

# A review of hydrogen storage and transport technologies

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## Abstract

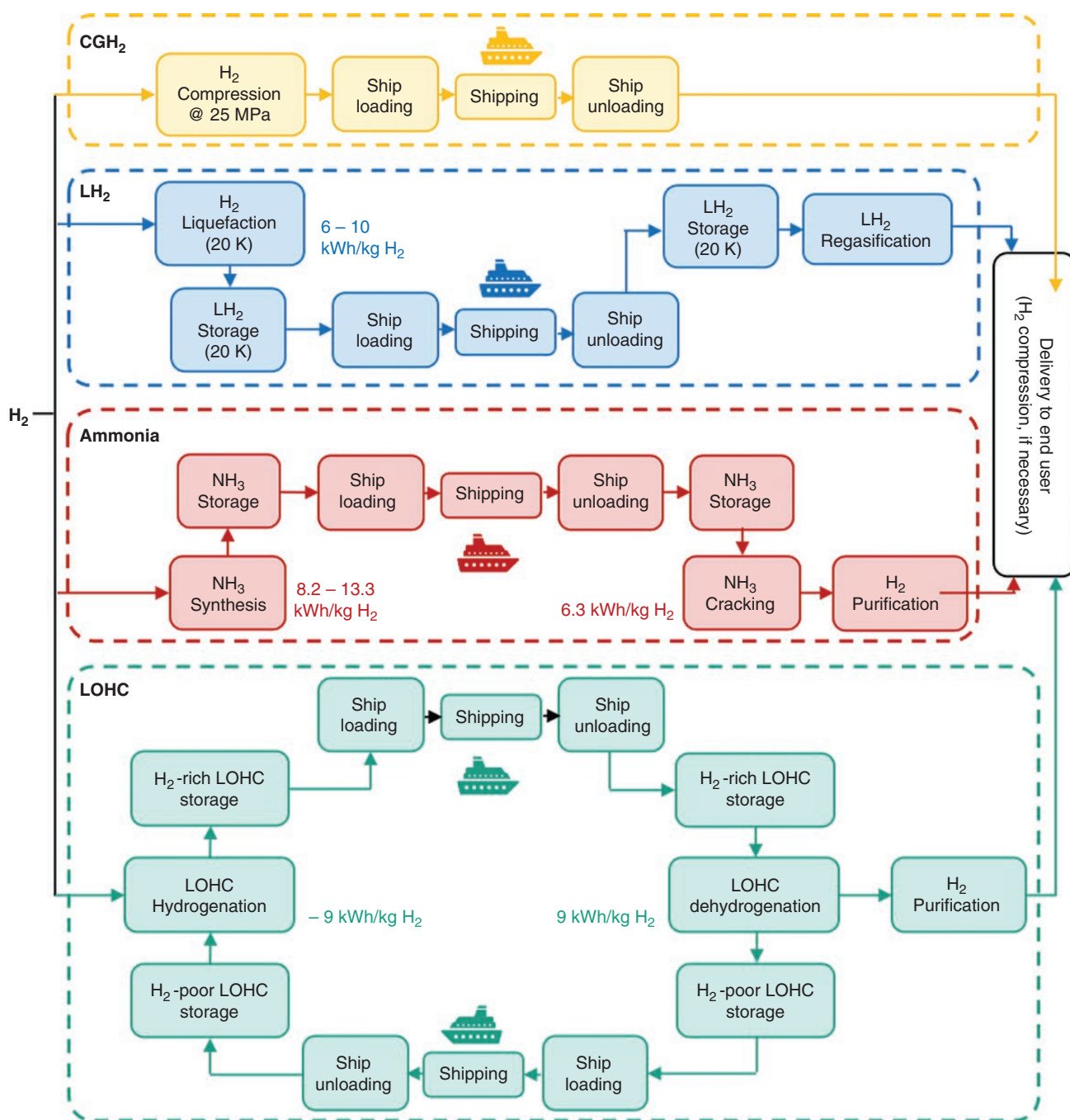
An important component of the deep decarbonization of the worldwide energy system is to build up the large-scale utilization of hydrogen to substitute for fossil fuels in all sectors including industry, the electricity sector, transportation and heating. Hence, apart from reducing hydrogen production costs, establishing an efficient and suitable infrastructure for the storage, transportation and distribution of hydrogen becomes essential. This article provides a technically detailed overview of the state-of-the-art technologies for hydrogen infrastructure, including the physical- and material-based hydrogen storage technologies. Physical-based storage means the storage of hydrogen in its compressed gaseous, liquid or supercritical state. Hydrogen storage in the form of liquid-organic hydrogen carriers, metal hydrides or power fuels is denoted as material-based storage. Furthermore, primary ways to transport hydrogen, such as land transportation via trailer and pipeline, overseas shipping and some related commercial data, are reviewed. As the key results of this article, hydrogen storage and transportation technologies are compared with each other. This comparison provides recommendations for building appropriate hydrogen infrastructure systems according to different application scenarios.

## Graphical Abstract

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**Keywords:** hydrogen infrastructure; hydrogen storage; hydrogen transportation

## Introduction

An essential component of the deep decarbonization of the worldwide energy system is to build up the large-scale use of carbon-neutral hydrogen as an industrial feedstock and replacement of fossil fuels. Hydrogen generated through the electrolysis of water using renewable energy, which is labelled 'green' hydrogen, is considered as the best candidate for this purpose. However, the higher cost of green hydrogen, ~3–6 USD/kgH<sub>2</sub> [1], today, versus 1–2.4 USD/kgH<sub>2</sub> for 'fossil hydrogen' is hitherto the main barrier against its implementation in industry and civil applications. In addition to green hydrogen, there are several

other colours labelling hydrogen depending on the production methods, which have different, but in most cases, negative environmental impacts. Hence, there is an intense discussion about using low-cost 'non-green' hydrogen as an intermediate state of the clean energy transition. In the end, it is a trade-off between the need to scale up to reduce the hydrogen cost in the long run and the environmental impact. One decisive and motivating idea in this transformation process may be that companies and countries that are ahead of the technological evolution will have economic benefits that can be further invested in to gradually develop the hydrogen ecosystem towards carbon-neutrality in the long run.

In addition to low-cost hydrogen generation technologies, a well-established, efficient and low-cost hydrogen infrastructure that covers hydrogen storage, transportation and distribution is another key. It can, on the one hand, increase the demand for hydrogen and thus enlarge the production scale of hydrogen and reduce its price. On the other hand, lower hydrogen production cost promotes further expansion of hydrogen infrastructure.

The aim of this paper is to survey the technology options and trends in two essential sectors of the hydrogen infrastructure: hydrogen storage and transportation. In general, the currently available technologies to store and transport hydrogen are directly developed from the related mature technologies in the chemical and gas industries. This is especially the case for the physical-based hydrogen storage and hydrogen transportation, either on the road or through the pipeline and by ship, as represented in Sections 2.1–2.3 and 3.1–3.4, respectively. However, due to special features of hydrogen such as high diffusivity in metallic materials, etc., extra measures are needed: e.g. the extremely low evaporation temperature of hydrogen of 20 K at 0.1 MPa (1 bar) necessitates a complicated liquefaction process and measures against the boil-off effect. The high diffusivity of hydrogen limits the applicable materials for hydrogen pipelines and requires additional reassignment works for the repurposing of the existing natural gas pipeline network.

A unique property of hydrogen compared with fossil fuels and their derivatives is that it can be stored by combining it chemically or physically with appropriate liquid or solid materials. Despite the relatively low technology readiness level (TRL), material-based hydrogen storage technologies improve the application of hydrogen as an energy storage medium and provide alternative ways to transport hydrogen as reviewed in Sections 2.4–2.6. The special focus of this paper lies in the comparison of different hydrogen storage technologies in Section 2.7. Therefore, not only the key technical features but also the energy consumption to achieve the storage condition and to release hydrogen, as well as the preferential application fields are taken into account. Section 3.5 compares different hydrogen transportation methods in relation to the transport distance, especially from an economic point of view. Finally, in Section 4 we give a brief guide to choosing the appropriate hydrogen storage and transportation methods for different application scenarios and to establish a hydrogen infrastructure development strategy at the national and regional levels.

## 1 Hydrogen storage

The technologies for hydrogen storage play an essential role in the establishment of the hydrogen infrastructure. The form in which the hydrogen is stored determines not only its transportation method but also the ways of hydrogen utilization. Progress in hydrogen storage technologies can further promote and extend the field of hydrogen applications. From a technical point of view, five main factors are usually taken into account to characterize the hydrogen storage system [2]:

- gravimetric density (5.5 wt%);
- volumetric density (0.04 kg H<sub>2</sub>/L);
- operating temperature (−40°C to 60°C);
- cycle life (1500 cycles); and
- system fill time (1.5 kgH<sub>2</sub>/min).

The data in the parentheses above are the technical goals of on-board hydrogen storage for light-duty fuel cell vehicles set by the United States Department of Energy (US-DOE) for 2020 as a reference [3].

In general, hydrogen storage systems can be divided into two categories: physical-based and material-based storage (see Fig. 1). In the former case, the hydrogen is stored by altering its physical state, namely increasing the pressure (compressed gaseous hydrogen storage, CGH<sub>2</sub>) or decreasing the temperature below its evaporation temperature (liquid hydrogen storage, LH<sub>2</sub>) or using both methods (cryo-compressed hydrogen storage, CcH<sub>2</sub>). In the case of material-based storage, additional materials as ‘carriers’ are applied. They can bond with hydrogen molecules or atoms, either physically or chemically, and thus enhance storage density and safety as compared with those of physical-based storage systems. However, most of the material-based storage technologies are still in the laboratory and demonstration stages.

### 1.1 Compressed gaseous hydrogen storage (CGH<sub>2</sub>)

#### 1.1.1 Pressure vessels

The easiest and most mature way to store hydrogen gas is to compress it and fill it into pressure vessels. There are currently four types of well-developed vessels available, as compared in Table 1. The choice to use which vessel type is based on the application field with a compromise between technical performance and cost.

Type I pressure vessels for hydrogen storage appeared at the end of the nineteenth century. They were able to store 25 Nm<sup>3</sup> of hydrogen at 12 MPa using a 500-kg steel cylinder. Today, their typical service pressure has increased to between 15 and 30 MPa. However, due to their low gravimetric density, they can only be used for stationary applications, especially on-site storage of hydrogen as industry gas. Under a given pressure, mechanical analysis shows that the cylinder body of a metallic pressure vessel with a homogeneous wall thickness is the weak point, where it suffers higher stress as compared with domes [4]. Therefore, to store hydrogen at a higher pressure level, one can easily strengthen the metallic vessel by hoop-wrapping the middle cylindrical portion with resin-impregnated fibre. Depending mainly on the thickness of the wrapped fibre, the pressure vessels produced thereby, called

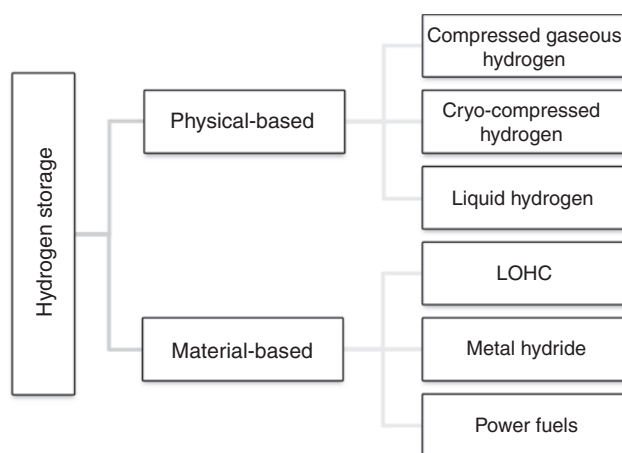


Fig. 1: Overview of hydrogen storage technologies.

**Table 1:** Categorization and comparison of different types of pressure vessels

Type	Material/description	Typical pressure (MPa)	Cost (\$/kgH <sub>2</sub> )	Typical gravimetric density (wt%)	Main application fields
I	Fully metallic pressure vessel (e.g. steel, Al)	15–30 [4]	240 <sup>a</sup>	1.7 [5]	Store the H <sub>2</sub> as industrial gas [4]
II	Metallic pressure vessel hoop-wrapped with glass fibre composite	10–95 [4], highest pressure tolerance (up to over 100 MPa possible)	360 <sup>a</sup>	2.1 [5]	Stationary applications, such as high-pressure H <sub>2</sub> storage (cascade) at H <sub>2</sub> refuelling station (HRS) [6]
III	Full composite wrap with metal liner	30–70	700 [5]	4.2 [5]	H <sub>2</sub> tube trailer [7]; H <sub>2</sub> trailer [4]; on-board H <sub>2</sub> storage
IV	Fully composite (e.g. high-density polyethylene inner with glass or carbon fibre)	30–70	500–1200 [8]	5.7 [5]	Stationary low-pressure hydrogen storage at HRS [6]; H <sub>2</sub> tube trailer [7]; H <sub>2</sub> trailer [4]; on-board H <sub>2</sub> storage

<sup>a</sup>Calculated from [9].

Type II vessels, exhibit the highest tolerance on service pressure. According to the technical data sheet of FIBA Technologies, Inc., Type II seamless steel vessels with wrapped carbon fibre are designed for gas pressures of  $\leq 100$  MPa [10]. For this reason, Type II pressure vessels are usually used for stationary high-pressure gas storage, such as cascade hydrogen storage at a hydrogen refuelling station (HRS) with 87.5 MPa [6]. When the metallic or polymeric inner liners are fully wrapped with fibre, the resulting pressure vessels (named Type III or IV, respectively) are significantly lightened and thus can fulfil the requirements on the gravimetric density of stored hydrogen for on-board applications. For the same reason, Type III and IV pressure vessels are preferential to be used in tube trailers and integrated into containers to transport hydrogen. As for low-pressure stationary hydrogen storage at refuelling stations, there is increasing interest in using Type IV vessels. Although one can store the same amount of hydrogen in Type I vessels with similar investment costs, they require a larger footprint [6].

Processes to manufacture the seamless metal cylinder and liner for Type I, II and III pressure vessels are very similar: the incoming metal slugs or plates are deep-drawn into the shell, with subsequent neck formation through stamping or hot-spinning. The liners of Type IV vessels are typically made of high-density polyethylene (HDPE) or polyamide (PA) using roto moulding, blow moulding or welding injected domes to an extruded tube of polymer. To strengthen the vessel liners, fibres (such as glass, aramid, carbon, etc.) can be hoop-wrapped, polar-wrapped or helical-wrapped thereon. Type II vessels are hoop-wrapped, whereas the wrapping for Type III and IV vessels is a combination of two or three of them. After this, the fibres are protected by cured resins (mostly epoxy).

### 1.1.2 Underground hydrogen storage

Besides pressure vessels, one other promising method to store compressed gaseous hydrogen is to use existing and appropriate salt caverns, aquifers and depleted gas reservoirs. Underground hydrogen storage (UHS) was developed especially for the medium- and long-term storage of a great volume of surplus hydrogen coming from importation or generated by seasonal renewable energy. Obviously, geological criteria are the main concerns for researchers and engineers when evaluating a potential UHS site. The salt cavern is generally the best candidate for pure hydrogen storage. It is not only due to the tightness of its deposits, the favourable mechanical properties of salt and its resistance to chemical reactions [11] but also due to its viscoelastic evaporitic rocks, which act as very good sealing for the gases [12]. Furthermore, the

saline condition suppresses the microbial consumption of stored hydrogen [12]. Unfortunately, the volumes of the salt caverns are relatively small and they are not widely distributed. Depleted gas reservoirs are larger in volume and exhibit significant advantages in that their geological structure and characteristics are well identified during exploration and exploitation [11]. However, the purity of stored hydrogen can be reduced by residual natural gas. If there exist good reservoir characteristics of the host rock and an impermeable layer to prevent migration of the stored hydrogen, the aquifer, which has a very large volume and is easily found, will be an option for hydrogen storage. However, the disadvantages are the potential leakage along undetected faults because of the porous nature of the aquifer, biochemical reactions and the reactions of hydrogen with minerals in the reservoir rock. Hitherto, pure hydrogen storage in aquifers has not been reported. Zivar *et al.* [13] summarized some existing UHS cases worldwide and compared different hydrogen applications with their suitable UHS, as listed in Tables 2 and 3, respectively.

## 1.2 Liquid hydrogen storage (LH<sub>2</sub>)

Hydrogen in its liquid form has obviously much higher gravimetric and volumetric density compared with compressed gaseous storage. However, the technique to liquefy hydrogen is much more difficult and consumes more energy than the compression of hydrogen or the liquefaction of other conventional gases. This is mainly due to the fact that

- (i) the evaporation temperature (20.28 K at 1 a.t.m.) and critical point (33 K) of hydrogen are very low;
- (ii) the molecule size of hydrogen is so small that it is very close to the ideal gas at a relative higher temperature—its Joule–Thomson coefficient is positive only if the temperature is  $< 202$  K (Joule–Thomson inversion temperature of hydrogen); and
- (iii) the enthalpy of parahydrogen vaporization at 20 K (447 kJ/kg) is lower than the enthalpy of exothermic conversion from normal to equilibrium hydrogen at the same temperature (532 kJ/kg) because of the ortho-to-para-conversion of hydrogen [14].

Note that the rate of temperature changes of a real gas with respect to isenthalpic pressure is defined as the Joule–Thomson ( $J$ – $T$ ) coefficient. By decreasing the pressure (increasing the volume), if the gas temperature is below its inversion temperature, the  $J$ – $T$  coefficient is positive and gas cools down. If the gas temperature is above its inversion temperature, the  $J$ – $T$  coefficient is negative

**Table 2:** List of some underground hydrogen storage projects around the world [13]

Location (country)	Storage type	H <sub>2</sub> (%)	Working condition	Depth (m)	Volume (m <sup>3</sup> )	Status
Teesside (UK)	Bedded salt	95	4.5 MPa	365	210 000	Operating
Clemens (USA)	Salt dome	95	7–13.7 MPa	1000	580 000	Operating
Moss Bluff (USA)	Salt dome		5.5–15.2 MPa	1200	566 000	Operating
Spindletop (USA)	Salt dome	95	6.8–20.2 MPa	1340	906 000	Operating
Kiel (Germany)	Salt cavern	60	8–10 MPa		32 000	Closed
Ketzin (Germany)	Aquifer	62	Not reported	200–250	Not reported	Operating with natural gas
Beynes (France)	Aquifer	50	Not reported	430	33 000 000	Operating with natural gas
Lobodice (Czech Republic)	Aquifer	50	9 MPa/34°C	430	Not reported	Operating
Diadema (Argentina)	Depleted gas reservoir	10	1 MPa/50°C	600	Not reported	Not reported
Underground Sun Storage (Austria)	Depleted gas reservoir	10	7.8 MPa/40°C	1000	Not reported	Operating

**Table 3:** Convenient storage site and application of energy based on the composition of the injected stream (percentage of hydrogen in the gas mixture) [13]

Gas stream	Conversion	Application	Convenient storage site
Pure hydrogen	Fuel cells	Electricity and vehicles	Salt caverns, which are almost completely hermetic, have a high degree of cleanliness and are characterized by a very low risk of probable gas contamination by impurities
Natural gas lean in hydrogen (6–15% H <sub>2</sub> )	Power to gas	Gas-fired turbines or to inject it into the natural gas pipeline	Depleted gas reservoir
Rich hydrogen mixture with CO, CH <sub>4</sub> and CO <sub>2</sub> (syngas or town gas) (20–40% H <sub>2</sub> )	Power to gas to power	Electricity, through thermomechanical conversion in gas turbines, and as fuel (in the case of town gas) for lighting and heating without any conversion	Aquifer, depleted gas reservoir or salt cavern
A mixture of hydrogen and CO <sub>2</sub>	Power to gas	Fuel and electricity	Aquifer or depleted gas reservoir

and gas warms up. The content of para- (or ortho-) hydrogen  $x_{pH_2}$  depends on the ambient equilibrium temperature. Varying the temperature from 300 to 20 K,  $x_{pH_2}$  increases from ~25% to 99.8%.

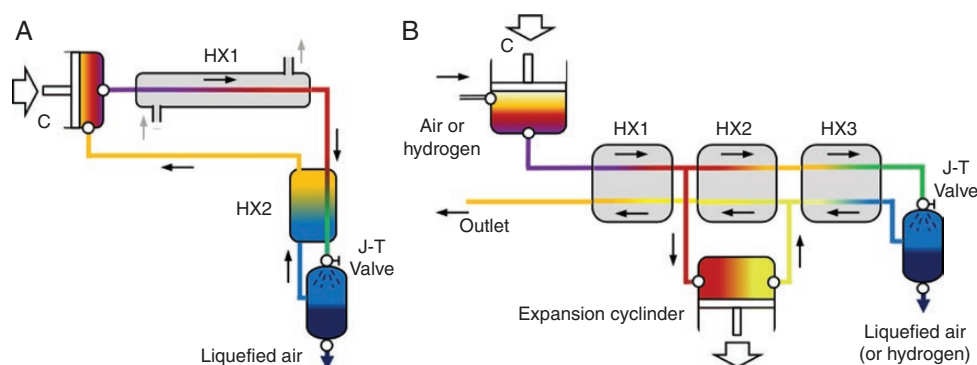
In 1895, Carl von Linde and William Hampson separately invented a cyclic process to liquefy the air that is suitable for industrial use. As shown in Fig. 2a, a compressor (C) compresses the air first from 2 to 6 MPa and then transfers the compressed air through a water heat exchanger (HX1). Subsequently, pre-cooled compressed air is fed into a countercurrent heat exchanger (HX2) and relaxed through a J–T valve (isenthalpic volume increase). One part of the air is liquefied thereby, whereas the other part of cooled air in its gaseous form goes through HX2, where it cools the incoming air, and back to the compressor. However, the Linde–Hampson cycle is unable to liquefy hydrogen, unless it is combined with a liquid nitrogen pre-cooling system [15].

Improving the Linde–Hampson cycle by combining the liquefaction cycle with the expansion machine, the Claude system, invented by George Claude in 1902 (Fig. 2b) is another method to liquefy the hydrogen: the incoming hydrogen is compressed to 4 MPa before it goes through heat exchange I (HEX I) where it will be cooled down to approximately –100°C. One part of this compressed and pre-cooled hydrogen is further cooled by increasing

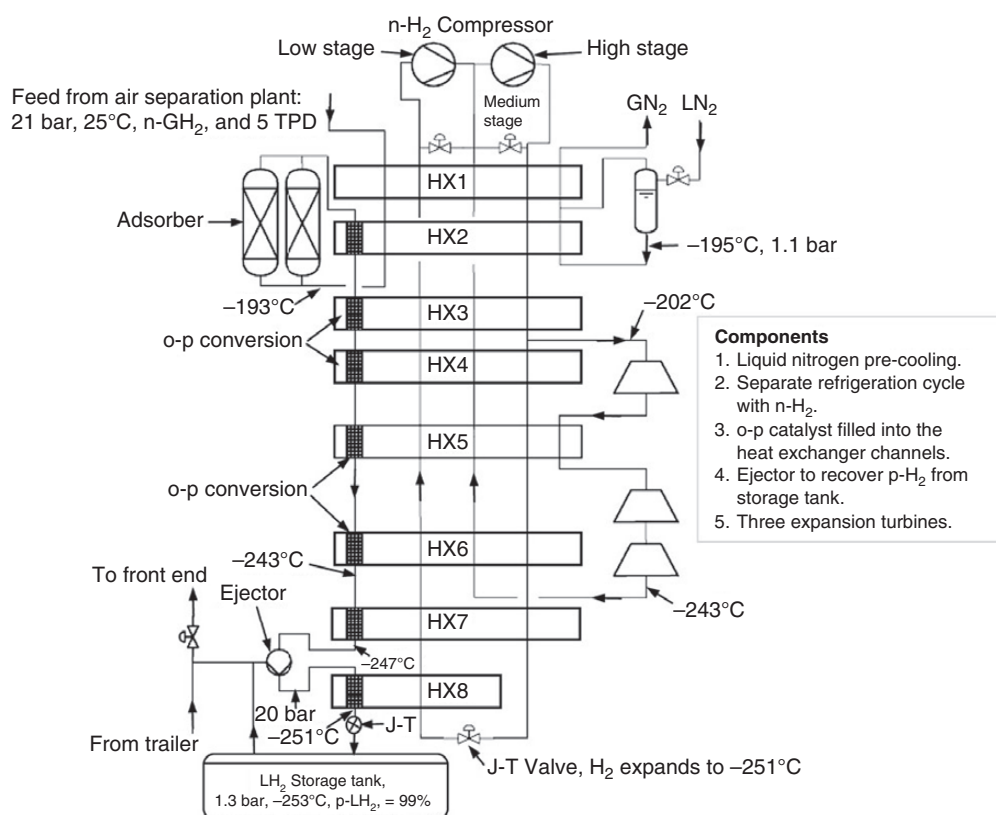
its volume via an expansion cylinder and then it is fed back to heat exchanger II (HEX II). The expanded hydrogen exchanges its cold in HEX II with the other part of the compressed hydrogen, whose major part will be liquefied through the J–T valve. The flash hydrogen created by throttling is warmed up in heat exchanger III (HEX III), mixed with the discharge from the expansion cylinder and further warmed up in HEX II and I.

In Germany, for example, there is currently one hydrogen liquefaction plant located in Leuna with a production capacity of 5.5 metric tons per day (mTPD) that has operated since 2007. The second liquefier in Leuna with the same capacity was scheduled to be online in 2021. The plant in Ingolstadt, which has operated since 1992, was decommissioned and had a capacity of 4.4 mTPD. All of these plants are based on the Claude system with liquid nitrogen pre-cooling and are provided and operated by Linde AG. Compared with the original Claude system, modern hydrogen liquefaction plants (as shown in Fig. 3) exhibit more sets of expansion turbines working at low temperatures and more heat exchangers with integrated catalytic ortho-to-parahydrogen converters. Moreover, the Claude cycle is separated from the cooling path to liquefy the hydrogen. According to calculations by Cardella *et al.* [17], one conventional modern plant with a





**Fig. 2:** Schematic description of (a) the Linde-Hampson cycle and (b) the Claude system for air/hydrogen liquefaction.

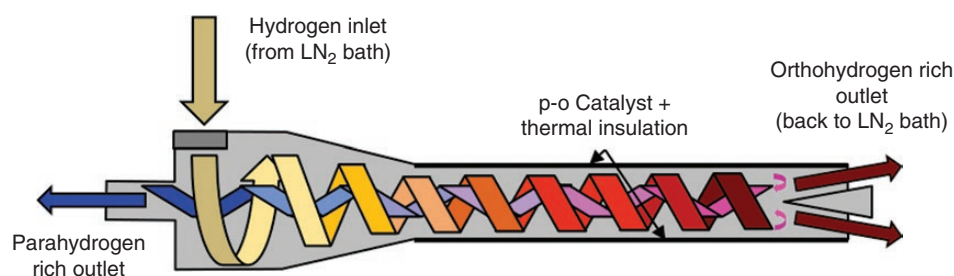


**Fig. 3:** Process flow sheet of Linde's hydrogen liquefaction plant in Leuna. Reproduced from [16] with permission from Elsevier Ltd.

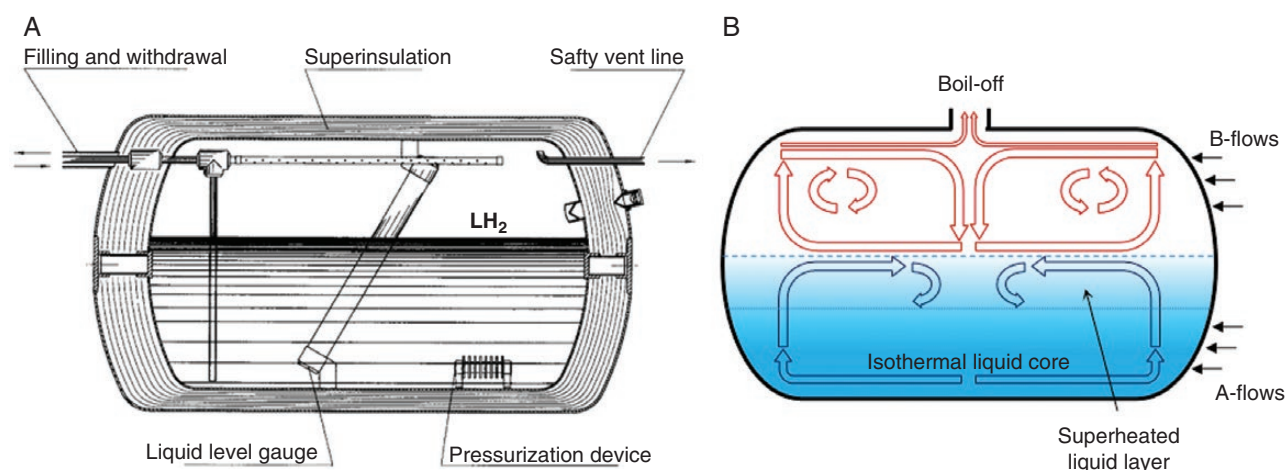
capacity of 5 mTPD consumes 10 kWh of electricity to liquefy 1 kg of hydrogen. They expected to reduce 40% of the energy consumption if the production capacity can be increased up to 100 mTPD with the application of mixed-refrigerant pre-cooling in the future.

As a potential alternative to the widely used refrigeration system based on the Claude cycle, Dr Jacob Leachman of the University of Washington and his team invented an interesting cooling system by combining a Ranque-Hilsch vortex tube with endothermic conversion of para-to-orthohydrogen conversion [18, 19]. As can be seen in Fig. 4, a pressurized stream of hydrogen (~3.5 bar) is first pre-cooled in a liquid nitrogen (LN<sub>2</sub>) bath at 77 K with an equilibrium para composition of ~50% and then injected into a vortex tube. In the swirl chamber, the hydrogen stream is accelerated to a high rotation speed and gradually separated into two fluids with different temperatures. The hydrogen molecules

in the outer shell of the rotating stream are getting warmer and rotating faster, and the molecules in the inner are getting colder and rotating slower. The para-to-ortho catalyst coating on the inner wall of the tube further endothermically converts the warmer parahydrogen into orthohydrogen. Because the insulation on the tube wall prevents thermal conduction from the environment, the thermal energy required for the conversion is extracted from the inner colder hydrogen fluid and thus enhances bulk cooling. Through a conical nozzle, the warm and orthohydrogen-rich outer stream (~120 K, 75% orthohydrogen, 1 bar) is allowed to escape the tube and is recycled, whereas the cold and parahydrogen-rich inner stream (~30 K, 25% orthohydrogen, 1 bar) is forced to return and leaves the tube through the other outlet, where it can be guided into a secondary vortex tube for further cooling or to a conventional J-T valve or flash separator for the liquefaction.



**Fig. 4:** Conceptual diagram of the conversion of para-ortho-hydrogen in a Ranque–Hilsch vortex tube (sketched on the basis of the results from [18])



**Fig. 5:** (a) A typical on-board liquid hydrogen tank system, reproduced from [20] with permission from Elsevier Ltd; (b) a sketch on heat flows in the cryogenic tank.

Although this technology has not been commercialized, the inventors declared that its efficiency in liquefying hydrogen is almost 20% over the current state of the art. Furthermore, it is a modular approach and therefore can be applied as a small to large hydrogen liquefier [19].

One major technological challenge of a cryogenic tank (as shown in Fig. 5a) to store LH<sub>2</sub> is to reduce its boil-off loss. Heat absorbed by LH<sub>2</sub> causes its evaporation. Because the metallic inner vessel is not designed to hold higher pressure, the evaporated hydrogen must be released, which results in a material boil-off loss. Thermal conduction, radiation, convection and ortho-to-para conversion are the main sources of heat leakage. Table 4 summarizes the current measures to keep the cryogenic tank thermally insulated.

State-of-the-art cryogenic tanks for LH<sub>2</sub> storage originate from the storage tank developed for LN<sub>2</sub> with barely any changes. Perlite and a vacuum of  $\sim 10^{-2}$  mbar are used for insulation and give a  $k$ -value of  $\sim 1.0$  mW/m<sup>2</sup>K. The typical boil-off loss of current LH<sub>2</sub> tanks varies from 1% to 5% per day [21]. In practice, it has become more and more popular to adequately utilize the evaporated hydrogen and thus to reduce the effective boil-off loss. In the HRS with LH<sub>2</sub> as storage, for example, low-temperature hydrogen vapour can be used to cool the hot compressed hydrogen gas. Therefore, the effective boil-off loss can be kept to <1% per day [21, 22].

Recently, many approaches have been made to further reduce the boil-off loss of LH<sub>2</sub> tanks. A representative one is to adopt the multilayer insulation technology in combination with a high vacuum (in the range of  $10^{-4}$  mbar), which is used as a standard technology to store liquid helium. The calculated boil-off loss of

LH<sub>2</sub> stored thus lies at 0.01% and 0.04% per day for large ( $4 \times 120$  m<sup>3</sup>) and small tanks (5 m<sup>3</sup>), respectively. When integrating a refrigeration system into such a multilayer insulated tank, it is possible to fully eliminate the loss [23]. In this integrated refrigeration and storage (IRAS) system, cryogenic gaseous helium is used as a coolant to absorb heat in the LH<sub>2</sub> through an emerged pipe system as shown in Fig. 6. Both of these approaches are not suitable for civil applications yet.

### 1.3 Cryo-compressed hydrogen storage (CCH<sub>2</sub>)

Although hydrogen storage in liquid form reaches a higher density (71.0 kg/m<sup>3</sup> at 20 K and 0.4 MPa) than its compressed gaseous state (39.1 kg/m<sup>3</sup> at 300 K and 70 MPa), the up-to-date unavoidable boil-off loss limits its application, especially in the case of on-board storage for automobiles. Therefore, BMW launched a study >10 years ago to investigate the opportunity to store hydrogen at low temperature, higher than 20 K, and high pressure, lower than 70 MPa, namely cryo-compressed hydrogen storage (CCH<sub>2</sub>) [24].

The essential advantage of CCH<sub>2</sub> storage is that it can achieve a higher density than LH<sub>2</sub> at relative higher temperatures, as compared in Fig. 7a. At 35 K, for example, 15 MPa of pressure is sufficient to make the hydrogen denser than its liquid state. The cryogenic hydrogen is thereby supercritical or in its two-phase region (saturated liquid and vapour) at this condition. Preparing the CCH<sub>2</sub> from gaseous hydrogen requires a multistage compression unit with a repeated compressor and cooling system in combination with a subsequent refrigeration unit, as shown in Fig. 8. It is obvious that simply increasing the pressure and decreasing

the temperature results in a very high hydrogen density, but it is less economically feasible in terms of energy consumption and storage facilities. Zhao *et al.* [25] defined a parameter  $\psi$  as the ratio of hydrogen density to the energy required for CcH<sub>2</sub> at different pressure and plotted it against the temperature. As can be seen in Fig. 7b, by increasing the pressure from 5 to 70 MPa, the  $\psi$  value grows at a decreasing rate. This means that it is economical to increase the hydrogen storage density through compression. But this advantage will be gradually neutralized if the pressure is

**Table 4:** Description of heat leakage sources and the measures against them (summarized from [21])

Heat leakage source	Measures for thermal insulation
Heat conduction through support system	Materials applied for support system with low thermal conductivity and high mechanical strength
Heat conduction through interconnecting piping system	Reduce the cross section and increase the length of the pipes
Radiation from warmer parts of the container	Shield the tank by using baffles, optimize the design and avoid direct view to warm parts
Natural convection in vapour above liquid due to heating	Minimize the A heat flows <sup>a</sup> and ensure that the B heat flows <sup>b</sup> are primarily absorbed by convection of the cold vapour. With a good tank design, B heat flows may not contribute to evaporation at all (for vapour convection in a cryogenic tank, see Fig. 5b)
Ortho-para conversion	Convert the orthohydrogen into parahydrogen during the liquefaction

<sup>a</sup>A heat flow: heat flows absorbed in the liquid resulting in evaporation of the liquid.

<sup>b</sup>B heat flow: heat flows adsorbed in the cold vapour.

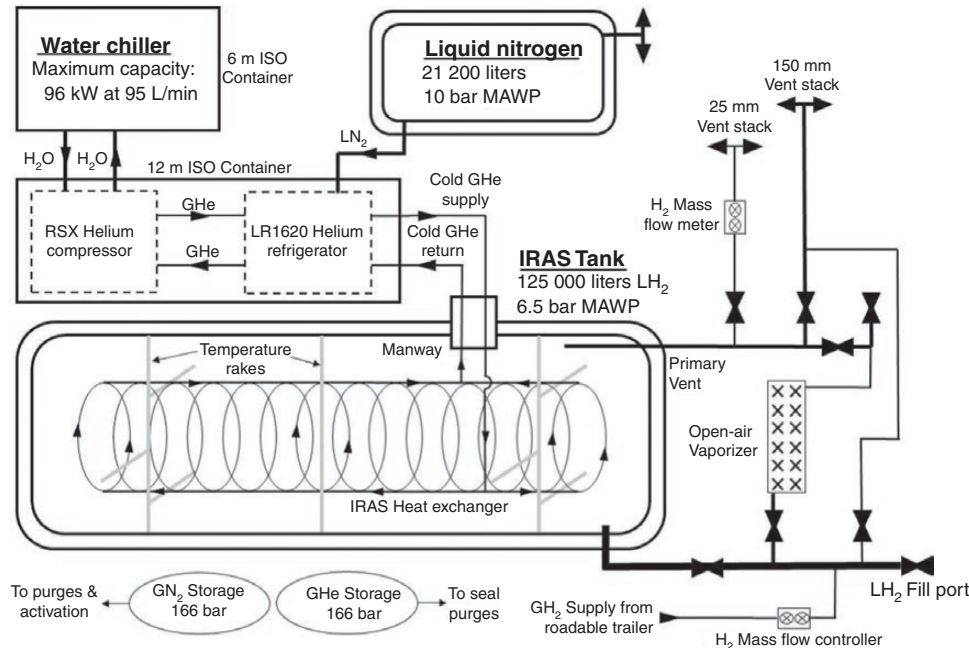
too high. On every isobaric curve at >10 MPa, a maximum value of  $\psi$  exists, which indicates the corresponding optimal temperature of CcH<sub>2</sub> storage. Furthermore, the  $\psi$  value of most CcH<sub>2</sub> prepared from gaseous hydrogen is significantly larger than that of LH<sub>2</sub> due to latent heat, which costs noticeable power during the liquefaction process.

In a joint project between BMW AG and Linde AG that started in 2011 [26], engineers used a system containing a high-pressure hydrogen cryopump and vaporizer to prepare the CcH<sub>2</sub> from LH<sub>2</sub>. Disregarding the complex liquefaction steps (Section 2.2), this process is much simpler than the CcH<sub>2</sub> production process from gaseous hydrogen (Fig. 8). If the as-prepared CcH<sub>2</sub> is directly dispensed into a fuel cell electric vehicle (FCEV), an intermediate storage unit is not necessary. Therefore, this technology could be easier to adapt to LH<sub>2</sub>-based hydrogen refuelling stations.

Unlike CGH<sub>2</sub> and LH<sub>2</sub>, the majority of studies about CcH<sub>2</sub> focus on its on-board storage applications and the related fields [27–29]. The CcH<sub>2</sub> vessel is in the praxis a combination of the CGH<sub>2</sub> pressure vessel and LH<sub>2</sub> tank. It contains in general a Type III pressure vessel for CGH<sub>2</sub> that is covered by multilayer insulation used for LH<sub>2</sub>. Among them, the vessel must be enclosed under a vacuum [30]. Therefore, the cost of the CcH<sub>2</sub> vessel will be much higher than that of the CGH<sub>2</sub> vessels and LH<sub>2</sub> tanks, and it will not be adequate for large-scale hydrogen storage. An advantage of the CcH<sub>2</sub> vessel is, of course, that it is also compatible to store CGH<sub>2</sub> [26].

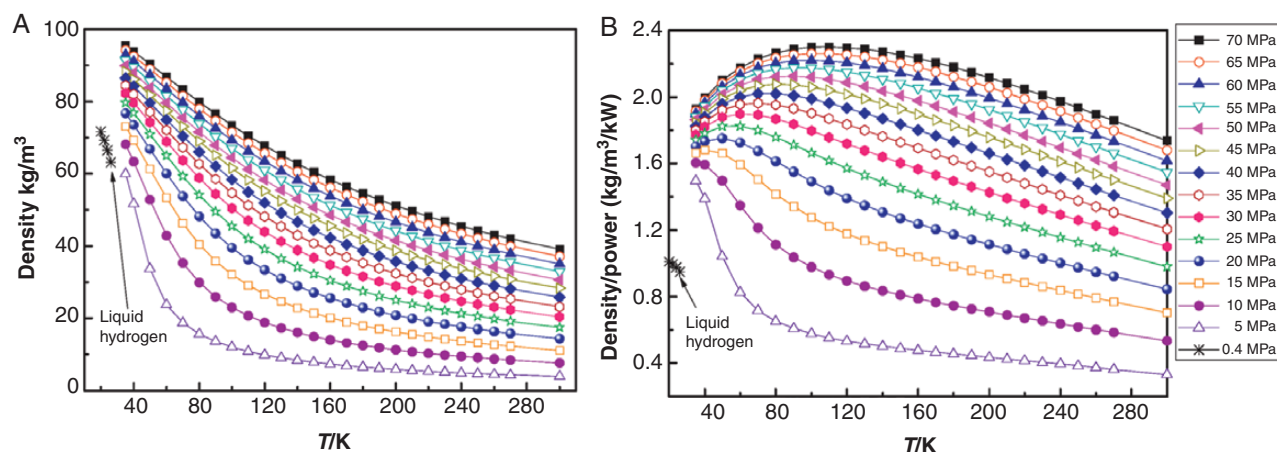
#### 1.4 Hydrogen storage in a liquid-organic hydrogen carrier

In addition to the physical-based hydrogen storage technologies introduced in previous sections, there has been an increasing interest in recent years in storing hydrogen by chemically or physically combining it with appropriate liquid or solid materials (material-based hydrogen storage). Liquid-organic hydrogen carriers (LOHCs) are one type of promising material for this purpose.

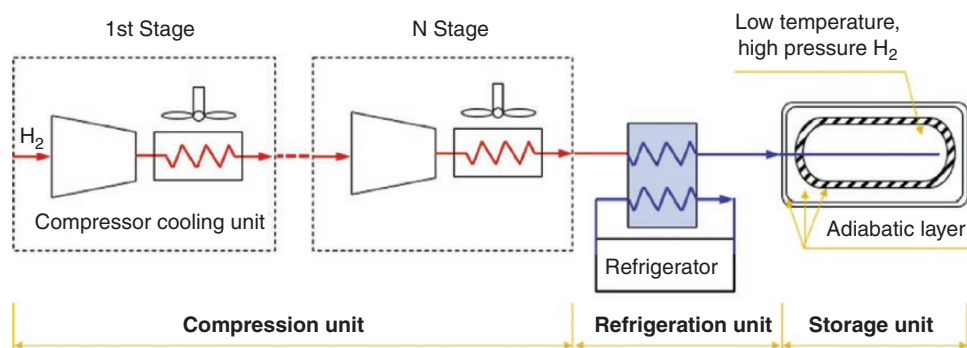


**Fig. 6:** Simplified functional diagram of the NASA-funded IRAS system used in the project ‘Ground Operations Demonstration Unit for LH<sub>2</sub> (GODU-LH<sub>2</sub>)’ [23].





**Fig. 7:** (a) isobaric densities of hydrogen at various temperatures; (b) density of hydrogen per total power consumption at different temperatures and pressures with liquid hydrogen. Influences of ortho- to parahydrogen conversion are considered. Reproduced from [25] with permission from Elsevier Ltd.



**Fig. 8:** Sketch of the processes for preparing and storing cryo-compressed hydrogen using gaseous hydrogen. Reproduced from [25] with permission from Elsevier Ltd.

At ambient temperatures, they are liquid or semi-liquid-organic substances and contain unsaturated bonds that enable them to store hydrogen molecules through a chemical reaction (hydrogenation) in the presence of catalysts. This reaction is exothermic and must be reversible. To release the hydrogen, the endothermic catalytic dehydrogenation reaction takes place under appropriate temperature and pressure conditions. Beyond this, the following criteria must be considered by designing/engineering a LOHC material [31, 32]:

- safe and non-toxic during transportation and usage;
- sufficient higher volumetric (e.g.  $>56 \text{ kg/m}^3$ ) and gravimetric (e.g.  $>6 \text{ wt\%}$ ) hydrogen storage density;
- low melting points, e.g. less than  $-30^\circ\text{C}$ ;
- relative higher boiling point, e.g.  $>300^\circ\text{C}$ ;
- sufficient chemical stability of the hydrogenated LOHC and lower energy consumption for its dehydrogenation reaction (this reveals that the hydrogen bonding energy of the LOHC should not be too low or too high; the optimal range lies between 40 and  $70 \text{ kJ/mol H}_2$ );
- sharp selectivity between the hydrogenated and dehydrogenated LOHC over a long life cycle;
- no or very few decomposed products left after the dehydrogenation reaction;
- ability to be directly integrated into current well-established fuel infrastructures;

- low production cost.

Since the early 1980s, a lot of novel work on LOHCs was carried out. However, it must be mentioned that none of the available LOHCs can meet these criteria perfectly. The state-of-the-art studies mainly focus on two material classes: homocyclic and heterocyclic compounds.

The homocyclic methylcyclohexane (MCH)/toluene is commercialized and was one of the first investigated LOHC systems. Toluene is converted by using different heterogeneous catalysts. Under ambient conditions, the liquid MCH exhibits a gravimetric hydrogen storage density of 6.2 wt%. But due to the relative higher energy demands ( $68.3 \text{ kJ/mol H}_2$ ), dehydrogenation at  $350^\circ\text{C}$  is always accompanied by the formation of coke and other side products. Using bimetallic catalysts, Pt-Sn, and catalytic supports of Mg-Al metal oxide, Yan *et al.* reported that  $>90\%$  of MCH could be dehydrogenated at  $300^\circ\text{C}$  with a hydrogen evolution rate of  $262.1 \text{ mmol/g}_{\text{met}}/\text{min}$  [33]. Decalin/naphthalene is an interesting homocyclic LOHC system. This is not only due to the high gravimetric hydrogen storage density in decalin (7.3 wt%) but also due to the fact that the dehydrogenated compound, naphthalene, is a solid at room temperature. This feature widens the application field of the decalin/naphthalene LOHC system through the innovative design of the catalyst and substrate. Using a bimetallic catalyst on granular activated carbon (Pt-Re/C) in a 'superheated liquid-film-type' state, Hodoshima *et al.* developed

a batch and a continuous reactor to dehydrogenate decalin in a temperature range of 210–280°C [34]. With the continuous reactor, hydrogen can be continuously converted from decalin with a power of 50 kW (>70% conversion), thus enabling the decalin/naphthalene LOHC to be a potential on-board hydrogen storage system for FCEV. The most promising homocyclic LOHC is a multicomponent system that contains perhydro-benzyl toluene (H12-BT)/benzyl toluene (H0-BT) and perhydro-dibenzyl toluene (H18-DBT)/dibenzyl toluene (H0-DBT) [31]. Compared with H18-DBT (65.4 kJ/mol H<sub>2</sub>, 370°C), dehydrogenation of H12-BT requires less energy (63.5 kJ/mol H<sub>2</sub>). Furthermore, H12-BT has a lower viscosity, releases hydrogen faster using a Pt/Al<sub>2</sub>O<sub>3</sub> catalyst at 270°C and produces fewer complex intermediates during the hydrogenation and dehydrogenation processes. However, its boiling point at 270°C is lower than that of H18-DBT (370°C) and this results in a higher vapour pressure at elevated temperatures. Therefore, Wasserscheid *et al.* suggested mixing H18-BT with 20% H12-BT to achieve an optimized viscosity at low temperature (10°C) and a higher rate of hydrogen release with acceptable vapour pressure [35].

As a competitor to homocyclic LOHCs, heterocyclic LOHCs, especially *N*-heterocyclic-based LOHCs, have attracted more and more attention in the last few years because of their reversibility, favourable kinetics and thermodynamics, low dehydrogenation temperature, etc. An example with these benefits is indole and its derivatives, such as *N*-methyl perhydroindole/*N*-methylindole, 2-methyl perhydro-indole/2-methylindole, 1,2-dimethyl perhydroindole/1,2-dimethyl indole LOHC system etc. However, the overall lower gravimetric hydrogen storage density (<6 wt%) may restrict them in high-end application scenarios. On the contrary, as investigated by Kempe *et al.*, the perhydro-phenazine/phenazine system is an interesting heterocyclic LOHC with a storage density of 7.2 wt% but in a solid state at room temperature [36]. Therefore, its hydrogenation (at 150°C) and dehydrogenation (at 190°C) require an aqueous-organic (dioxane/water) and organic (diglyme) solvent, respectively. In 2017, Suh *et al.* found that the perhydro-2-(*n*-methylbenzyl pyridine) (H12-BMP)/2-(*n*-methylbenzyl pyridine) (H0-BMP) system, which is liquid at ambient temperatures and exhibits a higher hydrogen storage density (6.15 wt%) [37, 38], has great potential to be easily integrated into current transportation infrastructures. The corrosion rate of H0-BMP and H12-BMP was estimated at 1a or 1b ('slight tarnish') according to the results of their copper-strip corrosion test (ASTM D130-12). The commercial catalyst Ru/Al<sub>2</sub>O<sub>3</sub> works well for its hydrogenation and so does Pd/C for its dehydrogenation. For better conversion, selectivity and higher hydrogen yield, the authors suggested applying a Pd-based heterogeneous catalyst with carbon-coated alumina support (Pd/CCA). Other types of heterocyclic compounds, namely O- and S-heterocyclic compounds, are comparatively less favourable for LOHC as a result of the formation of inconvenient products during dehydrogenation.

The hydrogenation and dehydrogenation reactions of the LOHC systems mentioned are illustrated in Fig. 9. The reaction temperatures, applied catalysts and essential physical properties of the materials are summarized in Table 5.

## 1.5 Hydrogen storage in metal hydrides

In general, as long as a solid material can physically or chemically combine with hydrogen and the resulting compound is stable at ordinary storage temperatures and able to release the hydrogen at moderate temperature and pressure, it can be used

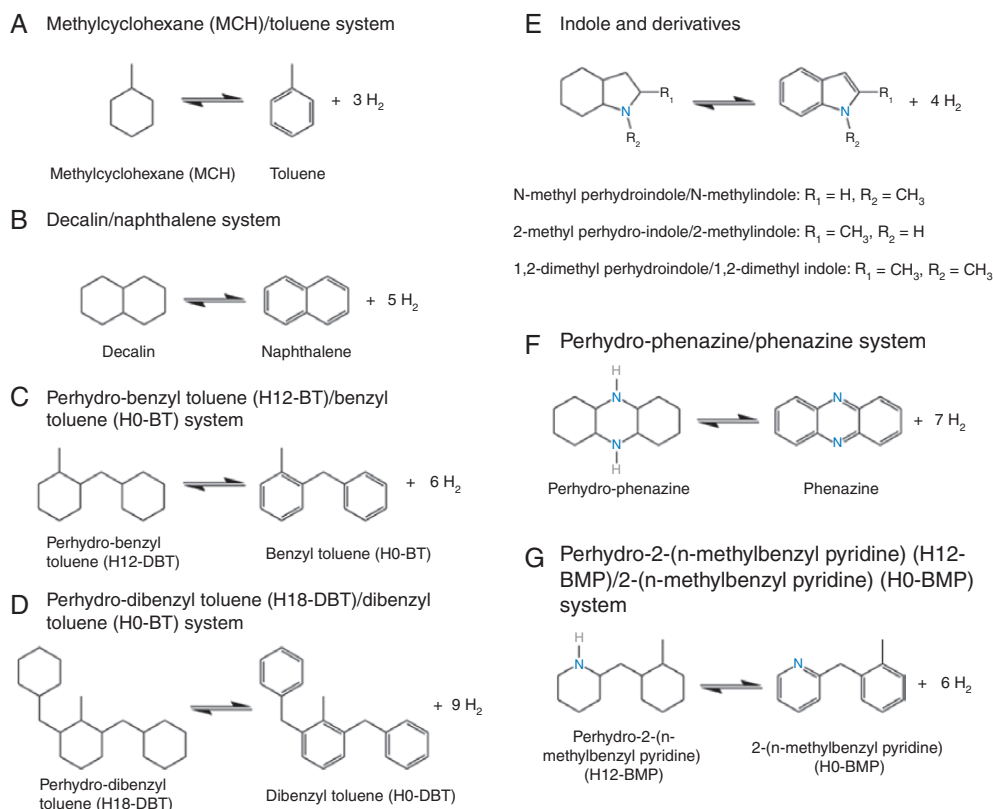
as a medium to store hydrogen in a solid form. It is obvious that solid-state hydrogen storage is the safest and is able to achieve the highest volumetric storage density (as compared in Table 6, Section 2.7).

Some intermetallic compounds, such as AB<sub>2</sub> type (Laves phase), AB<sub>5</sub> type phases (e.g. LaNi<sub>5</sub> with 1.28 wt% hydrogen storage density [39]) and Ti-based body-centred cubic alloys (e.g. FeTi with 1.9 wt% hydrogen storage density [40]), have been believed to be potential hydrogen storage materials since the 1980s. The Laves phases for hydrogen storage are AB<sub>2</sub> compounds with Ti and Zr on the A site and a combination of 3D transition atoms (V, Cr, Mn and Fe) on the B site. At room temperature and 1 MPa, V–7.4%Zr–7.4%Ti–7.4%Ni alloys (77.78%V), for example, absorb ~2 wt% of hydrogen after the 10th cycle [41]. This is mainly due to the particular crystal structure with large interstitial sites, which facilitate the dissociated hydrogen atoms on the surface to diffuse into the bulk material. The essential disadvantage of intermetallic compounds is, however, their low gravimetric hydrogen storage density. The porous/nanostructured carbon, such as the carbon nanotube, was also believed to be a potential hydrogen storage material. However, the amount of adsorbed hydrogen and the C–H binding energy (*E<sub>b</sub>*) highly depend on the specific surface area and the local arrangement of carbon (*E<sub>b</sub>*(channel) > *E<sub>b</sub>*(grooves) > *E<sub>b</sub>*(pores) > *E<sub>b</sub>*(surface) [42]). Furthermore, since the production of a large batch of pure carbon nanotubes with narrow morphological deviations and reliable characterization methods is still lacking, the reported experimental results for hydrogen storage density therein are scattered over several orders of magnitudes and are hardly reproducible [43–45].

Hence, in order to obtain a relative higher gravimetric density, the selection of storage materials has to be restricted to the light solid elements, namely Li, Be, B, Na, Mg and Al. In addition to considering the storage density, the following properties should be taken into account [46]:

- low dissociation temperature and moderate pressure;
- low heat dissipation during exothermic hydride formation;
- low heat of formation in order to minimize the energy necessary for hydrogen release;
- limited energy loss during charge and discharge of hydrogen (limited spontaneous hydrogen release);
- fast kinetics;
- cycle stability;
- high stability against oxygen and moisture for long cycle life;
- low cost of recycling and charging infrastructure;
- safety.

Because of the high hydrogen uptake potential, relative lower cost and good reversibility, metal hydrides based on Mg and its alloys are the most promising materials for solid-state hydrogen storage. At high temperatures and pressures, say 400°C and 3 MPa, hydrogen molecules react with Mg and form magnesium hydride (MgH<sub>2</sub>). Theoretically, MgH<sub>2</sub> contains 7.6 wt% of hydrogen. But it can never be achieved in the bulk material. Hydrogen uptake by Mg is a dissociative chemisorption on the surface of Mg followed by hydrogen diffusion. As the reaction proceeds, the MgH<sub>2</sub> layer grows, which is nearly impermeable and thus terminates further hydrogenation. Moreover, because of the high oxygen affinity of Mg, the compact oxide layer formed after a short exposure to air obstructs hydrogen diffusion. Raising the surface-to-volume ratio is the easiest way to increase the hydrogen storage density and the hydrogenation rate. It was found two decades ago that



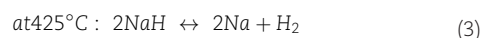
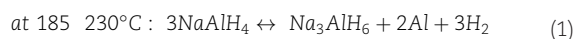
**Fig. 9:** Illustration of hydrogenation and dehydrogenation reactions of (a) methylcyclohexane (MCH)/toluene, (b) decalin/naphthalene, (c) perhydro-benzyl toluene (H12-BT)/benzyl toluene (H0-BT), (d) perhydro-dibenzyl toluene (H18-DBT)/dibenzyl toluene (H0-BT), (e) indole, (f) perhydro-phenazine/phenazine and (g) perhydro-2-(n-methylbenzyl pyridine) (H12-BMP)/2-(n-methylbenzyl pyridine) (H0-BMP) LOHC systems.

after 120 min at 300°C, the hydrogen adsorption in magnesium particles with micrometre-sized grains was neglectable, whereas nanocrystalline particles with a grain size of 20–30 nm adsorbed  $\leq 6$  wt% of hydrogen with an enhanced hydrogenation rate compared with that with a grain size of 50 nm (see Fig. 10a) [47]. Ball milling was applied, thereby, not only to create new surfaces and nanocrystalline structures but also to introduce defects on the surface and in the interior of magnesium, which significantly promote hydrogen diffusion.

To maintain the cycle stability of  $MgH_2$ , magnesium particles must be well protected against gaseous impurities that slow down or inhibit the hydrogen uptake, especially  $N_2$ , O,  $CO_2$  and CO [49]. Agglomeration of Mg particles during hydrogenation/dehydrogenation cycles also reduces cyclability. Optimized cyclability was experimentally confirmed if several percent of Ni (stable for  $\leq 800$  cycles, see Fig. 10b) or V (stable for  $\leq 2000$  cycles) were doped in the  $MgH_2$  particles [48, 50]. Furthermore, Ni and V performed in  $MgH_2$  as catalysts for enhanced hydrogen affinity and promoted hydrogen dissociation, respectively. In addition to these, the introduction of a small amount of other metallic (e.g. Al, Ge, Fe, Cu, Pd, Nb, Ti, Mn and Cr), oxide (e.g.  $Cr_2O_3$ ,  $V_2O_5$ ,  $Fe_3O_4$ ,  $TiO_2$ ,  $Nb_2O_5$ ), halide (e.g. NaF, NaCl,  $MgF_2$ ,  $CrCl_3$ ) and intermetallic (e.g. La–Ni, ZrNi, ZrMn, and Mg–Ni systems) additives was proven as effective in improving the hydrogenation/dehydrogenation performance of  $MgH_2$  [46, 51]. Through innovative material engineering, many new Mg-based hydride materials, such as  $Mg_2Fe(Ni)_6$  nanowires [52], have been frequently reported in recent years. However, the comparatively lower gravimetric storage density and higher cost in the material and production process may restrict their commercialization potential.

In the practical application of Mg-based hydrides for hydrogen storage, the hydride particles are formed into porous pellets via powder metallurgy processes [54]. For better thermal conductivity, the researchers from Fraunhofer IFAM in Dresden, Germany mixed  $Mg_{90}Ni_{10}$  particles with 10 wt% of expanded natural graphite (ENG) as shown in Fig. 11 [53]. Using this mixture, the compacted pellets at 300 MPa absorbed  $\leq 4$  wt% of hydrogen within 10 min at 180°C and 2 MPa [55]. Fig. 11a and b shows a photo of the compacted pellets and an optical micrograph of a compacted  $MgH_2$ –ENG, respectively.

Complex hydride is a class of Mg-free lightweight materials for solid-state hydrogen storage. The alanates and borates, mainly  $NaAlH_4$ ,  $LiAlH_4$  and  $LiBH_4$ , are especially interesting because of their potential to achieve higher gravimetric hydrogen storage density. However, their hydrogenation is a three-step reaction. Taking  $NaAlH_4$  as example:



Both high temperatures (425°C for NaH and 680°C for LiH) and catalysts are necessary to fully dehydrogenate the complex hydrides as summarized in [46].

## 1.6 Hydrogen storage as power fuels

There is a special class of material-based hydrogen carriers, either in gaseous or liquid form, that can not only combine with hydrogen molecules and release them according to demands, but also can be used as fuels. These hydrogen carriers

**Table 5:** Essential hydrogenation and dehydrogenation parameters of the LOHC system, as mentioned in the context and their physical properties (edited according to the results in [32])

LOHC system	Hydrogenation		Storage density (wt%)	Dehydrogenation		Melting point (°C)		Boiling point (°C)		Flash point (°C)	
	H <sub>2</sub> -lean	H <sub>2</sub> -rich		Temperature (°C)	Catalyst	ΔH (kJ/mol H <sub>2</sub> )	H <sub>2</sub> -lean	H <sub>2</sub> -rich	H <sub>2</sub> -lean	H <sub>2</sub> -rich	H <sub>2</sub> -lean
Toluene		Methyl-cyclohexane	6.2	n/a	n/a	68.3	-95	-126	111	101	6
Naphthalene		Decalin	7.3								
Dibenzyl toluene		Perhydro-dibenzyl toluene	6.2								
Benzyl toluene		Perhydro-benzyl toluene	6.2	80–300							
1-Methyl indole		1-Methylperhydro indole	5.8	160–190	Ru/Al <sub>2</sub> O <sub>3</sub>	51.9	95	n/a	238	180	110
2-Methyl indole		2-Methylperhydro indole	5.8	120–170	Ru/Al <sub>2</sub> O <sub>3</sub>	n/a	60	n/a	272	178	141
1,2-Dimethyl indole		1,2-Dimethyl perhydroindole	5.23		Ru/Al <sub>2</sub> O <sub>3</sub>	n/a	55	<-15	260.5	≥260.5	≥230
Phenazine		Perhydro-phenazine	7.2	150							
2-(n-Methylbenzyl pyridine)		Perhydro-2-(n-methylbenzyl pyridine)	6.15		Ru/Al <sub>2</sub> O <sub>3</sub>	67.3	-50.1	-19.3	291	293	n/a



**Table 6:** Comparison of the key technical features, energy consumption and application field between different hydrogen storage technologies

Items		Physical-based H <sub>2</sub> storage					Material-based H <sub>2</sub> storage			
		CGH <sub>2</sub>			LH <sub>2</sub>	CcH <sub>2</sub>	Power fuels		LOHC	Metal hydride
		35 MPa	70 MPa	UHS			NH <sub>3</sub>	CH <sub>3</sub> OH		
Technical features	Gravimetric density (wt%, without tank)	100	100	100	100	100	17.7 [56]	12.5 [56]	6.2 [31]	1.8 (FeTiH <sub>2</sub> ) [40] 10 (LiAlH <sub>4</sub> ) [71] 7.6 (MgH <sub>2</sub> ) [72]
	Gravimetric capacity (wt%, with tank)	4.2 (III) <sup>a</sup> [73] 5.5 (IV) <sup>a</sup> [73]	3.6 (III) [73] 5.2 (IV) [73] 5.7 (IV) [5]		7–12 [74]	10 (66 K, 35 MPa) [27] 8.7 (72 K, 50 MPa) [27] 7 (78 K, 70 MPa) [27]	n/a	n/a	n/a	n/a
	Volumetric density (g/L, without tank)	23.3 (300 K) [75]	39.0 (300 K) [75]	n/a	71.7 (20 K, 0.4 MPa) [25]	60 (35 K, 5 MPa) [25] 67.8 (120 K, 70 MPa) [25] 69.1 (66 K, 35 MPa) [27] 74.7 (72 K, 50 MPa) [27] 80.3 (78 K, 70 MPa) [27]	107 (293 K) [76] 123 (1 MPa) [56]	99 [56]	56 [32]	150 [54] 86 (MgH <sub>2</sub> ) [56] 110 (MgH <sub>2</sub> ) [72]
	Volumetric capacity (g/L, with tank)	17.4 (III) [73] 17.6 (IV) [73]	25 (III) [73] 26.3 (IV) [73]	n/a	40 [74]	50.9 (66 K, 35 MPa) [27] 51.3 (72 K, 50 MPa) [27] 49.6 (78 K, 70 MPa) [27]	n/a	n/a	n/a	n/a
	Operating temperature (°C)	−40 to 80	−40 to 80	Ambient temperature	−253	Cryogenic temperatures	n/a	n/a	n/a	n/a
	Cycle life	5500 for LDV; 15 000 for HDV <sup>b</sup>	5500 for LDV; 15 000 for HDV <sup>b</sup>	1–10 cycles/year <sup>c</sup>		5500 for LDV; 15 000 for HDV <sup>b</sup>	n/a	n/a	n/a	n/a
	System fill rate (kg/min)	1.5–2 [77]	1.5–2 [77]	n/a	1.5–2 [77]	1.5–2 [77]	n/a	n/a	n/a	n/a
	H <sub>2</sub> release rate (g/s)	n/a	>2 [71]	n/a	n/a	n/a	n/a	n/a	0.25 <sup>d</sup>	0.005–0.28 [78]
		Physical-based hydrogen storage					Material-based storage			
		CGH <sub>2</sub>			LH <sub>2</sub>	CcH <sub>2</sub>	Power fuels		LOHC	Metal hydride
Energy consumption (kWh/kgH <sub>2</sub> )		35 MPa	70 MPa	UHS			NH <sub>3</sub>	CH <sub>3</sub> OH		
	To prepare storage condition	1–2.8 [79]	1–3.3 [79]	n/a	6–10 [17]	n/a	8.2–13.3 (calculated in the text)	−2.3 [68]	−9 <sup>e</sup> [31]	Pressure + exothermic
	To release H <sub>2</sub>	0	0	n/a	0	0	6.3 [56]	6.7 [56]	9 <sup>f</sup> [31]	10.3 (MgH <sub>2</sub> ), 0.97 (AlH <sub>3</sub> ) [56]
	TRL	>9	>9	4–6	>9	4–6	> 9	>9	4–6	4–6
	Long-distance H <sub>2</sub> transport	Yes <sup>g</sup>	No	No	Yes	No	Yes	Possible	Yes	possible
	Transport to HRS	Yes <sup>h</sup>	No	No	Yes	No				
	Long-term H <sub>2</sub> storage	Yes <sup>h</sup>	No	Yes	No	No	Yes	Possible	Yes	possible
	H <sub>2</sub> storage at HRS	Yes <sup>h</sup>	No	No	Yes	No	No	No	No	no
	H <sub>2</sub> storage in FCEV	Yes	Yes	No	Possible	Possible	n/a	n/a	n/a	n/a

Table 6. Continued

Items		Physical-based H <sub>2</sub> storage					Material-based H <sub>2</sub> storage		
		CGH <sub>2</sub>			LH <sub>2</sub>	CcH <sub>2</sub>	Power fuels		Metal hydride
		35 MPa	70 MPa	UHS			NH <sub>3</sub>	CH <sub>3</sub> OH	
Application fields	Current technical limitations for application	Relatively low storage system capacity (gravimetric and volumetric)	Relatively low storage system capacity, high cost of the tank, only for LDV	Difficulties in finding a geographically suitable UHS site	Boil-off; energy consumption for the liquefaction process	Validation of performance, durability, safety, and mass production capability due to higher cost [30]	For all: high energy consumption for dehydrogenation process; gas separation/purification needed for CH <sub>3</sub> OH: DAC for green methanol production for NH <sub>3</sub> ; high energy consumption for the hydrogenation process		High material cost, low H <sub>2</sub> release rate, relatively high release temperature
	Current/potential application	H <sub>2</sub> storage in HDV	H <sub>2</sub> storage in LDV	A great amount of H <sub>2</sub> storage for a long period	H <sub>2</sub> transport to HRS; H <sub>2</sub> storage in HDV (in R&D)	H <sub>2</sub> storage in HDV and LDV (in R&D)	Long-distance H <sub>2</sub> transport; long-term H <sub>2</sub> storage, H <sub>2</sub> storage in HDV and LDV possible		

<sup>a</sup>III: type III pressure vessel; IV: type IV pressure vessel.

<sup>b</sup>Cycle life as regulated in SAE J2579; LDV, light-duty vehicle; HDV, heavy-duty vehicle.

<sup>c</sup>For aquifers as well as depleted oil and gas fields: 1 to maximum of 2 cycles/year; for salt caverns: ≤10 cycles/year [11].

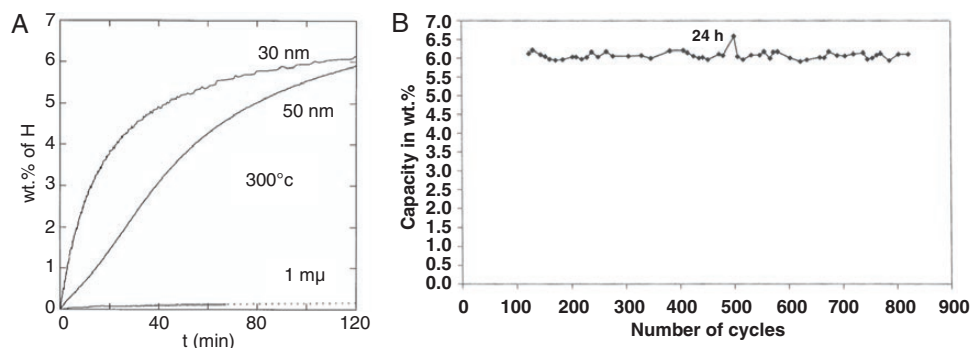
<sup>d</sup>From the technical datasheet of 'Release Box 10' from Hydrogenious LOHC technologies GmbH [80].

<sup>e</sup>Heat released during catalytic hydrogenation of H<sub>2</sub>-DBT at 10–50 bar and 80–320°C.

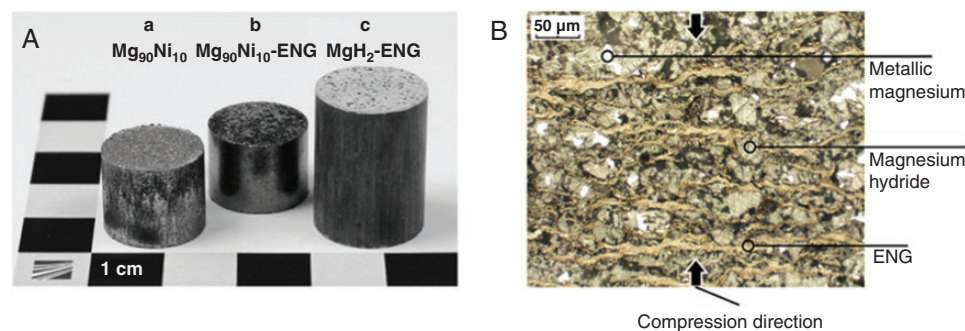
<sup>f</sup>Heat consumed during catalytic dehydrogenation of H<sub>18</sub>-DBT at 1–5 bar and 260–320°C.

<sup>g</sup>Or with lower pressure, CGH<sub>2</sub> transportation through pipeline and/or shipping (see Sections 3.2 and 3.3).

<sup>h</sup>Or with lower pressure.



**Fig. 10:** (a) Effect of grain size on hydrogen absorption of ball-milled magnesium powders, reproduced from [47] with permission from Elsevier Ltd; (b) cyclic stability of chemical Ni-doped Mg (at 503–643 K and 4.0 bar) reproduced from [48] with permission from Elsevier Ltd.



**Fig. 11:** (a) Compacted metal hydride pellets, (b) optical micrograph of an MgH<sub>2</sub>-ENG composite containing 25.5 wt% of ENG compacted at 600 MPa. Reproduced from [53] with permission from Elsevier Ltd.

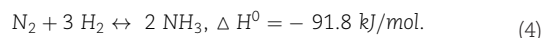
are called 'power fuels' or 'E-fuels' if the hydrogen is generated using electricity. In general, electrochemically synthesized methane, Fischer-Tropsch fuels (including synthetic diesel, petrol,

etc.), methanol and its derivatives, ammonia and hydrogen themselves are counted as power fuels, as shown in Fig. 12. However, except for ammonia and methanol with higher gravimetric and

volumetric storage density (ammonia: 17.7 wt%, 123 g/L; methanol: 12.5 wt%, 99 g/L) [56] as well as relatively lower energy consumption and less complexity in hydrogenation and dehydrogenation reactions, most of the power fuels are economically not suitable to be deployed as hydrogen carriers.

### 1.6.1 Ammonia

The Haber–Bosch process is a mature process and the main industrial procedure to produce ammonia throughout the world. Using a metallic catalyst, e.g. Fe, it converts gaseous hydrogen and nitrogen into ammonia at high temperature and pressure (typically 300–500°C and 20–35 MPa [57]):



The traditional Haber–Bosch process is usually connected to a steam methane reforming process, which delivers hydrogen as a reactant. The overall energy consumption for this is ~7.78–9.06 kWh/kg ammonia [58]. As an alternative, electrolysis provides the possibility of generating green hydrogen. Demonstration projects from industrial and academic pioneers, including ThyssenKrupp, Proton Ventures BV and Morris Plant from the University of Minnesota, showed that large-scale alkaline-electrolysis-based conventional Haber–Bosch plants (production capacity:  $10^3$ – $10^5$  kg ammonia per hour) require ~9–11 kWh to synthesize 1 kg of ammonia [59]. Taking into account the energy required to electrolyse water (~3.8–4.4 kWh/Nm<sup>3</sup> of hydrogen, corresponding to 7.3–8.4 kWh/kg of ammonia) and to separate/produce nitrogen gas from the air (0.25 kWh/kg), it can be estimated that the net energy input to produce 1 kg of ammonia directly using hydrogen and nitrogen as feedstock is ~1.45–2.35 kWh [59]. This is equivalent to 8.2–13.3 kWh to store 1 kg of hydrogen in the form of ammonia. The higher heating value (HHV) of 1 kg of hydrogen is 39.4 kWh/kg<sub>H<sub>2</sub></sub>.

Unlike hydrogen, ammonia can be easily liquefied at –33°C under atmospheric pressure or at 20°C under a pressure of 7.5 bar. Therefore, it is the most conventional way to store large amounts of ammonia (between 4500 and 45 000 t) in its liquid form. According to storage scales, application fields and customer demands, pressure storage at ambient temperature in pressure vessels (typically at 16–18 bar) and reduced pressure storage at ~0°C in insulated pressure vessels (typically at 3–5 bar) are common alternative ways for ammonia storage with smaller capacity (<270 t and between 450 and 2700 t, respectively) [60].

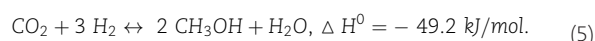
The cracking of ammonia into hydrogen and nitrogen occurs slowly at 200°C. To fully dehydrogenate ammonia at an acceptable rate, a higher temperature (>650°C) and a catalyst (Ru/SiO<sub>2</sub>) are inevitable [61]. This process consumes ~6.3 kWh to release 1 kg of hydrogen [56]. With a significantly lower theoretical thermodynamic energy consumption of 1.55 kWh/kgH<sub>2</sub>, electrolysis or electro-oxidation of ammonia was thought to be a potential alternative to thermal cracking. Unfortunately, this value does not account for the reaction kinetics. Using Pt-based catalysts (Pt–Rh, Pt–Ir, and Pt–Ir–Rh), its practical energy consumption is approximately an order of magnitude higher (14–18 kWh/kgH<sub>2</sub>) [62–64].

Compared with these indirect application scenarios, direct ammonia combustion for power generation using an ammonia-based solid-oxide fuel cell (SOFC) or a gas turbine is more favourable because of its efficiency [59]. Although both are currently in the demonstration stage, they are believed to be very promising CO<sub>2</sub>-free technologies for small- and large-scale

power generation, respectively. According to the green ammonia road map of the Danish company Haldor Topsøe, the electrical efficiency through direct use of ammonia for SOFC will be >60% of its lower heat value (LHV) [65]. As a result of low laminar burning velocity, high ignition temperature, slow burning speed and low flame stability, ammonia has to be mixed with other fuels, e.g. methane and coal, before it is burnt in the gas turbine. Further development of state-of-the-art gas turbines that are 100% ammonia-capable is on the way [66]. Fig. 13 illustrates an overview of the main components of the ‘power-to-ammonia-to-power’ pathway.

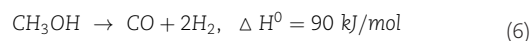
### 1.6.2 Methanol

The process of storing hydrogen in the form of methanol is mature and has already been commercialized since the early twentieth century, where carbon dioxide is hydrogenated on the surface of Cu-based heterogeneous catalysts, such as Cu/ZrO<sub>2</sub>, Cu–ZnO/ZrO<sub>2</sub>, etc., at a temperature of ~200–300°C and a pressure of ~5–10 MPa [67, 68]:

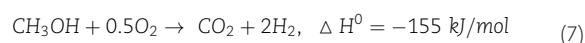


Therefore, the mechanism is the same for methanol synthesis from fossil fuel-based syngas, as confirmed experimentally [69]. Carbon dioxide, as a hydrogen carrier, can be collected in multiple ways. However, it should be noted that the current low-cost carbon dioxide from various industry sources, such as power plants and steel and cement factories, is fossil-based. Although carbon is used twice in this scenario, the carbon footprint of the overall process is positive as long as the carbon dioxide generated by the dehydrogenation and/or burning of methanol is released into the atmosphere. Reuse of the emitted carbon dioxide lowers its carbon footprint, but carbon capture and storage technology reduces its cost-competitiveness. Hence, it is widely accepted that, in the long term, carbon dioxide obtained from the atmosphere either directly by direct air capture (DAC) or through biomass will become more and more attractive. Fig. 14 illustrates these two categories of carbon dioxide feedback to produce methanol.

Because the hydrogenation reaction of carbon dioxide is exothermic, the process is able to be coupled with a heat exchanger to distil methanol from its water solution. Purified methanol can be used as an industrial feedstock to produce olefins (methanol-to-olefins or MTO), methyl tert-butyl ether, formaldehyde, acetic acid, dimethyl ether, etc., or as an alternative fuel for vehicles and heating. If methanol is produced only to store hydrogen, there is basically no need to separate it from water. Along the reverse direction of the reaction, as shown in Equation (5), at 230–330°C, the steam from the methanol–water mixture will be transformed into carbon dioxide and hydrogen in the presence of a Cu-based heterogeneous catalyst. Compared with other catalytic reactions of methanol to release hydrogen, methanol steam reforming is the most favourable because of its higher hydrogen yield per methanol molecule and relatively lower energy consumption (reverse direction of Equation (5) with 6.7 kWh/kg H<sub>2</sub>) [56, 70]. This relates to methanol decomposition (MD):



and partial oxidation of methanol (POM):



## 1.7 Technology comparison and discussion

Based on the introduction described above and our elaborate literature research and discussions with internal and external

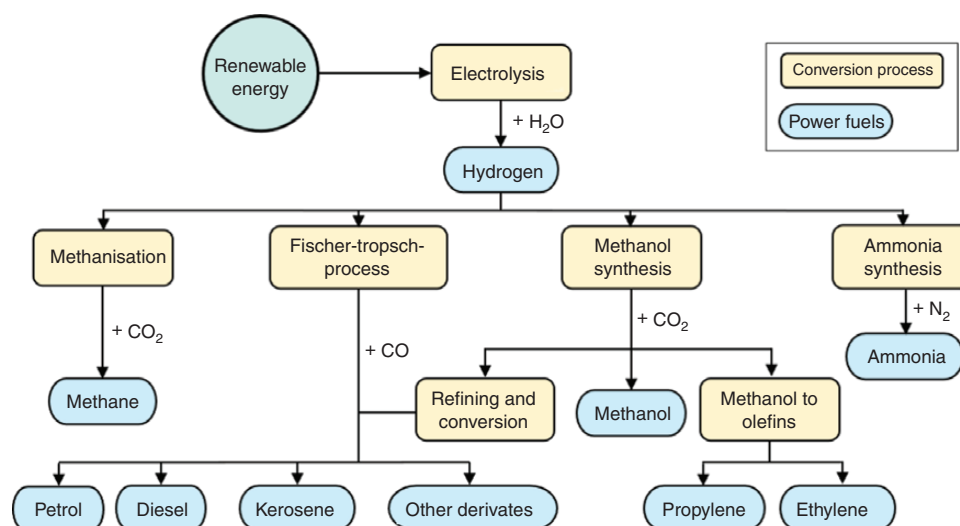


Fig. 12: Simplified process flow to convert power and/or hydrogen into power fuels and their main application fields.

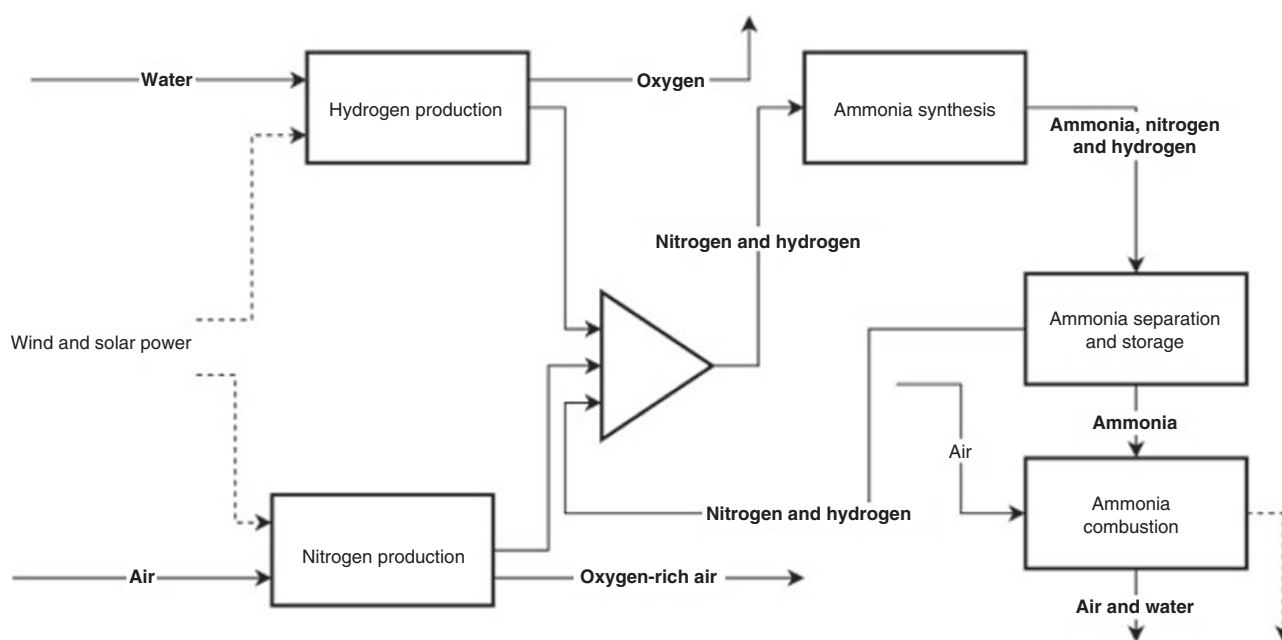


Fig. 13: Process flow of storage of electrolysis-generated hydrogen in the form of ammonia and ammonia combustion for power generation ('power-to-ammonia-to-power') [59].

experts, in this section we make a comprehensive comparison between different hydrogen storage technologies in three categories: key technical features, energy consumption and adequate application field (see Table 6).

The key technical features mostly consist of the five factors to evaluate the storage system suggested by US-DOE as listed at the beginning of this section. In terms of gravimetric and volumetric hydrogen storage capability, values without and with consideration of vessel/tank weight (corresponding to pure density and system capacity) are taken into account. It is obvious that the physical-based hydrogen storage technologies have the highest gravimetric density (100%), whereas the material-based technologies exhibit generally larger volumetric density. This makes the material-based carriers promising candidates for medium-to long-term hydrogen storage and long-distance transportation. Although the volumetric density of  $LH_2$  is comparable to

theirs, its cryogenic temperature and boil-off issue make  $LH_2$  preferable as a short-term storage solution. For the application of hydrogen as fuel in FCEVs, so far, no commercialized case using material-based hydrogen carriers is known. Due to the long cycle life of the system, high system fuel rate and hydrogen release rate and of course the purity,  $CGH_2$  is hitherto the only on-board hydrogen storage solution. In order to increase the storage density, developments in on-board  $LH_2$  and  $CcH_2$  have become more and more popular among the major automotive manufacturers.

The category of energy consumption focuses, on the one hand, on the energy required to achieve the storage conditions, such as the electricity used for the hydrogen compression and liquefaction, the energy used to combine the hydrogen with the chemical carriers, etc. On the other hand, it considers the energy needed to drive the dehydrogenation reactions. Except for



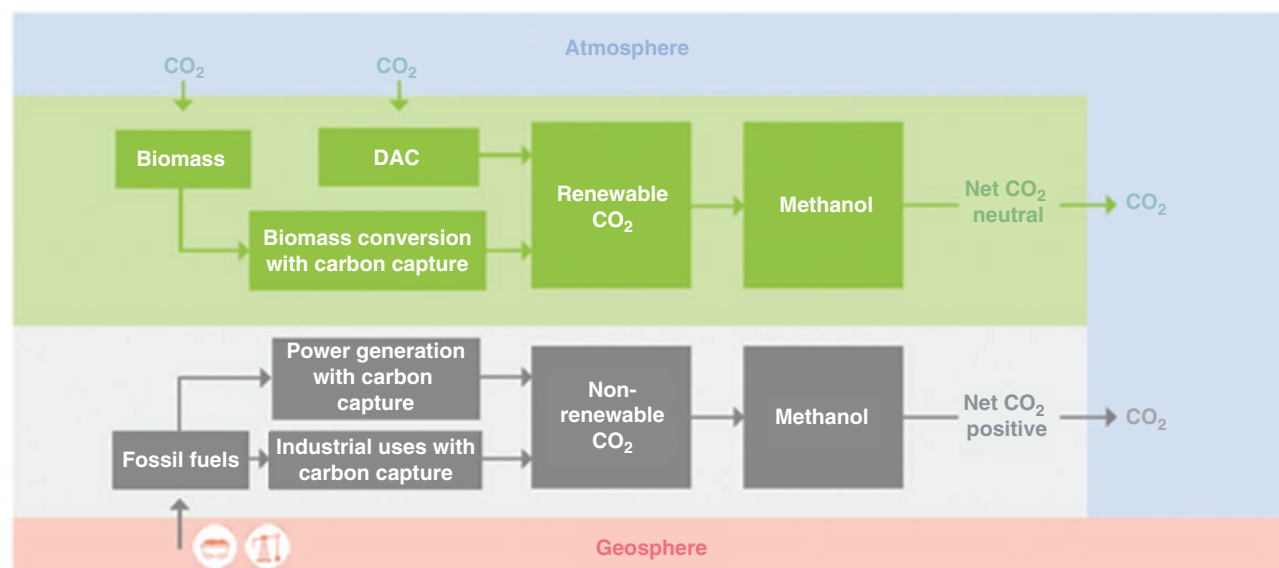


Fig. 14: Source of carbon dioxide as a hydrogen carrier [67].

CGH<sub>2</sub> and LOHC, one has to spend about one-third of the energy contained in hydrogen (LHV) or more to store it. LOHC is believed to be the most energy-saving hydrogen storage technology. However, this understanding is based on the full utilization of the heat released during the hydrogenation process. In the case of using LOHC for long-distance hydrogen transportation, the sites for hydrogenation and dehydrogenation are usually geographically far apart and probably not in the same country.

Since every hydrogen storage technology has its specific advantages and limitations and there is no 'one for all' solution for different application scenarios. In the last part of Table 6, we list some of our suggestions as examples.

## 2 Hydrogen transportation

Depending on hydrogen volumes, delivery distances and local circumstances [81], hydrogen can be transported from the production site and distributed to the end consumer in multiple ways. As shown in Fig. 15, at present, there are three main categories based on currently existing and mature gas transportation systems: road transportation, pipeline transportation and shipping.

In the case of road transportation, hydrogen is transported either in its compressed gaseous form or in liquid form via trucks/trailers. The mature hydrogen storage technologies, pressure vessels and cryogenic liquid tanks as reviewed in Sections 2.1 and 2.2, are used. Similarly to natural gas, pressurized gaseous hydrogen can be transported through pipelines, too. Although the investment cost for pipeline transportation is high, it is economically efficient for transporting large quantities of hydrogen and is therefore well suited as a transportation method for delivering hydrogen to large industrial users. Shipping is an alternative way to transport hydrogen in large amounts and is especially convenient for intercontinental transport. Therefore, hydrogen can be delivered not only in its elemental form (CGH<sub>2</sub>, LH<sub>2</sub>) but also in its compound form (LOHC, ammonia).

In addition to these major hydrogen transportation options, there exist other innovative methods and ideas, such as the air transport of hydrogen via Zeppelin airships. However, since there

is no practical example or relevant data available, they are excluded from this paper.

### 2.1 Road transportation of hydrogen

#### 2.1.1 Compressed gaseous hydrogen trailer

For a small hydrogen demand, the transportation of pressure vessels filled with compressed hydrogen is the simplest way. In case of larger hydrogen demands, several Type III or IV pressure vessels (Section 2.1) can be fixed in standard containers or a protective frame, and be towed by truck. Taking into account the cost and safety factors, the pressure of hydrogen is normally kept at between 20 and 50 MPa, which means that one truck can transport 200–1000 kg of hydrogen. In the gas container modules provided by Hexagon Purus GmbH, for example, containers with varying lengths from 3 to 12 m consisting of 22–103 vertically installed Type IV pressure vessels can carry 240–1115 kg of hydrogen at a pressure of 50 MPa [82]. The gas tube trailers that deliver natural gas are also suitable for hydrogen transportation. Thus, Type III vessels are most commonly used and horizontally bundled together. The maximum hydrogen pressure is normally regulated at 25 MPa in the USA, regardless of exceptions [83]. This results in a hydrogen capacity of ~380 kg per trailer. When replacing Type III vessels with Type IV, one tube trailer would be able to carry 560–900 kg of hydrogen. However, CGH<sub>2</sub> trailers are only suitable for short-distance hydrogen transportation (100–200 km) with customers with small hydrogen needs [84], e.g. hydrogen delivery to low-capacity refuelling stations.

#### 2.1.2 Liquid hydrogen trailer

Alternatively, hydrogen can be transported in its liquid form. The delivery of hydrogen using LH<sub>2</sub> trailers is particularly suitable for medium distances (>130 km according to a case study for Germany [85]). Here, hydrogen is liquefied at a central liquefaction plant and delivered to the customers. Since the volumetric storage density of LH<sub>2</sub> is significantly higher than that of CGH<sub>2</sub> (see Table 6), one LH<sub>2</sub> trailer can transport much larger amounts of hydrogen compared with CGH<sub>2</sub> trailers.

The LH<sub>2</sub> trailer with a 13.7-m-long cryogenic tank provided by Linde AG, for example, can transport ~4000 kg of hydrogen at 20 K [86]. The boil-off issue as introduced in Section 2.2 is an essential technical challenge for the transportation of LH<sub>2</sub>. However, the cryogenic tank designed for transportation can hold a pressure of 12 bar, which is three to five times higher than that of stationary bulk hydrogen storage tanks [86]. As marked on Linde's LH<sub>2</sub> trailer #7016, if the tank is filled with 3853 kg of hydrogen (91% full), the vapour pressure in the trailer is expected to increase from 2.1 to 3.4 bar in 158 hours [22]. This means that in a normal delivery run, the vented hydrogen will not be released into the atmosphere but be taken back to the liquefaction plant and recycled.

It must be mentioned that it is impossible to deliver all of the CGH<sub>2</sub> and LH<sub>2</sub> to the customer that has been transported. The residual amount of hydrogen remaining in the CGH<sub>2</sub> trailer is correlated with the pressure level of the supply chain. For liquid delivery, in order to maintain the cryogenic temperature, ~10% of the liquid should remain in the LH<sub>2</sub> tank [86].

## 2.2 Pipeline transportation of hydrogen

Like natural gas, gaseous hydrogen can be transported using pipelines. This is the most economical way to transport hydrogen in great amounts, and therefore especially satisfies the large hydrogen demands in densely populated and industrialized regions. However, it is obvious that investing in a completely new pipeline system to transport hydrogen will be costly. Hence, as soon as conditions permit, the repurposing of existing natural gas pipelines for hydrogen transportation would be a preferred, cost-minimizing solution.

Thanks to the higher compressibility factor of hydrogen (slightly larger than 1), its pressure drop in a pipeline over a long distance is significantly lower than that of natural gas. Therefore, it is possible to decrease the inlet pressure to transport pure hydrogen in a pipeline to 2–3 MPa [87]. However, because of the lower heating value of hydrogen, hydrogen transportation is less energy-efficient than that of natural gas. In addition to this, a major risk from the introduction of hydrogen in metallic pipe-

lines is the potential of material failures arising from hydrogen migration. There are two main mechanisms that contribute to the degradation of pipeline materials: the degradation of heat-affected zones (HAZ) and fatigue crack growth (FCP) in the base material of the pipeline [88]. Results from Research Centre Jülich, Germany [89] indicated that steel X70, which is widely used as pipeline material in Europe, has no HAZ issue and a reduced FCP degradation as compared with other pipeline steels, such as X60. The researchers further made a comprehensive cost analysis between different reassignment options for existing pipelines to transport pure hydrogen and compared them with the cost of building new hydrogen pipelines based on the German market. Regarding the cost of the subsequent purification process, they concluded that the admixture of 0.015% oxygen in the transporting hydrogen, which is proven to be effective to limit hydrogen embrittlement in metallic materials [88, 90, 91], is the most cost-effective option to reassign existing pipelines with small diameters (<250 mm) to transport hydrogen. To transport hydrogen through pipelines with larger diameters, only the direct use of existing pipelines without modifications could be cheaper than building a new one. Since there is no on-site coating technology available, the excavation of existing natural gas pipelines to coat a protective layer on their inner wall increases the cost. The integration of a specialized pipelines for hydrogen delivery within the existing natural gas pipelines (pipe-in-pipe approach) is expected to be the most expensive approach.

With regard to pipeline transmission of hydrogen, hydrogen purity needs to be considered. A repurposed pipeline, and even a new hydrogen pipeline, may not be able to provide hydrogen with a purity that satisfies the corresponding requirements for fuel cell applications. Depending on subsequent hydrogen processing and application, an additional purification process is required at the end. For example, using pressure swing adsorption (PSA) purification technology, a maximum purity of 99.9999% is achievable [92].

In Germany, for example, there are already three pipeline networks for hydrogen transportation (but only grey H<sub>2</sub>) available mainly for industrial purposes. The longest dedicated hydrogen pipeline is operated in the Ruhr region by the industrial gas company Air Liquide. It extends from the company's site in the Marl

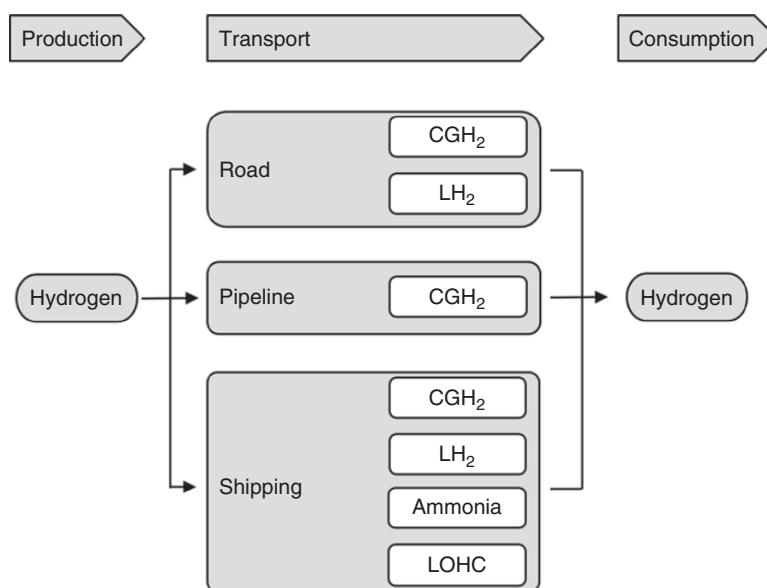


Fig. 15: Transport options for hydrogen.

chemical park to Castrop-Rauxel and Leverkusen, with a total length of 240 km. The so-called Central German Chemical Triangle around the large sites of Bitterfeld, Schkopau and Leuna also has a particularly high demand for  $H_2$  and, therefore, has had its network already for decades. The  $H_2$  pipeline in this region is owned by Linde and has a total length of 150 km. The third German hydrogen pipeline is located in Schleswig-Holstein, covering 30 km from the Heide refinery to the Chemcoast Park in Brunsbüttel.

In 2020, the operator of the natural gas transmission system (FNB Gas e.V.) presented the concept of the 'Vision Hydrogen Network'—a plan that envisages a total length of ~5900 km of pipelines connecting the main hydrogen production and consumption centres in the industrial, mobile and heating sectors in Germany, as well as numerous underground storage facilities, as shown in Fig. 16. The highlight of this proposal is that >90% of this visionary pipeline system is based on the existing natural gas network, which reduces the total cost [93]. The starting signal for this nationwide network is to be given in north-western Germany. By 2030, the ' $H_2$  Start Grid 2030' with a length of 1200 km could be created in North Rhine-Westphalia and Lower Saxony.

The 'European Hydrogen Backbone' is an initiative that includes 31 European energy infrastructure operators that aim to develop the European hydrogen market by defining the hydrogen infrastructure on the basis of existing and new-build pipelines. According to its vision [94], the hydrogen pipeline system will become a pan-European network connecting 25 European countries (including Norway, the UK and Switzerland) with a total length of almost 53 000 km by 2040. The total investment to realize this vision was estimated at between 80 and 143 billion euros. If the pipeline system is completed, the cost to transport 1 kg of hydrogen over 1000 km would be between 0.11 and 0.32 euros, depending on the location of the pipeline.

## 2.3 Hydrogen shipping

In a global green hydrogen economy, transporting hydrogen over sea becomes a necessity and the most economical option. This is especially the case for hydrogen trade between countries, in which the countries with a high excess of renewable energy that can be used to generate green hydrogen for export and countries that need to import hydrogen are far apart from each other [95]. Fig. 17 indicates that the cost of hydrogen transportation by ship would be more economical than building a new pipeline connection if the transportation distance were >7000 km. Although hydrogen transportation through pipelines (Section 3.2) is considered as a viable option for long-distance transport, it is geographically fixed. Possible changes in the political situation of the crossing countries may hinder long-term commitment to a pipeline project. Compared with pipeline transport, shipping hydrogen is more flexible and independent.

Unfortunately, there are hitherto just a few pilot projects aiming to ship hydrogen across countries and even over continents. Some studies predicted that, according to distance, energy consumption, related supporting infrastructure, etc., hydrogen supply chains based on shipping of great amounts of hydrogen in elemental form ( $LH_2$  or  $CGH_2$ ) or compound form (ammonia or LOHC), as shown in Fig. 18, would be established in the future [96, 97].

### 2.3.1 $CGH_2$ shipping

Shipping hydrogen in its gaseous state is the easiest way because gas compression consumes the lowest energy, ~1.1 kWh/

kg $H_2$ , to compress the hydrogen from 2 to 25 MPa, as calculated by a marine transportation company in Australia, Global Energy Ventures Ltd (GEV) [96]. Furthermore, the hydrogen after compression can be injected directly into the ship and thus the simplest supporting infrastructure is needed compared with other shipping options, as shown in Fig. 18. The main challenge for this approach is the low volumetric storage density, as with  $CGH_2$  storage.

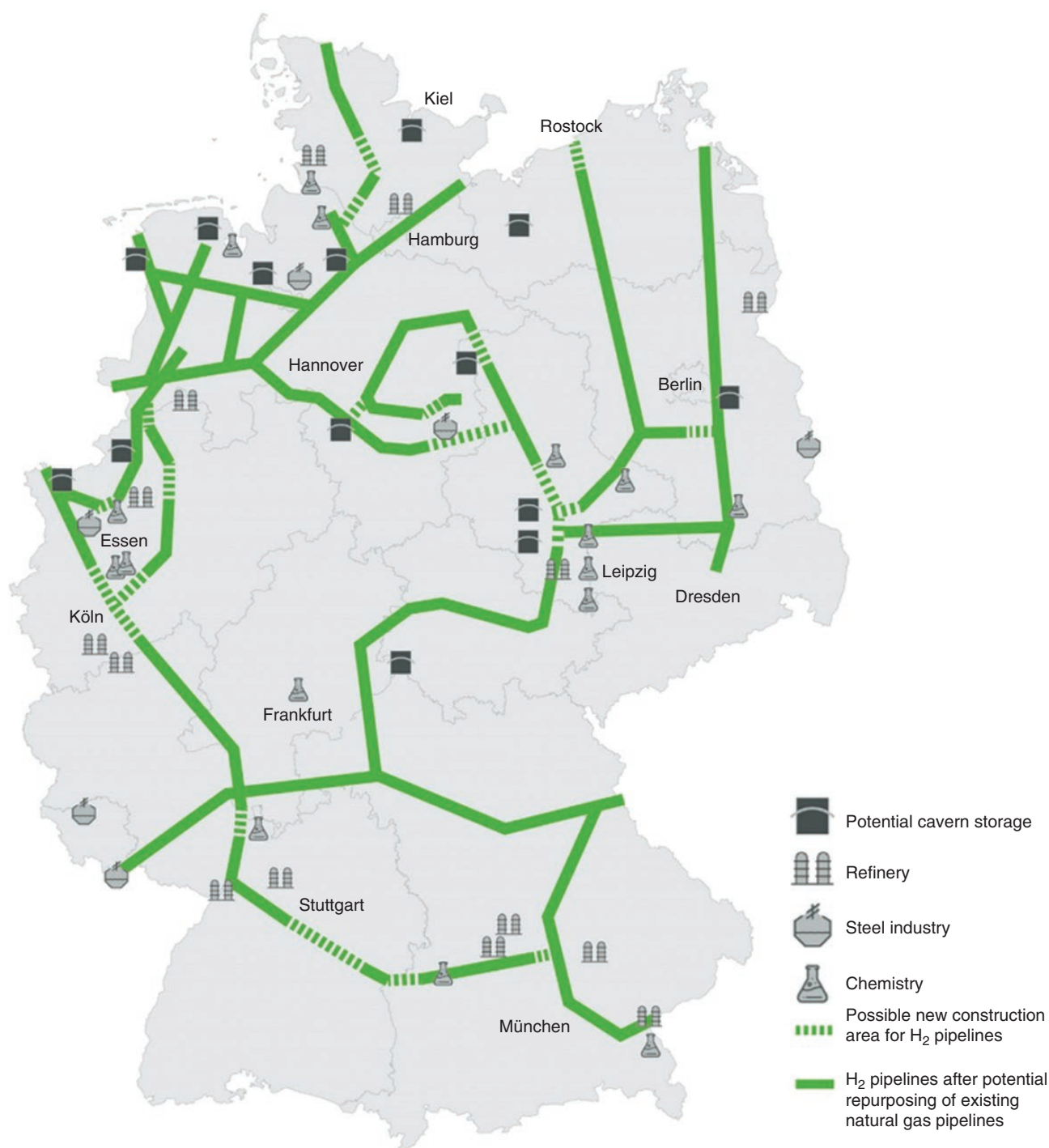
The world's first compressed hydrogen cargo ship, C-H2, is being developed by GEV [98]. It contains two cylindrical tanks with a diameter of 12 m. At an operating pressure of 25 MPa, the ship is able to transport 430 t of hydrogen. The first technology demonstration project is planned to be constructed in 2023 and ready for commercial use by 2025. The design and engineering goal of this project is to use C-H2 as a blueprint and develop a larger cargo ship with two 20-m-diameter cylindrical tanks transporting 2000 t of hydrogen. GEV announced that the hydrogen supply chain with  $CGH_2$  shipping is very competitive within a distance of 2000 nautical miles (3700 km, which corresponds to the route between Australia and Singapore) and remains competitive for transporting hydrogen from Australia to Japan, South Korea and China [96].

### 2.3.2 $LH_2$ shipping

The shipment of hydrogen in its liquid state has become increasingly attractive in recent years. This is, on the one hand, due to its high volumetric density (see Table 6). On the other hand, the experiences summarized from other mature cryogenic technologies can be easily integrated into the development of an  $LH_2$  shipping system. For example, the technology for  $LH_2$  shipping is somewhat derived from liquefied natural gas (LNG) shipping technology, which transports natural gas already at -162°C internationally [99]. Moreover, by the end of 2021, Europe had 37 large-scale LNG terminals with an additional 27 planned [100]. These terminals can be upgraded for  $LH_2$  import and/or export because of the shared used facility and the upgradability of existing systems [101]. Another advantage of  $LH_2$  shipping is that the energy-intensive liquefaction plants are located on the side of the exporter where the energy is already readily available and cheap (such as the cheap renewable energy for the generation of green hydrogen). And on the importer side, as shown in Fig. 18, only minor energy is required for  $LH_2$  storage and regasification, and high-purity hydrogen gas is directly available for every application without a purification process [102]. These are the main advantages of  $LH_2$  shipping when comparing it with hydrogen shipping in the form of ammonia or LOHC (which will be introduced in the following parts).

Compared with LNG, the boiling point of  $LH_2$  is 91 K lower, at -253°C (1 bar).  $LH_2$  shipping faces the same challenge as stationary storage technology—the boil-off loss. Re-liquefaction on the ship is currently not available. The storage of the excess boil-off in a  $GH_2$  tank would require extra space for the tanks, and a complete compressor system would have to be added on board, in competition with the cargo space. Hence, both of these approaches are non-economical. The boiled-off hydrogen vapour must be vented to the atmosphere as soon as its pressure exceeds the limit of the tank. In the future, tanks with higher pressure limits and/or active  $LH_2$  cooling systems, as well as progress in small-sized and energy-saving liquefaction equipment, could eliminate boil-off loss on board.

Making full use of evaporated hydrogen as a fuel is currently the most feasible way to cope with the boil-off loss. Using fuel cells, hydrogen energy can be converted to electric power that



**Fig. 16:** The 'visionary hydrogen network' for Germany connects major producers and consumers and has a length of ~5900 km [93]. Adapted from FNB Gas e.V.; legends are translated into English.

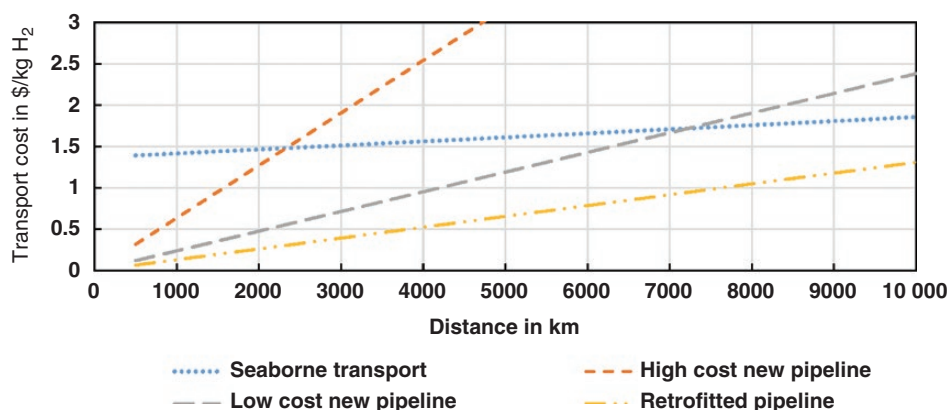
drives the ship. A battery system may serve to store excess electricity [96]. Direct burning of hydrogen in combustion engines, with technologies derived from LNG ships (turbine engines or dual-use combustion engines), is an alternative to drive the ship.

Nevertheless, the boil-off effect restricts the maximum sailing time, and therefore the maximum sailing distance, of LH<sub>2</sub> shipping. As compared in Fig. 19, the Joint Research Centre (JRC), the European Commission's science and knowledge service, found that its preferable shipping distance lies between 2500 and 16 000

km [97]. This covers the LH<sub>2</sub> shipping route from Saudi Arabia to Rotterdam [102].

HySTRA is the most successful project to transport LH<sub>2</sub> intercontinentally. A cooperation between Australia and Japan currently uses brown coal for hydrogen production (grey hydrogen). In a later step, a carbon capture and storage (CCS) system will be installed to convert it into blue hydrogen. This project provides a huge test field for the shipping, loading/unloading and handling of LH<sub>2</sub> at the portside with a lot of progress. The SUIISO FRONTIER, the first LH<sub>2</sub> ship built by Kawasaki, was launched in December





**Fig. 17:** Comparison of options for long-distance hydrogen transportation. Seaborne transportation costs include the liquefaction operating expenditure (OPEX) (including electricity), export terminal capital expenditure (CAPEX), shipping CAPEX and OPEX and import terminal CAPEX and OPEX. Pipeline transportation costs include CAPEX and OPEX and are assumed to be uniform across countries. Seaborne transportation cost are also dependent on the price of the electricity used to liquefy the cargo. The cost shown here assumes liquefaction in Saudi Arabia. Reproduced from [95] with permission from Elsevier Ltd.

2019 and finished by mid-2020 [99]. The first hydrogen was produced at the beginning of 2021 with a purity of 99.999% [103]. After delays due to COVID-19, the voyage of the SUIO FRONTIER started at the beginning of 2022. It transports 1250 m<sup>3</sup>, 75 t of LH<sub>2</sub> at 10 K on a journey of 9000 km and 16 days [104]. The SUIO FRONTIER is still equipped with a standard diesel engine, but the next ships are supposed to use hydrogen as fuel.

### 2.3.3 Hydrogen shipping in the form of ammonia

Unlike the extreme requirements on tanks to hold the high pressure for CGH<sub>2</sub> shipping and to maintain cryogenic temperature for LH<sub>2</sub> shipping, the requirements for shipping hydrogen in the form of ammonia are much more convenient. The shipping at atmospheric pressure and only -33°C or at 25°C and 10 bar is well developed and has already been applied for ≥100 years. With the support of a mature infrastructure, the amount of ammonia by sea worldwide is already ~17.5 million tons per year. One hundred and seventy ships are currently operating throughout the world, loading at 38 export terminals and unloading at 88 import terminals [105].

Eighty per cent of the ammonia currently transported is used as fertilizer or goes into fertilizer production. As shown in Fig. 18, in principle, the hydrogen supply chain that takes ammonia as the carrier can be integrated into the existing ammonia chain. The production, storage and transportation of ammonia are industrially standardized. However, the ammonia synthesis process on the exporter side is even more energy-intensive than hydrogen liquefaction. The ammonia cracking process on the importer side consumes additional energy equivalent to ~20% LHV of hydrogen. Then the mixture of nitrogen and hydrogen after cracking must be separated before delivery of the hydrogen to the end consumer. The ammonia-based hydrogen supply chain is therefore less attractive at present, and its construction plan remains on paper [96].

### 2.3.4 Hydrogen shipping in form of LOHC

An alternative to transporting H<sub>2</sub> under high pressure or at extremely low temperatures is conversion into other chemicals. Promising candidates are ammonia and LOHC.

As mentioned in Section 2.4, the LOHC carries hydrogen via hydrogenation and releases it through dehydrogenation reac-

tions. LOHCs can be transported and handled more easily and securely than LH<sub>2</sub> and have higher H<sub>2</sub>-density than CGH<sub>2</sub> [101]. With 56 kg of H<sub>2</sub> per m<sup>3</sup>, H18-DBT for example can contain ≤78% of the amount of LH<sub>2</sub> (calculated using the data from Table 6). With physical properties similar to those of diesel fuel, it can be transported using the existing infrastructure and transport technologies. The hydrogenation of LOHC is an exothermic process. On the other hand, dehydrogenation (9 kWh/kgH<sub>2</sub>) and purification are energy-intensive endothermic processes. Additional energy has to be invested on the importer side. If there is no significant sector coupling for the required heat, high energy prices are a big cost factor for this system.

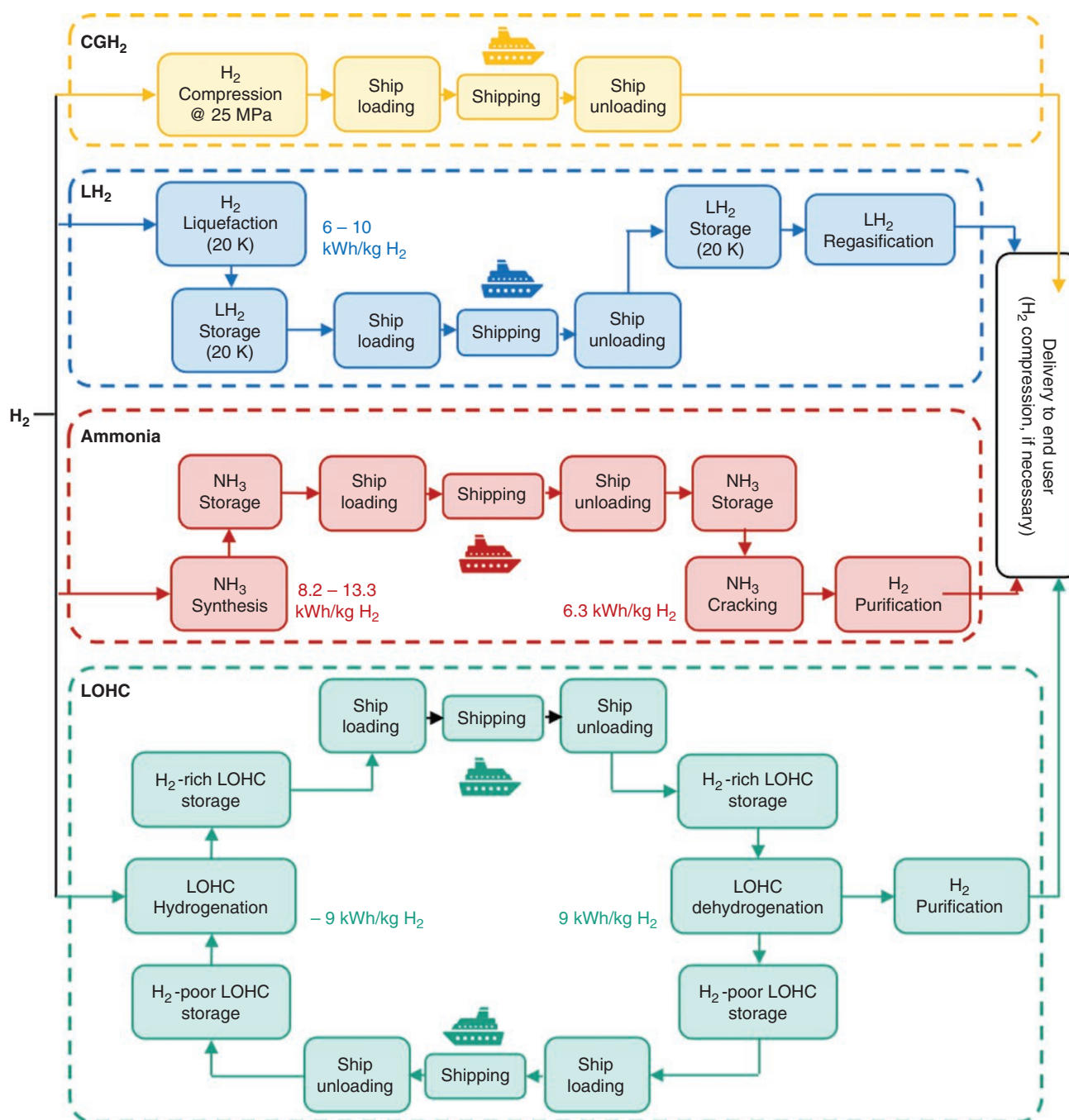
During transport, the lack of boil-off, the less hazardous storage and the high payload favour the LOHC-based hydrogen supply chain (Fig. 18). The drawbacks are the additional fuel system for the ship, the back-transport of the dehydrogenated LOHC and the initial cost of the LOHC. Especially the back-transport of depleted LOHC increases the OPEX of the ship. Concerning the health effects of LOHCs, such as H18-DBT or toluene, it should be mentioned that they are made from crude oil and are still dangerous to health and dangerous for water organisms.

In spite of the estimations from the JRC that LOHC would be the best choice to transport hydrogen over a very long distance from an economic point of view (see Fig. 19), no LOHC shipping system has been implemented so far. There are several facilities that are testing the LOHC cycle, but none of them has a scale comparable to that of shipping. Further technological development is still necessary to reduce the energy needs for dehydrogenation and the stability of the catalysts.

## 2.4 Technology comparison and discussion

Table 7 collects and compares related data from the publications (collected mainly for Germany and Europe) for the hydrogen transportation methods mentioned in previous sections, with the focus on pressure, depreciation period, capacity, transportation cost, CAPEX and OPEX.

Regarding the question of how to choose the most cost-effective way to transport hydrogen, one should not only consider the amount of hydrogen transported, the distance and the investment, but also have to take the cost of integration of the supply chain into account. As listed in Table 7, the overall transportation



**Fig. 18:** A sketch of the hydrogen supply chain based on the shipping of CGH<sub>2</sub>, LH<sub>2</sub>, ammonia and LOHC. According to the data in Table 6, the energy inputs consumed by hydrogen liquefaction, ammonia synthesis and cracking, as well as hydrogenation and dehydrogenation of LOHC, are marked. The energy content of 1 kg of hydrogen, i.e. the lower or higher heating value (LHV or HHV), is 33.3 or 39.4 kWh/kgH<sub>2</sub>, respectively.

cost for LH<sub>2</sub> is obviously cheaper than that for CGH<sub>2</sub>. However, this advantage could be compensated for by the high cost of the liquefaction process if LH<sub>2</sub> is transported only for a short distance. Based on a case study for Germany, within a transportation distance of 130 km, the final product cost of CGH<sub>2</sub> is the most competitive, despite the fact that its transportation cost is higher. Hence, on-road transportation of LH<sub>2</sub> is cost-effective for medium distances. If the transport distance is long, the boil-off loss, however, will become non-negligible and will have a negative impact on the cost. Table 7 further indicates that the pipeline appears to be the cheapest way to transport CGH<sub>2</sub>. This is true under the precondition that it is possible to deliver a great amount of hydrogen

over a long distance. Therefore, it is very applicable as a transport method to deliver hydrogen directly to large industrial user groups. Although real-world experience and data are lacking, transportation of hydrogen for civil users, e.g. to hydrogen refueling stations, is maybe another profit point for a pipeline. This could be a direction that needs to be further explored and studied in the future.

As for the cases in which the hydrogen exporter and importer are not connected by pipeline but by sea, ship transport will be the most economical option. The technologies for hydrogen shipping in the form of LH<sub>2</sub>, CGH<sub>2</sub>, NH<sub>3</sub> or LOHC have different advantages and disadvantages. In addition to the CAPEX and OPEX costs

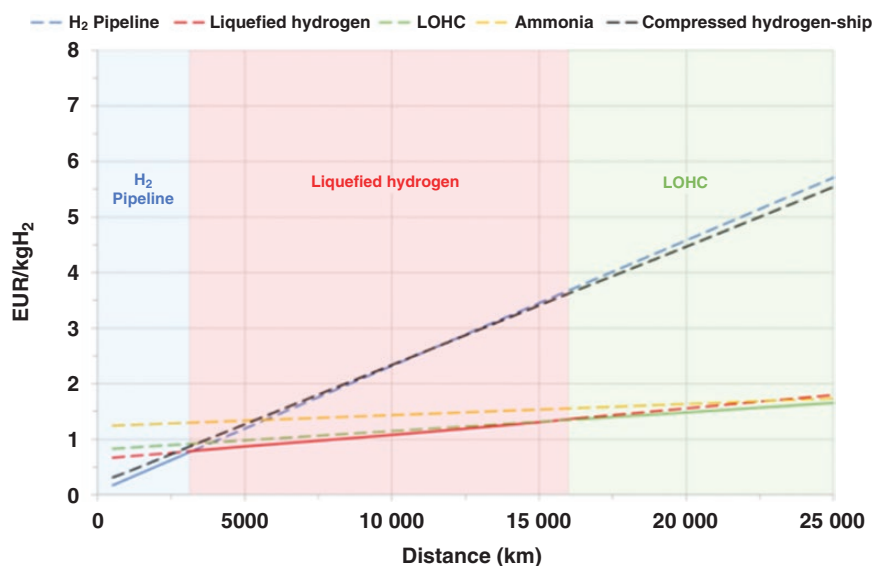


Fig. 19: Hydrogen delivery costs for a simple (point-to-point) transport route, for 1 Mt of  $H_2$  and a low electricity cost scenario 2050 [97]

of the ships, as well as inland transportation, additional costs due to the preparation of hydrogen for transportation and hydrogen release (compression, liquefaction, hydrogenation, dehydrogenation, etc.) may have dominating impacts on the final price of hydrogen.  $LH_2$  shipping has the advantage of the high amount of energy transported and the liquefaction can be operated where energy is cheap, i.e. on the exporter side. But the drawbacks are the cryogenic storage conditions, the boil-off losses and the very high initial cost of the total supply chain (liquefaction plants, storage tanks, ships). The  $CGH_2$  shipping has the advantage that there is no conversion necessary, but the low volumetric density makes it non-favourable for longer distances. Shipping through  $NH_3$  or LOHC has the potential to play a key role in hydrogen transportation. In addition to the hazardous properties of the chemicals, both systems have the advantage that their storage conditions and handling are more convenient during shipping. This significantly reduces the initial cost of ships and infrastructure. The main drawback of both systems is the high energy input for dehydrogenation. This could somewhat be remedied by a good sector coupling, if high-temperature waste energy, for instance, can be used for dehydrogenation. The advantage of ammonia prior to LOHC as a hydrogen carrier is that it can be employed to release the hydrogen through dehydrogenation/cracking reactions or can be directly used as fuel or as feedstock in the chemical industry. Thus, ammonia fuel has high versatility towards differing end uses.

Our discussions above are in good agreement with the results of a study by Graf and Turkovska [114], in which the final costs of hydrogen transported through different paths (including hydrogen generation price, costs for conversion, costs for transport and the loss of hydrogen during transport and conversions) were investigated and compared (cf. Table 8). They concluded that the delivery of hydrogen in the form of ammonia, both via a trailer on the road and by ship, was basically the most expensive option in the whole range of transportation that could be considered (on the road:  $\leq 5000$  km; shipping:  $\leq 180\,000$  km). This was due to the high cost of conversion. The transportation of  $CGH_2$  by trucks was especially competitive for short-distance transport, but became the most expensive option at 5000 km. The most economical inland pathways for long-distance transportation of hydrogen, say  $>1000$  km, were using  $LH_2$  trucks or  $CGH_2$  pipelines. The study

further confirmed that  $LH_2$  shipping was also the cheapest way to transport over the sea, followed by LOHC shipping. According to this study, Table 8 may serve as a guide for the future on how to choose the most cost-effective way to transport hydrogen.

### 3 Conclusions

Generally speaking, until now, no single form of hydrogen has dominated the whole hydrogen value chain. According to different storage needs (quantities, duration, etc.), different specifics of transportation (distance, volume, etc.) and different end uses, the physical and chemical state of hydrogen should be modified in order to meet the economic goals. Therefore, it may be necessary to establish different infrastructure systems to support different application scenarios.

Since hydrogen fuel cells are very sensitive to gaseous contamination, the corresponding hydrogen infrastructure (for fuel cell electric vehicles, fuel cell power generation, etc.) tends to be built on the technologically more mature infrastructure of pure hydrogen, in its gaseous and/or liquid state. A pipeline is the most cost-efficient way to transport huge amounts of  $CGH_2$  over long distances. However, their construction requires a high capital investment. Nevertheless, investigations in Europe have been carried out to study the technological potential and economic feasibility of the repurposing of existing pipelines from current natural gas use to future hydrogen transport. The results of these works and the ideas behind them are undoubtedly of great reference value for countries and regions other than Europe.

In application scenarios involving medium- and long-term hydrogen storage, material-based storage technologies are preferred because of their higher volumetric density, chemical stability and safety. As soon as the problem of their energy-intensive hydrogen release process is solved, ammonia and LOHC could be promising hydrogen carriers in addition to  $LH_2$  for long-distance hydrogen shipping. Adverse thermodynamics and kinetics during the hydrogenation and dehydrogenation processes are currently the main obstacles that prevent metal hydrides from large-scale application and commercialization.

In summary, each country and region must design its own strategy for the construction of hydrogen-based infrastructure in

**Table 7:** Comparison of different hydrogen transport methods

Features	CGH <sub>2</sub> trailer	LH <sub>2</sub> trailer	CGH <sub>2</sub> pipeline	LH <sub>2</sub> -ship	NH <sub>3</sub> -ship	LOHC	Reference
<b>Pressure (MPa)</b>	20–50	0.1–0.4 (–253°C)	2–3	~0.1	~0.1	~0.1	[87, 106–108]
<b>Depreciation period (years)</b>	12	12	40 30–55	n/a	n/a	n/a	[106, 108–109]
<b>Capacity (kg H<sub>2</sub>)</b>	500 (20–25 MPa) 1000 (50 MPa)	4000–4300	n/a	75 000 (SUIISO FRONTIER); ~11 336 000 (estimated for 160 000 m <sup>3</sup> LH <sub>2</sub> ship)	~19 200 000 (estimated for 160 000 m <sup>3</sup> NH <sub>3</sub> ship) <sup>a</sup>	~8 265 600 (estimated for 160 000 m <sup>3</sup> LOHC ship carrying H18-DBT)	[85, 102, 110, 104]
<b>Transportation cost (€/kg H<sub>2</sub>)</b>	2.69	0.74	0.64/500 km 0.11–0.21/1000 km	0.7–1.5 (with liquefaction 2–2.5)	0.8–0.9 (with dehydrogenation 1.8–2.9)	1.6–2.7	[85, 106–111]
<b>CAPEX (€)</b>	660 000/ trailer (50 MPa) (2019)	860 000/ trailer (2019)	$Invest(e/m) = 0.0022D^2 + 0.86D + 247.5$ (pipeline diameter D in mm)		179 944 000/ ship <sup>b</sup>	134 924 800/ ship <sup>b</sup>	[108, 109, 112, 111]
<b>OPEX (/year)</b>	2%	2%	4–4.7%	9 900 000 + 4% CAPEX <sup>b</sup>	9 047 000 + 4% CAPEX <sup>b</sup>	15 604 000 + 4% CAPEX <sup>b</sup>	[112, 94–111]

<sup>a</sup>The common cargo volumes of liquid ammonia ship are 30 000, 52 000 and 80 000 m<sup>3</sup> [113], corresponding to ~3 600 000, ~6 200 000 and ~9 600 000 kg of hydrogen, respectively.

<sup>b</sup>Estimated for a ship with a cargo volume of 160 000 m<sup>3</sup>.

**Table 8:** Appropriate distance for different hydrogen transport methods (summarized from the results in [114])

Transport	Appropriate distance	
<b>Land transportation</b>	<b>CG trucks</b>	Short-distance transport → up to 100 km
	<b>LH<sub>2</sub> trucks</b>	Medium-distance transport → over 500 km
	<b>Pipeline</b>	Long-distance transport → up to 1000 km
<b>Overseas transportation</b>	<b>LH<sub>2</sub> ship</b>	Long-distance transport → over 1000 km

close accordance with its own energy characteristics and its role in the global hydrogen energy system. For countries and regions with a higher rate of distributed renewable energy and a lower share of traditional power generation plants, energy-intensive industries and chemical industries (e.g. Germany), research and development in hydrogen generation with advanced coupling with renewable energies and infrastructure construction for short- to medium-term storage and domestic transportation of hydrogen should be the top priority. For countries and regions highly dependent on hydrogen import or export (e.g. Japan and Australia), efficient, low-cost and safe medium- and long-term storage and intercontinental transport of hydrogen and/or its carriers (such as LOHCs and metal hydrides) should be their focus. For the countries and regions with dominant traditional power plants, centralized renewable energy, high energy consumption and great demands on chemical feedstocks (e.g. China), large-scale hydrogen generation, short- to medium-term storage and domestic transportation of hydrogen should be the major targets when building up the hydrogen infrastructure. In addition, power fuels may serve as coupling between different energy sectors and chemical industries.

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## Conflict of interest statement

M.Y., R.H., S.B., B.S., and B.W. declare that they have no conflict of interest or financial conflicts to disclose.

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