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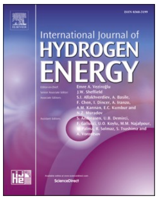

Liquefied hydrogen, ammonia and liquid organic hydrogen carriers for harbour-to-harbour hydrogen transport: A sensitivity study

Elvira Spatolisano [a,*], Federica Restelli [a], Laura A. Pellegrini [a], Simone Cattaneo [b], Alberto R. de Angelis [b], Andrea Lainati [b], Ernesto Roccaro [b]

[a] GASP - Group on Advanced Separation Processes & GAS Processing, Dipartimento di Chimica, Materiali e Ingegneria Chimica "G. Natta", Politecnico di Milano, Piazza Leonardo da Vinci 32, 20133, Milano, Italy

[b] Eni S.p.A. Research and Technological Innovation Department, Via F. Maritano 26, 20097, San Donato Milanese, Italy

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ABSTRACT

Hydrogen is commonly perceived as the key player in the transition towards a low-carbon future. Nevertheless, H_2 low energy density hinders its easy storage and transportation. To address this issue, different alternatives (liquefied hydrogen, ammonia and liquid organic hydrogen carriers) are explored as hydrogen vectors. The techno-economic assessment of H_2 transport through these carriers is strongly dependent on the basis of design adopted, such that it is difficult to draw general conclusions. In this respect, this work is aimed at performing a sensitivity analysis on the hypotheses introduced in the layout of H_2 value chains. Different scenarios are discussed, depending on harbour-to-harbour distances, cost of utilities and raw materials and H_2 application to the industrial or mobility sector. The most cost-effective carrier is selected for each case-study: NH_3 is the most advantageous for industrial sector, while LH_2 holds promises for mobility. Critical issues are pointed out for future large-scale applications.

1. Introduction

Several countries around the world have expressed the intention to decrease humankind's dependency on non-renewable and polluting energy sources such as coal, oil, and gas [1-3]. In this respect, political actions take place to favour the decarbonization target [4-6]. For instance, the Energy Union (2015) established the five main aims of European energy policy, which are [5]:

1. Diversify Europe's sources of energy, guaranteeing cooperation between EU countries;
2. Ensure a fully integrated internal energy market, enabling adequate infrastructure for the free flow of energy through Europe;
3. Improve energy efficiency and reduce dependence on energy imports;
4. Decarbonise the economy, in line with the Paris Agreement, increasing the share of renewable energies in energy consumption;
5. Promote research in low-carbon and clean energy technologies.

The distribution of local potential for renewable energy is not homogeneous across different regions of the globe, resulting in a mismatch between energy consumption levels (which depend on population and industrialization density) and the availability of renewable energy sources. While some regions have abundant potentiality in terms of sources of green power, others may have limited access. This creates a need for a more diverse mix of renewable energy sources and technologies to ensure that the energy demand can be met across different regions. Furthermore, the implementation of renewable energy technologies and infrastructure requires significant investments in research, development and deployment, which will necessitate collaboration and support from both governments and industry [6]. The Renewable Energy Directive (EU) 2018/2001, substantially revised in 2018, established a minimum 32% share of renewable energy sources in the EU's final energy consumption by 2030.

In this framework, a special role is played by hydrogen. H_2 combustion produces no emissions such as CO_x, NO_x and SO_x, being an extremely clean fuel. Its outstanding gravimetric energy storage density, with each kilogram containing approximately 33 kWh of energy, makes it be perceived as the key player in the transition towards a low-carbon future, also considering its various applications in transportation,

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* Corresponding author.
E-mail address: elvira.spatolisano@polimi.it (E. Spatolisano).

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industrial processes, and power generation [7].

The hydrogen strategy (COM/2020/301) aims to install at least 6 GW of renewable hydrogen electrolysers by 2024 and 40 GW by 2030. It sets renewable hydrogen production targets of 10 million tonnes for European domestic production and of 10 million tonnes for imports by 2030. The key element that will impact the economic viability of hydrogen imports is whether factors such as scale, technologies, and other efficiencies can counterbalance the expenses associated with transporting hydrogen from regions where production costs are low to areas with high demand. To ensure cost-effectiveness in international trade, the production cost of green hydrogen in the exporting region must be significantly lower than that in the importing region, enough to cover the transportation expenses. This cost differential is expected to widen with the expansion of projects and advancements in technology aimed at reducing transport costs. According to the report by IRENA, hydrogen trade will develop largely in regional markets. North Africa and the Middle East are expected to be the primary trading partners for Europe, while Australia is poised to primarily supply the Asian market. Latin America's intra-regional market is projected to be substantial, with some exports directed towards Europe. Despite the significant political actions towards hydrogen implementation on a large scale, hydrogen-driven economy still suffers from important technical and economic challenges.

On the one hand, as opposite to traditional fossil fuels, which can be used whenever needed, any energy system that relies extensively on renewables must deal with their intermittent nature. Consequently, energy storage systems are of paramount importance to adjust the stochastic production pattern, to meet energy requirements.

On the other hand, hydrogen low energy density hinders its easy storage and transportation [8]. To face these issues, research is focused on providing long term and energy effective H_2 storage and transportation concepts, which are discussed in the following section.

2. Hydrogen storage and transportation concepts

Under ambient conditions, a single litre of gaseous hydrogen can store only 3 Wh of energy. This extremely low density makes H_2 storage and transportation difficult without high levels of compression or liquefaction. The appropriate storage method depends on size and duration.

For small scales, up to 1000 kg, hydrogen is typically stored as a compressed gas in carbon-fibre overwrapped pressure vessels at pressures ranging from 350 to 950 bar. For medium scales, below 20 tonnes, gaseous hydrogen can be stored in underground Type-1 pipe facilities at pressures lower than 100 bar [9]. An insulated, cryogenic spherical tank located above ground can store up to 250 tonnes of liquefied hydrogen, depending on the intended application [9–11]. For extremely large-scale storage, ranging from 100 to 3000 tonnes, underground geologic storage in salt caverns or lined rock caverns is typically the preferred method [12,13]. Nonetheless, finding appropriate locations for these types of caverns can be challenging due to geological limitations, and they may not always be available where they are required [14].

When dealing with hydrogen transportation, extremely high pressures are needed because of its low volumetric storage density, *i.e.*, 700 bar in existing technical applications. In this case, H_2 is referred to as Compressed Gaseous Hydrogen (CGH2) [15]. This concept implies huge compression costs, both in terms of capital expenditures and energy requirements. Alternatively, the preferred route for H_2 is the transport in its liquid state, which requires temperatures below $-253\ ^\circ C$. In this case, it is called Liquefied Hydrogen (LH2) [16]. Vacuum-insulated liquid tankers allow for the transportation of hydrogen in larger quantities (up to 4300 kg) and over longer distances [17,18].

The pilot project HySTRA [19] will demonstrate brown coal gasification and hydrogen refining at Latrobe Valley in Australia, hydrogen liquefaction and storage of liquefied hydrogen at Hastings, marine transportation of liquefied hydrogen from Australia to Japan and unloading of liquefied hydrogen in Japan.

Nonetheless, the process of liquefying hydrogen demands a significant amount of energy, even more than 10 kWh per kg of hydrogen, equivalent to more than 30% of its energy content, in addition to losses due to boil-off during transportation [20,21]. These two mentioned transportation concepts are intricate in terms of technology, entail a critical emphasis on safety, and require a significant financial investment for establishing a distribution infrastructure on a large scale. Recently, together with LH2 and CGH2, also solid hydrogen storage is under evaluation, despite still in an early development phase [22]. As a general remark, solid media can be susceptible to mechanical stress and abrasion, whereas these issues are minimized with liquid storage media.

As a result of the above-mentioned challenges, scientists are exploring alternative approaches for the transportation and storage of hydrogen, focusing on chemically bounded forms. These molecules can undergo a catalytic hydrogenation reaction, exploiting green hydrogen produced where renewable energy is extensively available. Then, they can be easily transported to the spot of energy demand and, upon arrival, dehydrogenated to favour H_2 release. The hydrogen thus produced can be used either to serve industrial or mobility sector. In this way, large quantities of energy can be stored and transported over extended periods of time.

Among all the available hydrogen carriers, ammonia is one of the most studied and well-established [23]. With a global production exceeding 200 million tons per year and a market value exceeding USD $60 billion, ammonia is the second-largest chemical produced worldwide [24]. Although scarcely used as an energy vector presently, it has the potential to serve as a renewable fuel in fuel cells, internal combustion engines, or gas turbines with almost zero carbon footprint [25]. When thinking of NH_3 application as hydrogen carrier, NH_3 main benefit lies in its high H_2 content, about 17.8 wt%, which is significantly greater than other carriers, together with its high volumetric hydrogen density (121 kg-H_2/m^3 at atmospheric pressure and 240 K, surpassing the densities of liquid hydrogen, of about 70.8 kg–H_2/m^3 at atmospheric pressure and 20K [26]). Moreover, ammonia can be produced using renewable hydrogen and nitrogen from the air by means of electric energy, without the need of involving carbon species during the synthesis process. These attributes make ammonia a convenient option as a carrier for renewable energy.

While producing ammonia for transportation purposes and converting it back into hydrogen requires a significant amount of energy, the infrastructure for handling and shipping ammonia is already available. It remains in a liquid state at room temperature under around 10 bar pressure, with a vapor pressure similar to propane. NH_3 can be stored in tanks or transported through pipelines, ships, or trucks [27,28].

ARENHA (Advanced materials and Reactors for Energy storage tHrough Ammonia) [29] will demonstrate the feasibility of ammonia as a dispatchable form of large-scale energy storage, enabling the integration of renewable electricity in Europe and creating global green energy corridors for Europe energy import diversification.

NEOM Green Hydrogen Company (NGHC) is an equal joint venture by ACWA Power, Air Products and NEOM. NGHC's mega-plant will integrate up to 4 GW of solar and wind energy to produce up to 600 tonnes per day of carbon-free hydrogen by the end of 2026, in the form of green ammonia as a cost-effective solution for the transportation and industrial sectors globally.

However, there are also some challenges associated with the use of ammonia as a hydrogen carrier. One of the major challenges is the safety issue, as ammonia is a toxic and corrosive chemical. Therefore, special safety measures need to be taken to prevent any accidental release of ammonia into the atmosphere. Nonetheless, with the development of more efficient and low-cost technologies, the storage and transportation of green hydrogen via ammonia vector could become effective and economically viable.

A potential substitute for conventional storage methods is the

Table 1
Summary of the main features of the H_2 carriers.

carrier	H_2 density [kg/L]	cost of raw material [€/kg]	infrastructure	H_2 conversion to carrier	carrier reconversion to H_2	sustainability issues
Liquefied hydrogen (LH_2)	0.071 @ P_{atm}[a], $T = -253\ ^\circ C$	–	not yet available	liquefaction is high energy intensive, so very costly	regassification is quite established and releases a significant energy content	can be produced exploiting renewables only
ammonia (NH_3)	0.12 @ P_{atm}[a], $T = -33\ ^\circ C$	–	already established (LPG[c] products)	NH_3 synthesis is well established on large scale. Process intensification is needed for downscaling	NH_3 cracking is high energy intensive and established in metallurgic industry, at very small scale only.	can be produced exploiting renewables only
methanol/ formic acid/	0.05–0.15 @ P_{atm}[a], T_{atm}[b]	0.03	already established (LPG[c] products)	production processes already established on large scale	it releases CO_2	can be produced from CO_2
LOHC (fossil-based)	0.047–0.056[d] @ P_{atm}[a], T_{atm}[b]	0.4 (TOL) – 4 (DBT)	already established (oil products)		high energy intensive	fossil-based substances
LOHC (bio-based)		–	already established (oil products)	not yet studied (low TRL[e])	not yet studied (low TRL[e])	can be produced from biomass

[a] P_{atm}: atmospheric pressure.
[b] T_{atm}: atmospheric temperature.
[c] LPG: Liquefied Petroleum Gas.
[d] Total hydrogen density of the hydrogenated compound.
[e] TRL: Technology Readiness Level.

technology based on Liquid Organic Hydrogen Carriers (LOHCs). LOHCs are organic molecules in which hydrogen is covalently bonded through hydrogenation, while, during periods of energy demand, can be dehydrogenated to release hydrogen. Meanwhile, the energy-deficient compound is recycled back to the hydrogenation hub. Thanks to these features, LOHCs allow for a decoupling of energy production and energy consumption in both spatial and temporal terms. As for the catalysts, the LOHC compound undergoes a cyclic process of hydrogen loading and release, rather than being consumed. This approach of energy storage and distribution may be nearly carbon-neutral, allowing for zero CO_2 emissions, if the value chain is properly designed.

The majority of LOHCs remain in a liquid state under normal atmospheric conditions and possess physical characteristics that closely resemble those of diesel. As a result, they can guarantee an easy and safe handling, and enable to exploit the widely available diesel distribution network.

Several substances have been proposed as potential LOHC molecule candidates, including methanol [30], formic acid [31], toluene [32], various cycloalkanes [33–36], and ammonia borane-based systems [37, 38]. Methanol and formic acid are not liquid organic hydrogen carriers strictly speaking, because they are converted to CO_2 during the dehydrogenation process, such that they cannot be recycled back to the loading terminal and the cycle cannot be closed.

Toluene is currently the most widely established molecule as liquid organic hydrogen carrier. The toluene (TOL)/methylcyclohexane (MCH) system has already been the subject of research, and a patent has been issued by Chiyoda Corporation [32]. The AHEAD project is the first small-scale demonstration of intercontinental hydrogen transport via LOHC. In this project, 210 tonnes of hydrogen are transported from Brunei to Japan [39]. While the costs of the project are estimated to be several billion yen, the cost of the delivered hydrogen has not been disclosed. Toluene is mainly synthesized through the catalytic conversion of petroleum products and the aromatization of aliphatic hydrocarbons. Toluene is primarily utilized as a precursor to a variety of chemicals, such as benzene, phenol, and toluene diisocyanate, which account for around 50% of its industrial usage. It is also a widely used solvent for paints and coatings (10%) and is utilized as an octane booster in gasoline (3%) [40]. It was projected that worldwide toluene production would experience only modest growth from an estimated 13 million tonnes in 2012.

In 2014, dibenzyltoluene (DBT), used as a heat transfer oil for many years, was suggested as a potential LOHC. Since then, the dibenzyltoluene (H0-DBT)/perhydro-dibenzyltoluene (H18-DBT) combination has attracted the attention of many researchers. Compared to other LOHC systems, it has numerous advantages such as a relatively high hydrogen storage capacity (6.2 wt%), exceptional thermal stability, a high boiling point (390 °C), low toxicity, and a low melting point (−39/–34 °C) [41]. These characteristics enable the hydrogenation and dehydrogenation of dibenzyltoluene and perhydro-dibenzyltoluene to take place in a liquid state, and the pairs can be easily stored or transported at ambient temperature. The technology based on dibenzyltoluene pair is commercialized by “Hydrogenious LOHC Technologies GmbH”, a company founded in 2013 [42].

Together with the abovementioned species, the use of oxygen-containing rings is attracting the research attention because they can be easily obtained from biomass and sustainable resources. However, their implementation is largely more challenging than the use of their nitrogenated counterparts, because of their lower maturity [43].

All the characteristics of the discussed hydrogen carriers are summarized in Table 1.

There are several studies in literature devoted to discussing the economic viability of hydrogen transportation by different carriers.

However, results are strongly dependent on the introduced hypotheses, on the considered basis of design and on the adopted methodology, so it is difficult to draw general conclusions. For this reason, it is more meaningful to focus on the technical assessment of the cost drivers of the overall value chain (*i.e.*, H_2 conversion to the carrier and carrier reconversion to H_2), rather than put the stress on its economics. To promote the industrialization of hydrogen transport through H_2 carriers, hydrogenation and dehydrogenation stages are of paramount importance. From the engineering point of view, the accurate design of these stages allows for the identification of weaknesses that require process intensification. Once these stages have been analysed and the layout of the overall value chain is clearly pointed out, a sensitivity study on the introduced hypotheses can be useful to understand their impact on results. Depending on the presented scenario and considering Table 1, excluding carriers that involve the CO_2 direct emissions, the best alternative for hydrogen transport can be identified. In this respect, this work is aimed at analysing and comparing the most promising H_2 carriers: liquefied hydrogen, ammonia and LOHCs (considering toluene and dibenzyltoluene as representative carriers).

Details for the technical analysis of each of them, as well as the simulation of hydrogenation and dehydrogenation stages in Aspen Plus V11®, have been already discussed elsewhere [44–46] and will be not reported in this work. In the following, a sensitivity analysis on the introduced hypotheses is presented, to evaluate the impact of each of

Table 2
Specific utility costs for the “present” and “future” scenarios [47].

Utility	Units	“present” (2022)	“future” (2027)
Electricity	€/MWh	500	220
Cooling Water (CW - 30 to 40 °C)	€/GJ	0.3583	0.3583
Refrigerated Water (RW -15 to 25 °C)	€/GJ	32.3408	14.4768
Boiler feed water (BFW)	€/t	1.15	1.20
IFO 380 1%S	€/t	580	450
Diesel	€/l	1.8155	1.8155
CO_2 emissions	€/t	90	105

them on the outcomes of the techno-economic assessment. In this way, results are rationalized and the most cost-effective option is identified according to the discussed scenario.

3. Basis of design and methodology for hydrogen value chains

The main hypotheses to be considered to define the layout of a hydrogen supply chain include.

1. Production rate of green H_2 to be fed to the system. Green hydrogen is, in most cases, produced by electrolysers driven by renewable sources, as wind or solar. Renewable sources are characterized by a power density several orders of magnitude lower than fossil fuels. The transition pathways towards sustainability must consider both the limitations of available land and the specific geophysical conditions as to wind and solar power [25]. In this respect, tuning the plant size according to the land requirement of renewables is crucial for the assessment of realistic scenarios. Understanding the extent of land needs allows to put the feasible scale of green hydrogen production into perspective. Taking into account these considerations, in the present analysis, flat H_2 production of 20000 Nm^3/h is supposed via 100 MW alkaline electrolysers, available at 20 bar and 25 °C [45].
2. Loading and unloading terminal location and, consequently, distance to be covered for H_2 transport. Different scenarios can be inferred, as the long-distance harbour-to-harbour hydrogen transport, which involves the H_2 seaborne transport or the short distance hydrogen transport, that implies the road or pipeline hydrogen transport [44]. In the present case study, harbour-to-harbour H_2 transport is assumed, varying the distance covered via ship transport in the range 2500–10000 km.
3. H_2 utilization and its application in industry or in the mobility sector. According to the industrial scenario, the produced H_2 is conveyed into a power plant for green electricity production. In this case, less stringent specifications on H_2 purity are needed, likely. On the other hand, for the H_2 utilization in the mobility sector, H_2 has to be distributed to several hydrogen refuelling stations. Thus, high H_2 purity is necessary. The selection of the type of scenario also affects the process design of the whole value chain and, consequently, the operating conditions of the delivered hydrogen (*i.e.*, temperature and pressure of discharge at the end user, together with required purity) [46]. In the present study, both applications are considered for each carrier. In the first case, hydrogen product is released at 30 bar and with a purity of 99.9 mol%, while in the second case, each H_2 Refuelling Stations (HRS) has a H_2 demand of 500 kg/d each (required H_2 purity of 99.97 mol%, according to standard ISO 14687:2019 Hydrogen fuel quality - Product specification), and the pressure of the H_2 delivered is set at 900 bar (the required pressure level for the H_2 application to the mobility sector is 700 bar, thus a sufficient ΔP is required as driving force to fill the car tanks).

Together with the above-mentioned aspects, also raw materials and utilities costs can affect results. These are strongly dependent on geopolitical and economic issues, according to the period the economic assessment refers to. For this reason, two temporal scenarios will be discussed, the present one and the future one, varying utilities and raw materials costs, as reported in Table 2 and Table 3, respectively. In the present scenario, the economic evaluations are referred to the year 2022, while the future one takes into account a cost reduction within the next 4–5 years due to the significant inflation experienced last year, which affected the electricity price, mostly.

Table 3
Specific raw materials costs for the “present” and “future” scenarios.

		“present” (2022)	“future” (2027)
Toluene	€/t	1300	850
Dibenzyltoluene	€/t	5000	3000
Nitrogen	€/Nm^3	0.20	0.15

The utility consumption is calculated through the energy balance retrieved from process simulations.

The overall hydrogen value chain for the three different analysed carriers is depicted in Fig. 1. System’s boundaries are marked by the dashed red line. In the present evaluation, green hydrogen production cost is not included, since the aim is to compare different methods for H_2 transport.

The H_2 value chain of Fig. 1 includes:

1. Green H_2 conversion into the selected carrier at the loading terminal;
2. Carrier storage at the loading terminal;
3. Seaborne transport of the selected carrier, covering the distance *D* variable in the range 2500–10000 km;
4. Carrier storage at the unloading terminal and its subsequent road distribution via trucks. A distance of 100 km is assumed from the unloading terminal to the hydrogen end user, to be covered via road transport;
5. Carrier reconversion to favour H_2 release. Hydrogen is released at variable specifications and operating conditions, according to the two different applications considered (*i.e.*, industrial or mobility sector).

With reference to the value chain depicted in Fig. 1, an economic assessment is carried out, evaluating the Levelized Cost of Hydrogen Transport (*LCoHT*) according to Eq. (1). The cost of hydrogen transport for the carrier considered is the sum of the cost of each step of the value chain disclosed in Fig. 1 [48].

$$LCoHT = \frac{\sum_{t=0}^{N-1} \frac{CAPEX_t + OPEX_t}{(1+WACC)^t}}{\sum_{t=0}^{N-1} \frac{P_{H_2,out}}{(1+WACC)^t}} \tag{1}$$

In Eq. (1), $P_{H2,out}$ is the annual hydrogen productivity, *WACC* is the weighted average cost of capital, *t* is the year to which *CAPEX* (capital expenditures) and *OPEX* (operating expenditures) are referred to (t = 0 is the current year and *N-1* is the end year). The financial assumptions considered in the present work are summarized in Table 4.

CAPEX and *OPEX* of Eq. (1) are calculated according to the Turton methodology [51], for the carrier conversion and reconversion stages. Specifically, the fixed costs are evaluated starting from the Aspen Plus process simulations detailed in previous works [44–46]. As for the operating costs, raw materials, utilities and labour costs have been accounted for, considering both present and future scenarios. The following assumptions have been introduced in the evaluation of the carrier conversion and reconversion costs, for all the hydrogen value chains discussed in this analysis:

- No spare units have been included when estimating capital costs.
- Costs associated with catalysts have been omitted, both initial catalysts costs and subsequent costs for replenishment. The rationale for

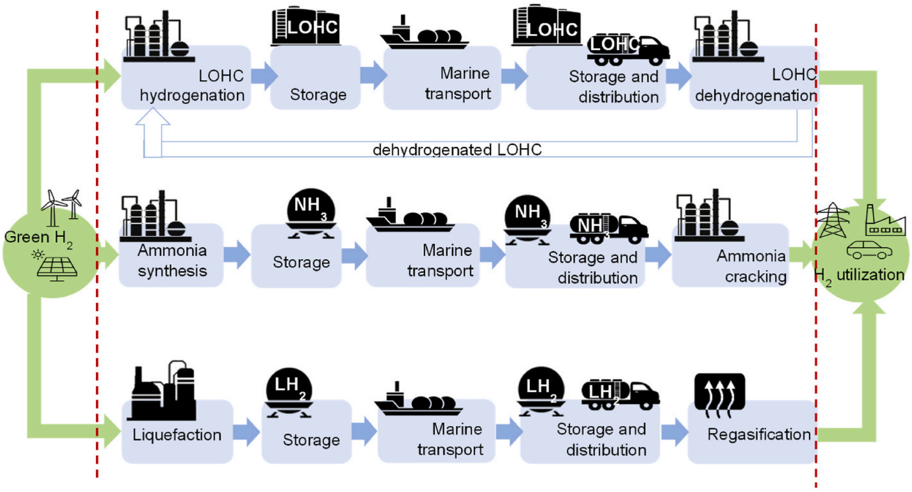

Fig. 1. H_2 value chain for the different carriers analysed.

Table 4
Financial assumptions.

Item	Value
WACC	5%
Base year ($t = 0$)	2022
Project lifetime	25 y
Construction period	3 y (*CAPEX* breakdown: 40%, 30%, 30%)
Decommission cost	5% *CAPEX* [49]
Plant availability (H_{eq})	8000 h/y
Exchange rate (2022)	0.951 €/US-$ [50]

this decision stems from preliminary estimations which demonstrate that the costs associated with noble metal catalyst replenishment do not significantly impact the overall assessment.

- Costs related to harbour infrastructures at both loading and unloading terminals—including pipelines, jetties, and flares—have been neglected.

As regards storage, seaborne transport and road transport, both capital and operating expenditures have been estimated, as well. Reference is made to what available in literature regarding oil products, ammonia or liquefied hydrogen tanks and tankers. Fixed costs are due to the item purchase and depend on its size, adjusted to the 2022 year

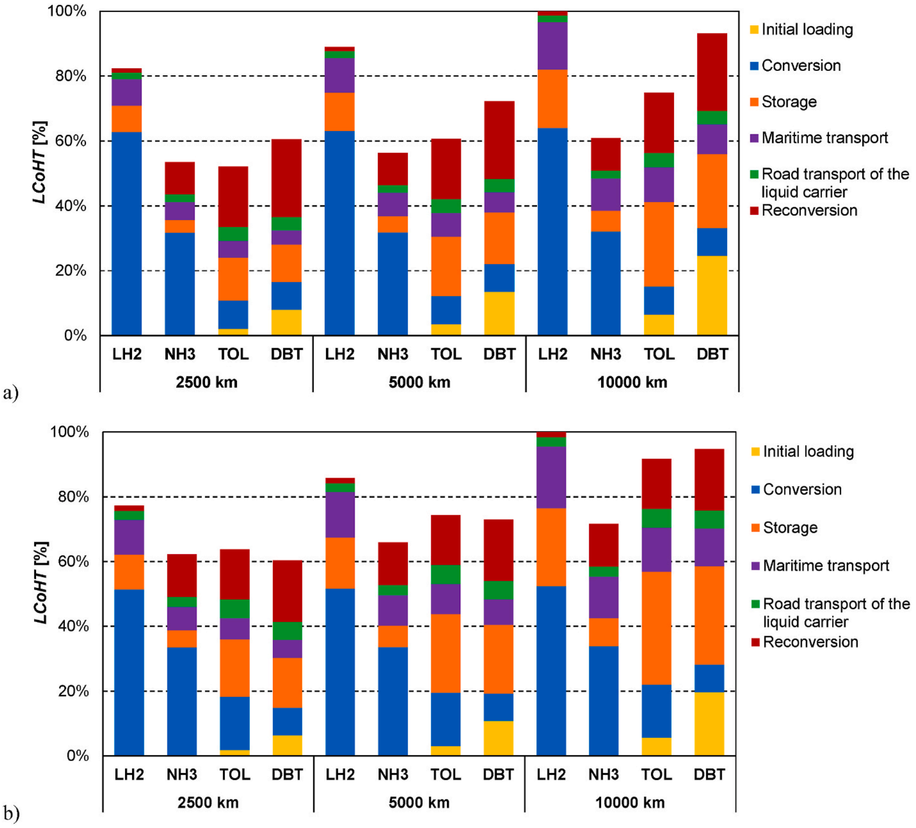

Fig. 2. Comparison between the different hydrogen transport value chains for its industrial application (H_2 valley), as a function of the distance D covered by seaborne transport, for the scenario: a) present and b) future.

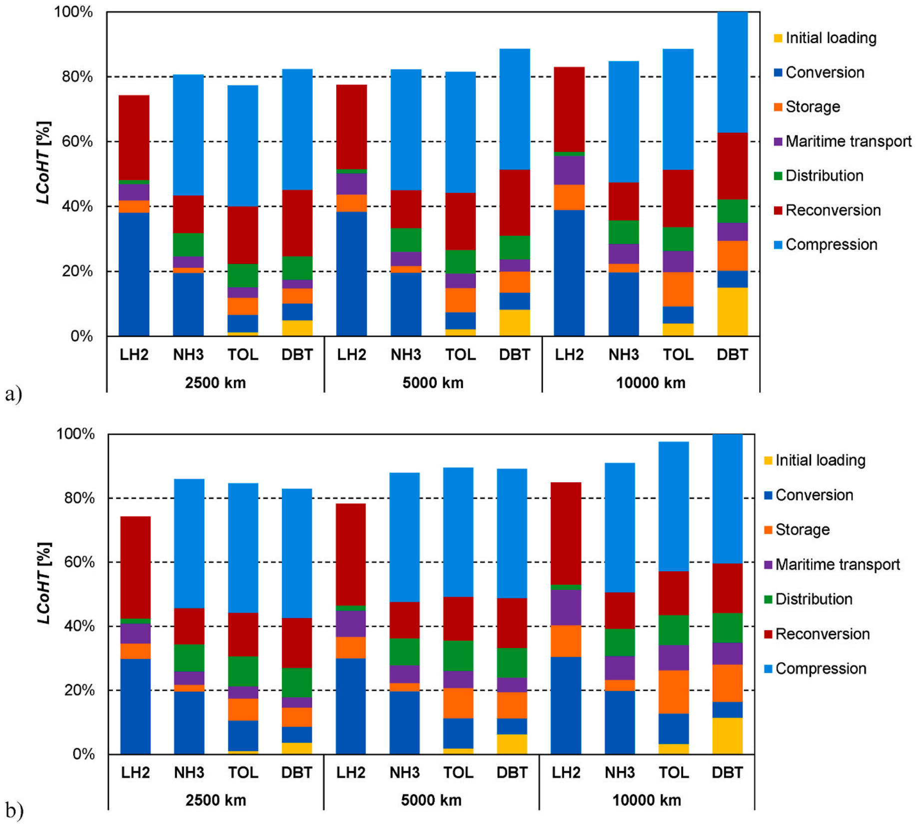

Fig. 3. Comparison between the different hydrogen transport value chains for its mobility sector application (H_2 refuelling stations), as a function of the distance *D* covered by seaborne transport, for the scenario: a) present and b) future.

through the *CEPCI* and attributed to the actual capacity through the Hill's law. Operating costs for both ship and road transport include labour cost, fuel cost and CO_2 emissions cost. Tankers are assumed to be driven by conventional fossil-based fuels (Intermediate Fuel Oil - IFO 380 1%S), while trucks are assumed to be diesel based. As a consequence of the usage of a fossil-based fuel, carbon dioxide is emitted during both seaborne and road transport. For this reason, additional costs associated with CO_2 emissions have also been taken into account, according to the cost items reported in Table 2. No other CO_2 emissions rather than the direct ones have been accounted for.

For both tankers and storage operating costs, a 10% CAPEX is assumed to take into account for maintenance and insurance.

Moreover, in the case of NH_3 and LH_2, also losses due to boil-off phenomenon during ship transport have been estimated.

In addition, for the case of hydrogen transport through liquid organic hydrogen carriers, the fixed cost of the initial LOHC loading has also been introduced. This initial loading volume is considered to be equivalent to the combined capacity of three storage tanks (one at the loading terminal, one at the unloading terminal and one at the reconversion site). Essentially, it represents the initial carrier volume necessary to kickstart the hydrogen distribution process, acting as a foundational input to set the LOHC cycle in motion.

Finally, the small amount of by-products formed during LOHC dehydrogenation is burned, together with part of the H_2, to provide the necessary heat for the reaction to occur (see Ref. [44] for further details). Thus, no cost associated to by-products is introduced in the economic assessment.

4. Results and discussion

4.1. Hydrogen application to the industrial sector (H_2 valley)

Fig. 2 shows the results of the technical-economic evaluations carried out, as a function of the distance *D* covered via ship, for both the present and future scenarios. As a consequence of the different H_2 conversion and reconversion processes, for each carrier different H_2 flow rates are delivered to the H_2 valley. For a distance covered via ship transport of 2500 km, the delivered H_2 is: 42.8 ton/d for liquefied hydrogen, 34.2 ton/d for ammonia, 26.4 ton/d for toluene, 27.8 ton/d for dibenzyltoluene.

The cost driver of the LOHCs value chain is the dehydrogenation of the carrier to produce hydrogen. To reduce the costs associated with the transport of hydrogen via LOHC, therefore, a process intensification for the dehydrogenation section is necessary.

The most significant cost item for the ammonia value chain is NH_3 synthesis. For the application of ammonia as a hydrogen carrier, this section should be intensified to reduce its costs on a small scale.

For the liquefied hydrogen value chain, the highest cost comes from liquefaction. A process optimization is required to reduce electricity consumption.

Referring to the present scenario (Fig. 2a), for the distance *D* of 2500 km, ammonia and LOHCs (dibenzyltoluene and toluene) are the most cost-effective alternatives for transporting and storing hydrogen, while for a distance of 5000 km, ammonia is more cost-effective as a carrier of hydrogen. This reversal of trend is due to the fact that, as the seaborne transport distance increases, the initial loading of organic carriers increases, too, the cost of which, at the moment, is far from negligible. This is particularly true for dibenzyltoluene, as shown in Fig. 2a. Toluene shows lower hydrogen transport costs than dibenzyltoluene, due to the lower dehydrogenation enthalpy, together with the lower raw material cost.

The contribution of the initial loading of organic carriers is so high that, at a distance of 10000 km, the costs of hydrogen transport through dibenzyltoluene almost equal the costs of liquefied hydrogen. Liquefied hydrogen remains the most expensive alternative as H_2 carrier for industrial applications, as a consequence of the particularly high liquefaction costs.

In the future scenario (Fig. 2b), the calculated cost of hydrogen transport varies more or less significantly depending on the analysed carrier. In particular, for the liquefied hydrogen value chain, liquefaction costs are significantly reduced, since the energy consumption of the process is, almost entirely, electric. The trend of comparison remains unchanged.

The cost of transporting hydrogen also appears lower for the LOHC value chain compared to the current scenario, considering the important cost reduction of dibenzyltoluene.

4.2. Hydrogen application to the mobility sector (H_2 refuelling stations)

When hydrogen is intended to be applied to the mobility sector, it has to be distributed to a number of end users, whose H_2 demand is 500 kg/day each. In this case, two different alternatives arise for the carrier reconversion. As a matter of fact, the hydrogen vector can be either converted to hydrogen at the unloading terminal, involving subsequent compressed gaseous hydrogen distribution via truck, or converted to hydrogen at each end user, delivering the carrier via road transport from the unloading terminal to the end user (100 km far, as from the basis of design of this analysis). For liquid organic hydrogen carriers value chain, considering that the dehydrogenated organic molecule has to be routed back to the loading terminal via ship transport, the carrier reconversion stage for H_2 release has been assumed to be at the harbour.

For liquefied hydrogen, it is more cost-effective to decentralize conversion at the end user. In fact, hydrogen arrives at the user in its liquid state and can be pumped up to 900 bar to save compression work downstream of regasification, as demonstrated in a previous work [46].

In a similar fashion, both centralized and decentralized reconversion stages have been compared for ammonia as hydrogen carrier. Results revealed that, the centralized cracking at unloading terminal, the distribution of compressed hydrogen gas and its subsequent recompression at the individual user is the best choice. As a matter of fact, the cost of small-scale, electrically powered NH_3 cracking is higher than the sum of centralized compression up to 320 bar (considering that the pressure required by compressed hydrogen trucks is 250 bar) and decentralized compression from 15 to 900 bar (15 bar is assumed to be the pressure required to empty the truck).

Having identified the best alternative for centralized/decentralized carrier reconversion, Fig. 3 shows the results of the technical-economic evaluations carried out, as a function of the distance D covered via seaborne transport and for both the present and future scenarios, when hydrogen application is the mobility sector.

According to the present scenario, in all cases, liquefied hydrogen is the most cost-effective alternative for transporting and storing compressed hydrogen, followed by ammonia and LOHC. The sensitivity analysis as a function of distance did not reveal any reversal of the trend in this respect.

Liquefied hydrogen is the best carrier when hydrogen at 900 bar is required by small end users. This is due to the convenience in transporting hydrogen in liquid state and, therefore, in the possibility of pumping the liquid to save part of the compression work. Ammonia shows a lower cost than both dibenzyltoluene and toluene.

On the other hand, in the future scenario, the cost difference between the different carriers is more evident because, as the price of electricity falls, the costs for compression become less significant. Liquefied hydrogen is still the best alternative, while ammonia and LOHC show about the same cost.

Table 5
Pros/cons of the hydrogen carriers analysed.

carrier	pros	cons
LH_2	✓ Electric energy required, only, for the liquefaction process; ✓ most cost-effective H_2 *carrier* for mobility sector (in particular, according to the future scenario).	× Significant H_2 leakages (10–14% as from Air Liquide estimations), which cannot be released in the atmosphere because of environmental and safety issues; × most expensive H_2 *carrier* for industrial applications → process intensification of the liquefaction process needed; × no infrastructure for storage and distribution available.
NH_3	✓ Most advantageous H_2 carrier for industrial applications, also considering high harbour-to-harbour distances; ✓ highly flexible and versatile (can be used as both H_2 carrier and carbon-free energy vector); ✓ global commodity already transported worldwide via ships or pipelines.	× Toxicity issues; × low TRL for cracking on large scale; × synthesis costs should be reduced on small scale.
LOHC	✓ Cost-effective H_2 carrier for H_2 transport at reduced harbour-to-harbour distances, considering the hydrogen industrial application; ✓ effective in hydrogen storage at ambient temperature and pressure without leakages due to boil-off; ✓ already existing infrastructure for oil products can be exploited.	× Low TRL for other molecules rather than toluene; × high dehydrogenation operating costs; × high cost of the raw material (in particular for DBT) and uncertainties in the market of DBT.

5. Conclusions

The technical-economic analysis carried out on different hydrogen carriers, coupled with the sensitivity analysis, highlights potential and weaknesses of hydrogen transport through ammonia, liquefied hydrogen and liquid organic hydrogen carriers as H_2 vectors. Each stage of the H_2 value chain has been deepened, to pave the way for future process intensification, in view of cost reductions. The application of the produced hydrogen to both the industrial sector (H_2 valley case) and the mobility sector (Hydrogen Refuelling Station case) is discussed. As a general remark, H_2 application to the industrial sector shows the lowest costs in the present scenario. On the other hand, H_2 application to the mobility sector is affected by the high impact of compression costs. In addition, safety issues related to the management of hydrogen gas should be addressed in this case.

The comparison between the different carriers is shown in Table 5, together with pros/cons of each of them.

Considering the high flexibility and versality, together with its maturity and the already existing infrastructures, ammonia turns out to be the most promising hydrogen and energy carrier to achieve the decarbonization target.

CRediT authorship contribution statement

Elvira Spatolisano: Writing – original draft, Software, Methodology, Investigation, Data curation, Conceptualization. **Federica Restelli:** Software, Investigation, Data curation, Conceptualization. **Laura A. Pellegrini:** Writing – review & editing, Validation, Supervision, Methodology. **Simone Cattaneo:** Writing – review & editing, Validation, Supervision, Project administration. **Alberto R. de Angelis:** Writing – review & editing, Supervision, Project administration. **Andrea Lainati:** Writing – review & editing, Supervision, Project administration.

Ernesto Roccaro: Writing – review & editing, Supervision, Project administration.

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.

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