

## Perspective

## Large-scale stationary hydrogen storage via liquid organic hydrogen carriers

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## SUMMARY

Large-scale stationary hydrogen storage is critical if hydrogen is to fulfill its promise as a global energy carrier. While densified storage via compressed gas and liquid hydrogen is currently the dominant approach, liquid organic molecules have emerged as a favorable storage medium because of their desirable properties, such as low cost and compatibility with existing fuel transport infrastructure. This perspective article analytically investigates hydrogenation systems' technical and economic prospects using liquid organic hydrogen carriers (LOHCs) to store hydrogen at a large scale compared to densified storage technologies and circular hydrogen carriers (mainly ammonia and methanol). Our analysis of major system components indicates that the capital cost for liquid hydrogen storage is more than two times that for the gaseous approach and four times that for the LOHC approach. Ammonia and methanol could be attractive options as hydrogen carriers at a large scale because of their compatibility with existing liquid fuel infrastructure. However, their synthesis and decomposition are energy and capital intensive compared to LOHCs. Together with other properties such as safety, these factors make LOHCs a possible option for large-scale stationary hydrogen storage. In addition, hydrogen transportation via various approaches is briefly discussed. We end our discussions by identifying important directions for future research on LOHCs.

## INTRODUCTION

Decarbonization is necessary for the world to minimize the adverse effects of climate change. Central to decarbonization is establishing an alternative to unsustainable fossil fuels. Hydrogen is considered an attractive solution as an energy vector to decarbonize the energy value chain based on renewable energy sources. The advantage of hydrogen as a clean fuel of high gravimetric energy density is that it can help to replace fossil fuels in a wide range of applications, including heavy transport and industry. Hydrogen can be used, for example, in the iron and steel industry for green ironmaking and steelmaking (Tang et al., 2020b) and may offer practical solutions to environmental damage from mining (CSIRO Australia, 2021). Renewable energy resources (such as solar and wind) are a key component of decarbonization but are available only intermittently, often with significant fluctuations, and hence, a buffer is necessary between the inharmonious fluctuations in energy production and demand. Among the buffering options, hydrogen can be used as a storage medium for electricity from intermittent renewable sources to balance energy production and demand, becoming more critical as the fraction of photovoltaics and wind turbines in electricity grids increases and as the trend to electrification continues. Given the importance of hydrogen in the future energy system, the world has heavily invested in hydrogen-related research, industry, and infrastructure (COAG Energy Council, 2019; Germany Federal Ministry for Economic Affairs and Energy, 2020). However, for hydrogen to fulfill its promise, it will be necessary to establish large-scale hydrogen-embedded energy value chains.

Once produced, hydrogen can be stored in different forms such as gas, liquid, solid, and chemicals via binding to hydrogen-lean materials. Safe, economical, and efficient hydrogen storage/transport at a large scale is a key to the success of hydrogen-embedded energy value chains. However, storing hydrogen for the long term at a large scale and transport over a long distance are not trivial tasks (Sharma and Ghoshal, 2015). We note that "large scale" and "long term" are relative and depend on the applications, and in this work, we consider storing 500 tonnes of hydrogen for one month as a demonstration. The production

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capacity of 500 tonnes of hydrogen per day is a realistic startup scenario, and 30 days of storage for all products and reactants is a reasonable industrial practice for supply chain interruptions (Ulrich, 1984; M Walas, 1990). To date, the most common approach is to store hydrogen either as gas in high-pressure cylinders/canisters or liquid in cryogenic tanks, which incur high containment costs and concerns about safety and boil-off. An alternative approach, storage via solid hydrides, does not show enough potential due to factors such as low capacity, slow reaction kinetics, and/or poor reversibility (Abdin and Khalilpour, 2019). Though relatively new, hydrogen storage via liquid chemical molecules has emerged as a promising approach, thanks to other advantages such as recyclability, liquid state under ambient conditions, and compatibility with existing storage/transport infrastructure for fossil fuels.

Hydrogen storage via liquid molecules involves two reversible reaction steps: hydrogenation of hydrogen-lean molecules and dehydrogenation of hydrogen-rich molecules. The hydrogen-lean format of the molecules can either be gas or liquid. Hydrogen carriers for the former case, such as ammonia, methanol, and formic acid, are also called “circular” hydrogen carriers in the literature since the gas molecules (CO<sub>2</sub> or N<sub>2</sub>) captured from the atmosphere for synthesizing the hydrogen carriers are released back into the atmosphere, hence forming a circle. In contrast, liquid hydrogen-lean molecules are reusable during the reversible (de)hydrogenation process (Preuster et al., 2017b). Such organic hydrogen carriers are called liquid organic hydrogen carriers (LOHCs). LOHCs can store hydrogen without binding or releasing other substances to or from the atmosphere and can produce pure hydrogen from dehydrogenation after appropriate condensation. They also can be stored for an extended period at a large scale without any losses and transported over a long distance using the existing infrastructure for liquid fuels. The idea of using LOHCs for large-scale stationary hydrogen storage is still relatively new. However, hydrogenation of aromatics and dehydrogenation of cyclic hydrocarbons are performed at a large scale in industrial applications, e.g., in oil refineries. Thus, LOHC compounds, along with circular hydrogen carriers, could be potential candidates for stationary hydrogen storage at a large scale using the well-established infrastructure.

Several important reviews have contributed to our understanding of hydrogen storage materials and particularly LOHCs. Yadav and Xu (2012) discussed (de)hydrogenation of several liquid compounds for hydrogen storage and related catalysts. Andersson and Grönkvist (2019) delivered a general overview of large-scale hydrogen storage options based on fundamental thermodynamic and engineering aspects. Niermann et al. (2019a) reviewed the (de)hydrogenation process for various LOHCs and compared their important characteristics, and similarly, Preuster et al. (2017b) reviewed different LOHCs for their (de)hydrogenation process, catalyst, application, and outlook. Aakko-Saksa et al. (2018) reviewed the different LOHCs, compared to existing energy storage systems, and discussed their different features, e.g., storage density, materials, safety, and efficiency. Overall, these articles mainly focus on the materials aspects of hydrogen storage. Niermann et al. (2019b) simulated the technological and economic performance of a series of LOHCs (including formic acid and methanol) as well as compressed gas H<sub>2</sub> for intercontinental transport and illustrated the technological and economic advantages of LOHCs. However, two important candidates, ammonia (MacFarlane et al., 2020) and liquid H<sub>2</sub> (Li et al., 2020), were not considered in this study.

It is essential to understand how LOHC-based large-scale stationary hydrogen storage could be one of the possible options, on a technical and economic basis, against the current dominating hydrogen storage systems and other important alternative hydrogen carriers. So far, this issue has not been systematically addressed in the literature. In this work, by performing such analyses for LOHCs compared with current hydrogen storage systems and two leading alternative hydrogen carriers—ammonia and methanol—we will illustrate how competitive LOHCs are at a large scale as part of the transition toward a low-emission energy economy.

Typically, along with a storage system, a hydrogen dispensing system (integrated with a buffer tank and cooling system) needs to be installed for densified stationary hydrogen storage systems. For LOHCs and circular carriers, a dehydrogenation system is an extra step to extract hydrogen along with the dispensing system. It is noted that these carriers are currently mainly used as is or other derivatives; thus, we limit our focus in this study only on the storage, i.e., hydrogenation system.

The structure of this perspective article is as follows. We start with a succinct discussion of the existing and planned stationary hydrogen storage systems, followed by a section on the current state of key physical

(including densified and physisorption) and chemical (including solid hydrides, LOHCs, and circular carriers) hydrogen storage technologies in the context of large-scale application. In the next two sections, we focus on the current state of LOHCs and techno-economic comparison with the conventional physical approaches (gaseous and liquid hydrogen) for stationary storage, as well as two circular carriers (ammonia and methanol). Finally, we summarize the work and discuss important future research directions for LOHCs.

## EXISTING AND PLANNED STATIONARY HYDROGEN STORAGE SYSTEM

Stationary hydrogen storage systems are built primarily for on-site storage at either production site or end-use and for stationary power generation. At present, on-site stationary hydrogen storage and/or stand-alone stationary applications are mostly limited to compressed hydrogen storage in pressurized tanks (small scale) or underground (large scale). For example, [Gahleitner \(2013\)](#) analyzed 48 hybrid stationary hydrogen production plants (power-to-gas), whose hydrogen storage capacity ranges from 0.2 kg to 1350 kg (from 1990 to 2012); among them, 88% of projects stored hydrogen via compressed storage and 11% via metal hydride storage. [Abdin \(2017\)](#) also analyzed 19 renewable hybrid stationary hydrogen production plants, and hydrogen storage capacity ranges from 0.2 kg to 450 kg (from 1989 to 2017); among them, 74% stored via compressed storage and 26% stored via metal hydride. This is mainly due to the pressurized tank being a mature technology and commercial availability compared to other storage methods; perhaps, this explains why hydrogen storage is limited to compressed storage. However, compressed storage has the drawbacks of energy consumption for compression, safety concerns, low volumetric energy density, and transportation cost (i.e. if the fueling station is at a certain distance). Since these are hybrid stationary energy systems which store energy in a battery bank and hydrogen storage tank, the values are not directly related to the overall plant capacity.

In the future hydrogen economy, large-scale stationary storage (i.e. grid-scale energy storage ranging from GWh to TWh and beyond) could be used to store the excess energy of the grid and/or supply a large number of customers with hydrogen. The underground compressed hydrogen storage (UCHS) could be a possible alternative at a large scale, especially for seasonal hydrogen storage. There are five types of UCHS: depleted natural gas and oil reservoirs, aquifers, salt caverns, abandoned mines, and rock caverns; among them, salt caverns could be a good option since salt is inert to hydrogen ([Moradi and Groth, 2019](#)). Salt formations have been exploited worldwide in the last decades to store natural gas, oil, and chemicals. For example, hydrogen has been successfully stored in two caverns in Texas (USA) since 1983 (storage capacity: 580,000 m<sup>3</sup> and 566,000 m<sup>3</sup>) and in three caverns in Teesside (UK) since 1972 (storage capacity: 3 × 70,000 m<sup>3</sup>) ([Abdin et al., 2020](#)). [Gabrielli et al. \(2020\)](#) explored recent progress on UCHS from the analysis of the thermo-mechanical properties of the salt cavern to the identification of optimal regional sites and assessing the financial and environmental performance of underground storage of hydrogen and natural gas. Salt cavern provides higher safety than aboveground compressed storage methods, and the cost is 10 times less than that of aboveground tanks and 20 times less than that of hard rock mines ([USA Office of Fossil Energy and Carbon Management, 2021](#)). However, many challenges are associated with it, including (but are not limited to) geological constraints, pipelines materials durability, design concerns, hydrogen leakage, and legal and social obstacles ([Elbery et al., 2021](#)).

Green hydrogen is crucial to the world, potentially creating alternative benign and sustainable fuel industry, as indicated in the recently launched National Hydrogen Strategy in relevant countries, indicating several planned green hydrogen storage projects ([COAG Energy Council, 2019](#); [Germany Federal Ministry for Economic Affairs and Energy, 2020](#)). For example, Mitsubishi Power and Magnum Development announced the Advanced Clean Energy Storage Project in central Utah, USA, to build a storage facility for 1,000 MW/100,000 MWh of 100% green hydrogen storage into salt caverns ([Hydrogen valleys, 2021](#)). In addition, the HYPOS alliance of over 100 companies and institutions aims to build a salt cavern in the Central German Chemical Triangle in Saxony-Anhalt with about 150,000 MWh of energy from wind power-generated hydrogen, funded by the German government ([EU Commission, 2020](#)). Recently, Air Products and Chemicals, USA, announced that they would build a green (primarily based on solar and wind, 4 GW) hydrogen plant in Saudi Arabia that will produce 650 tonnes of hydrogen per day and store it as ammonia ([John, 2020](#)). In addition, InterContinental Energy and its partners plan to build a 26 GW solar and wind project in East Pilbara, Western Australia; the project would produce around 1.8 Mt/year of hydrogen and store it as ammonia ([The Asian Renewable Energy Hub, 2021](#)). Also, in Germany, the world's

largest plant for storing green hydrogen, 1800 tonnes/year of hydrogen, in LOHCs on an industrial scale is to build at CHEMPARK Dormagen (Hydrogenious LOHC Technologies, 2021).

## CURRENT STATE OF KEY STATIONARY HYDROGEN STORAGE TECHNOLOGIES

In a large-scale hydrogen distribution system, storage is vital to accommodate the variation between production levels and stochastic fluctuations in demand. The primary goal of stationary hydrogen storage at a large scale is to minimize the levelized cost of hydrogen at the end use by coordinating supply and demand or using it for backup purposes. Hydrogen demands in a specific application may significantly impact the storage's capital and operating costs on a large scale (Luo et al., 2015). For example, some applications, such as fuel cells, are susceptible to hydrogen dispensing because of high demands on the response time; some, such as urea production, only need to be flattened or refilled a couple of times at controlled flow rates in a year or so. Also, in some applications, such as proton exchange membrane (PEM) fuel cells, the purity of hydrogen is crucial. Hence, different storage technologies may be required to meet these varying constraints as well as the variability of energy generation and demand at different time scales, ranging from hourly to seasonal (Andersson and Grönkvist, 2019).

Figure 1A classifies hydrogen storage technologies based on the nature of the interaction between hydrogen and the storage container or materials, and Figure 1B shows the volumetric and gravimetric densities of these hydrogen storage technologies. From the perspective of the overall cost of the storage system, high volumetric density is more desirable than high gravimetric density for large-scale stationary hydrogen storage. Figure 1C shows the volumetric density of different hydrogen storage technologies as a function of pressure. Among those technologies, LOHCs and circular carriers operate at ambient pressure, whereas currently dominating hydrogen storage approaches, gaseous and liquid, require considerably higher operating pressure. Also, the volumetric hydrogen density of LOHCs and circular carriers is significantly higher than that of the gaseous systems within the standard industry pressure range.

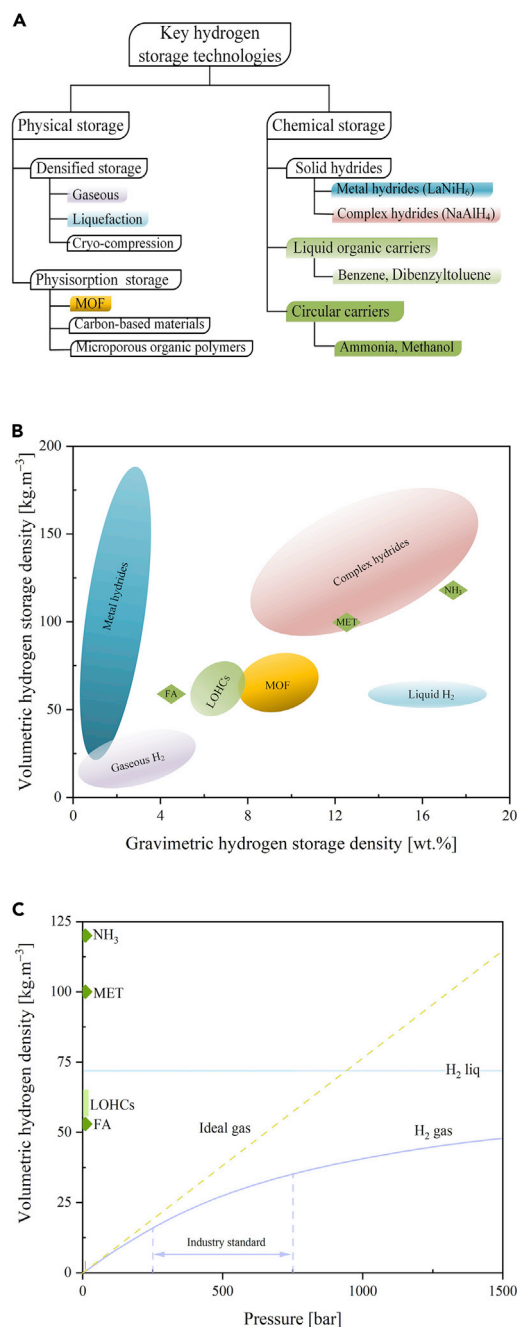
### Physical storage

Physical hydrogen storage includes densification of pure hydrogen and physisorption of hydrogen onto the surface of adsorbents. During this process, no chemical interactions between hydrogen molecules and the containing materials are involved.

#### Densified storage

Densified storage includes compressed gas (CGH<sub>2</sub>) and liquid hydrogen (LH<sub>2</sub>), in which hydrogen molecules do not physically or chemically bind with other materials. Gaseous hydrogen at a large scale can be stored either above or below the ground level. The pressure for hydrogen gas storage above ground is usually below 100 bar, considering the operating cost and container material requirements (Andersson and Grönkvist, 2019). Underground storage of hydrogen in depleted oil wells and salt caverns, with a pressure of not more than 200 bar, is a mature and well-established practice (Elberry et al., 2021). Hydrogen storage using lined rock caverns is also possible, although such technologies, already used for natural gas storage with a maximum pressure of 200 bar, need further validation (Tengborg et al., 2014). Compared with storage above ground, it has several desirable features: low construction cost, low leakage rate, fast charging and discharging, lower risk of contamination, and relatively less cushion gas needed. However, underground hydrogen storage at a massive scale is constrained by the factors discussed in section 'Existing and planned stationary hydrogen storage system'.

Liquid hydrogen storage has not been prominent for stationary applications at a large scale, although cryogenic storage at the scale of many cubic meters of liquid is a well-established technology in the space industry (Andersson and Grönkvist, 2019). A key concern for liquid hydrogen storage is the energy-intensive (~10 kWh/kg) and capital-intensive liquefaction process (~40–50% of capital expenditure (CapEx) of the liquid hydrogen storage system) (Cardella et al., 2017). Boil-off loss due to heat flow from the exterior is another issue for liquid hydrogen plants, although it is of less concern where the liquefaction process and storage are nearby. Some remedies include injecting the cold boil-off gas back into the liquefaction process, using it in downstream applications, and using containers with high insulation and low surface-to-volume ratio. Although liquefied hydrogen has the above issues, it is the prevalent option for the large-scale export of pure hydrogen. Kawasaki Heavy Industry (Japan) has already constructed small liquefied hydrogen carriers, initially at the 200-tonne scale (Abdin et al., 2020).



**Figure 1. Key hydrogen storage technologies and their energy densities**

(A) Classification of hydrogen storage technologies.

(B) Volumetric and gravimetric densities (based on storage materials and storage vessels) of different hydrogen storage technologies (Reuß et al., 2017; Sartbaeva et al., 2008); circular carriers: ammonia (NH<sub>3</sub>), methanol (MET), and formic acid (FA).

(C) Volumetric density of hydrogen as a function of pressure (Züttel, 2003); here, the effect of system volume is not considered for liquid H<sub>2</sub> while it is considered in Figure 1B.

### Physisorption storage

Physisorption is a reversible exothermic process whereby gas can readily adsorb onto a surface via van der Waals bonding and be released later without decomposition or loss. The amount of hydrogen adsorbed is typically proportional to the sorbent's surface area. As a result of the weak van der Waals bonding between

molecular hydrogen and the sorbent, this process requires low temperature ( $\sim -196^\circ\text{C}$ ) but elevated pressure (typically 10–100 bar) to store hydrogen at higher densities (Abdin, 2017). However, it depends on the adsorbent and application since high pressure is not helpful beyond a specific threshold.

Among the vast range of materials, porous carbon-based materials, metal-organic frameworks, porous polymeric materials, and zeolites are the most prominent adsorbents for hydrogen storage (Langmi et al., 2014). However, to date, most developed adsorption-based storage vessels are still at the laboratory scale. Apart from that, most of the currently available adsorbents have a low energy density and need a sophisticated thermal management system to remove the heat released by hydrogen absorption, limiting their potential usage for stationary storage.

### Chemical storage

In chemical storage, hydrogen is chemically bonded with storage materials, and these bonds are much more resilient than the van der Waals bonds in physisorption storage. According to the phase (solid, liquid, and gas) of hydrogen-lean media, chemical storage can be classified into solid hydrides, liquid organic carriers, and “circular” carriers, as discussed below.

#### Solid hydrides

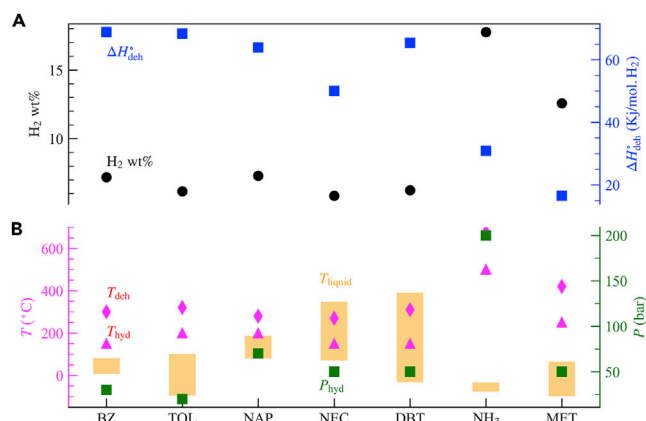
The solid hydrides are roughly classified into metal hydrides and complex hydrides. Metal hydrides encompass a wide variety of materials, including elemental metals, alloys, and stoichiometric non-metallic compounds, with the combined capability to dissociate hydrogen molecules at the material’s surface and absorb hydrogen atoms into the interior crystal structure. Studies (Abdin and Khalilpour, 2019) indicate that absorption/desorption of hydrogen to/from metal hydrides can take place over a vast range of pressures and temperatures. Therefore, metal hydrides with relatively high volumetric hydrogen density are generally considered for stationary storage. These can absorb and desorb hydrogen at room temperature, and with a few bar pressure, with the enthalpy of the absorption/desorption reaction generally between  $\pm 30$  and  $\pm 40$  kJ/mol.H<sub>2</sub>. However, the sluggish reaction kinetics, low thermal conductivity, and high cost of metal hydrides limit their application for stationary storage at a large scale, though a few installations at a small scale have been demonstrated (Abdin, 2017).

Complex hydrides, usually comprising more than one metal or a metalloid, are metal salts with complex anions formed by covalent bonding between hydrogen and the central atoms. Many complex hydrides have excellent hydrogen gravimetric storage capacity due to the relatively light elements involved, and some can even exceed that of liquid hydrogen. For example, LiBH<sub>4</sub> contains hydrogen of 18 wt.% (Abdin et al., 2015). Complex hydrides have mild dehydrogenation enthalpy. For instance, the dehydrogenation of Ti-doped NaAlH<sub>4</sub> is a multi-step process, with the first step having an enthalpy of 37 kJ/mol.H<sub>2</sub> and the second having an enthalpy of 47 kJ/mol.H<sub>2</sub> (Andersson and Grönkvist, 2019), corresponding to  $\sim 36^\circ\text{C}$  and  $\sim 116^\circ\text{C}$  hydrogen release temperature at 1 bar hydrogen partial pressure, respectively. However, the rehydrogenation of NaAlH<sub>4</sub> requires stringent conditions (200–400°C and 10–40 MPa) and has slow kinetics (Andersson and Grönkvist, 2019). Ti-based doping agents can increase the kinetic rates of rehydrogenation but lowers the storage capacity. Other factors, such as difficulty in safe handling, limit complex hydrides at a large scale for stationary storage (Rusman and Dahari, 2016).

#### Liquid organic and circular carriers

Liquid organic molecules with conjugated  $\pi$ -bonds can be used for reversible hydrogen storage. They can be hydrogenated by saturating the  $\pi$ -bonds with hydrogen and can be dehydrogenated in the reverse process. Also, hydrogen can be carried or stored via circular carriers, such as ammonia and methanol. Based on gas molecules, circular carriers in their hydrogen-rich state are liquid or liquefied under mild conditions and have similar desirable properties as liquid organics. Liquid organics and circular carriers have been demonstrated to be promising for convenient hydrogen storage and transportation at the bulk level. These chemicals are widely produced, have excellent compatibility with existing infrastructure, and can be propelled for continuous delivery and distribution.

Overall, the physical storage technologies fall short of the volumetric densities that can be achieved by chemical storage because of the large van der Waals dimension of molecular hydrogen in the former as compared to the dimension of atomic hydrogen in the latter, and they generally require low temperatures and/or high pressures. A significant advantage of liquid organic and circular carriers over solid hydrides is



**Figure 2. Salient features of some selected LOHCs and circular carriers for stationary storage**

(A) Hydrogen storage capacity (wt.%) and dehydrogenation enthalpy change of some typical liquid organic hydrogen carriers and other hydrogen carriers.

(B) Typical temperatures for (de)hydrogenation ( $T_{\text{hyd}}$  and  $T_{\text{deh}}$ ) and hydrogenation pressures. The orange blocks represent the carriers' temperature range in a liquid state; for LOHCs with different  $T_{\text{liquid}}$  ranges due to (de)hydrogenation, the narrower one is chosen. Except for ammonia ( $\text{NH}_3$ ) and methanol (MET), the carriers are indicated by their hydrogen-lean formats: benzene (BZ), toluene (TOL), naphthalene (NAP), N-ethylcarbazole (NEC), and dibenzyltoluene (DBT). The data for  $T_{\text{deh}}$ ,  $T_{\text{hyd}}$ , and  $P_{\text{hyd}}$  and relevant catalyst information for TOL, NAP, NEC, DBT, and MET can be found in (Niermann et al., 2019a, 2019b; Preuster et al., 2017b; Andersson and Grönkvist, 2019; Aakko-Saksa et al., 2018), those for  $\text{NH}_3$  in (Thomas and Parks, 2006), and those for BZ in (Modisha et al., 2019).

their compatibility with existing fuel transport systems for chemical storage. In the subsequent sections of this perspective article, we compare LOHCs with the relatively established gaseous and liquid hydrogen and the alternative carriers of ammonia and methanol.

## CURRENT STATE OF LIQUID ORGANIC HYDROGEN CARRIERS FOR STATIONARY STORAGE

An ideal LOHC compound should not only have a high hydrogen content but also satisfy other requirements regarding stability, reaction rate, cost, safety, compatibility with existing technology and facilities, and so on (Modisha et al., 2019). As mentioned in the introduction, there have been several reviews discussing the properties of LOHCs (Modisha et al., 2019; Niermann et al., 2019a; Preuster et al., 2017a, 2017b; Andersson and Grönkvist, 2019; Aakko-Saksa et al., 2018). Hence, here we only succinctly discuss some critical properties of a few typical LOHCs, especially those that have the potential for stationary storage, including benzene (BZ), toluene (TOL), naphthalene (NAP), N-ethylcarbazole (NEC), and dibenzyltoluene (DBT). Some of these (TOL and DBT) are already in industrial application, and the others either are structurally important or possess some unique properties. For example, BZ is a building block that commonly exists in LOHC molecules, and NEC demonstrates lowered dehydrogenation enthalpy via incorporating a heteroatom. Figure 2 shows some important properties of these LOHCs as well as ammonia and methanol for comparison.

Among the above compounds, the benzene/cyclohexane (BZ/CHE) system has the simplest structure and a high hydrogen storage capacity of ~7.2 wt.%. Several catalysts, including Pt group metals, Ni, Ni/Cu, and Ni/Pt, have been studied for (de)hydrogenation of BZ/CHE, and the catalyst performance was found to be a function of multiple factors such as catalyst composition, support materials, and reaction conditions (Modisha et al., 2019). The drawbacks of this system include the high toxicity of BZ and the flammability of CHE. In addition, the relatively low boiling point of CHE (81°C) makes it challenging to separate produced hydrogen from the reactants. Adding a methyl radical turns BZ/CHE into toluene/methylcyclohexane (TOL/MCH), reducing the hydrogen storage capacity to ~6.2 wt.%. With a wider liquid temperature range and lower toxicity than the BZ/CHE system, TOL/MCH has been used as the hydrogen carrier by Chiyoda (Japan) for its SPERA (out of the Latin word for 'hope') hydrogen supply business (Chiyoda Corporation, 2021). At ~350°C and with Pt/Al<sub>2</sub>O<sub>3</sub> catalyst, the dehydrogenation of MCH occurs with MCH conversion rate higher than 95% and toluene selectivity higher than 99.9%, as reported for Chiyoda's demonstration

plant, which has a production rate of 50 Nm<sup>3</sup>/hr (Okada and Shimura, 2013). Other catalysts such as Ni, Pt group metals, and bimetallic Pt/Mo on various support materials have also been explored for (de)hydrogenation of TOL/MCH (Modisha et al., 2019).

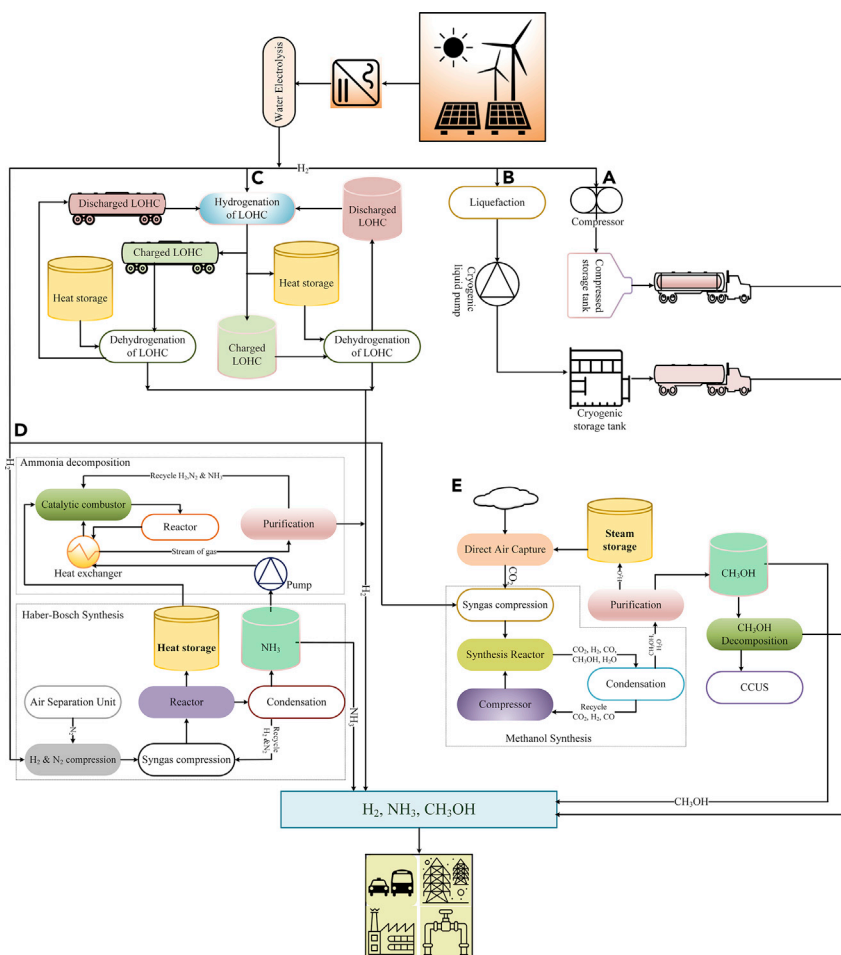
NAP has a hydrogen storage capacity as high as 7.3 wt.%. Hydrogenation of NAP can be carried out using Pt catalysts with mesoporous acidic supports at 200–300°C (Park et al., 2002; Albertazzi et al., 2003; He et al., 2013). Upon hydrogenation, tetralin forms as an intermediate before the final product decalin, with the support material impacting the product selectivity (He et al., 2013). For hydrogenation, the support's acidic nature, which helps the spillover hydrogen react with the adsorbed NAP, significantly improves the catalyst performance (He et al., 2013; Park et al., 2002). Carbon-supported Pt-based fine particles can realize the dehydrogenation of decalin at around 280°C (Hodoshima et al., 2003). It was found that the highest stationary rate of hydrogen evolution is reached at a moderate feed rate of decalin (Hodoshima et al., 2005). The NAP and decalin are safe commodity chemicals for LOHC applications, but the relatively high (80°C) melting point of NAP costs extra energy to keep the molecules in a liquid state.

NEC has a reasonably high (5.8 wt.%) hydrogen storage capacity. NEC's hydrogenation can be realized using Pt group metals or Ni catalysts (Ye et al., 2011; Eblagon et al., 2012). Ru is the most active among these catalysts, with a reported selectivity of 98% toward complete hydrogenation (Eblagon et al., 2010). Compared with other LOHCs, the NEC system has a very low (de)hydrogenation enthalpy change (~50 kJ/mol.H<sub>2</sub>) and hence low dehydrogenation temperatures, making it ideal for feeding hydrogen to PEM fuel cells, which also have low operating temperatures (below 200°C). The low enthalpy change is attributed to the introduction of the heteroatom (nitrogen) as well as the pentagon ring (Pez et al., 2006). However, the relatively weak N-alkyl bond could result in dealkylation above ~120°C (Gleichweit et al., 2013). Another drawback for this system is the relatively high melting point, 68°C, of NEC. Stark et al. (2016) attempted to decrease the melting point of NEC via mixing with its hydrogenation derivatives or various N-alkylcarbazoles, but generally, the melting points of the mixtures are above room temperature. In addition to these technical factors, NEC's availability also needs to be considered for its large-scale LOHC application since NEC's production, mainly from coal tar distillation, is below 10,000 tonne per year (Brückner et al., 2014).

Recently, mixtures of isomeric DBT, which had been widely used as heat transfer oils under the trade name Marlotherm SH for decades, were proposed as promising LOHCs for stationary applications (Brückner et al., 2014). DBT can be hydrogenated into H18-DBT with Pt group metals around 140°C (Shi et al., 2019), and the reverse process can be carried out at 270–320°C (Brückner et al., 2014; Shi et al., 2019). The DBT/H18-DBT system has several advantages for LOHC applications, including high hydrogen storage capacity (6.2 wt.%), low toxicity, and thermal stability. Furthermore, hydrogenation of DBT using hydrogen-containing gas mixtures is possible (Dürr et al., 2017; Jorschick et al., 2018) with suitable catalysts. This is attractive for large-scale applications as it connects seamlessly with industrial processes which produce hydrogen-containing gas mixtures. The DBT/H18-DBT system has been used as an LOHC by Hydrogenious Technologies GmbH (Germany) and HySA Infrastructure (South Africa). However, the hydrogenation capacity of the DBT/H18-DBT system is sensitive to the operation process. For example, it has been reported that the capacity reduces to ~23% of its theoretical value after several (de)hydrogenation cycles due to incomplete dehydrogenation (Shi et al., 2019); on the other hand, a recent study achieved stable hydrogen capacity upon extended (de)hydrogenation cycles using a swing reactor that processes dehydrogenation and hydrogenation in the same place (Jorschick et al., 2019).

As shown in Figure 2, the hydrogen storage capacity of the above LOHCs is significantly lower than that of ammonia and methanol. On the other hand, the (de)hydrogenation process of the LOHCs can occur at lower temperatures as compared to the latter (as detailed in section 'Hydrogen storage by circular hydrogen carriers'), despite the LOHCs having higher (de)hydrogenation enthalpy. Upon dehydrogenation of ammonia/methanol, hydrogen needs to be separated from N<sub>2</sub> or CO<sub>2</sub> gas, which is not the case for LOHCs. In brief, both LOHCs and circular carriers have their strengths and weaknesses from the perspective of material properties, and the choice of hydrogen carriers depends on the consideration of multiple factors, such as cost and application scenarios. There are a vast number of organic molecules that could be studied—for example, recently, some of the authors studied the potential of some bio-based molecules (amaryllidaceae alkaloids) as LOHCs based on first principles computations (Tang et al., 2020a). Thus, exploring ideal LOHCs, still in an early stage, is likely to reward more efforts to find promising materials.





**Figure 3. Schematic of a stationary hydrogen storage system**  
(A–E) (A) Gaseous, (B) liquid, (C) LOHCs, and (D&E) circular carriers form.

### Comparison between $\text{CGH}_2$ , $\text{LH}_2$ , and LOHCs

For stationary applications, the conventional approaches of compressed gas and liquid hydrogen are the current state of the art, and, in contrast, LOHC-based hydrogen storage systems are still in an evolving phase. Only a small number of commercialization activities and technology providers worldwide use LOHCs, including Hydrogenious GmbH,  $\text{H}_2$ -Industries AG, Areva H2Gen, and Hynertech, Chiyoda Corporation (Hurskainen, 2019) and Hydrogenia Pty Ltd, an Australian company. Having discussed these three approaches generally above, we now focus on the techno-economic analysis of stationary storage based on each approach in this section. For large-scale stationary storage, the sites of end use are usually different from the storage sites. Therefore, we also lightly discuss hydrogen distribution here because of its impacts on stationary storage cost and technology.

#### Stationary storage process

Figure 3 illustrates how hydrogen is stored and transported via gaseous, liquid, LOHC, and circular forms. In the pressurized hydrogen system, Figure 3A, the compressor is a core component along with storage vessels. The compressor can be distinguished based on capacity and pressurization needs. A reciprocating compressor with a high flow rate and relatively low working pressures between 50 and 300 bars is required for typical stationary applications. The most common pressure vessel for gaseous hydrogen storage is a type 1 (hot rolled electric resistance welded) steel tube suitable for pressure ranging from  $\sim 100$  to 400 bar and interconnected to surge the overall storage capacity. Composite pressure vessels can also be used and are under development for stationary applications. They are more expensive than steel vessels

of the same size but have a higher pressure capacity and higher storage capacity. For the liquefaction approach, [Figure 3B](#), a series of compression, isenthalpic expansion via a Joule-Thomson valve, expansion cooling via a turbine, and cooling by nitrogen through a heat exchanger are involved in transforming hydrogen from the gaseous to the liquid phase. Liquid hydrogen is stored in super-insulated cryogenic pressure tanks due to its boil off; the tanks can be spherical or cylindrical, but large tanks are usually spherical to reduce the surface area. The core components of LOHC storage systems, [Figure 3C](#), are (de)hydrogenation reactors, liquid organic carriers, and storage tanks.

[Table 1A](#) listed the energy consumption for the different hydrogen storage systems. As shown in [Table 1A](#), electrical energy consumption for the LOHC system is negligible compared to the gaseous and liquid storage systems (more discussion on energy consumption by circular carriers  $\text{NH}_3$  and  $\text{CH}_3\text{OH}$  compared to LOHC can be found in section '[Hydrogen storage by circular hydrogen carriers](#)'). Furthermore, the heat produced in the exothermic hydrogenation process of LOHC can be recycled via an intelligent thermal management system to mitigate the thermal energy demand for the on-site endothermic dehydrogenation, as shown in [Figure 3C](#).

### Capital cost

Fixed capital cost plays a significant role in the overall costs of a large-scale stationary hydrogen storage system. Thus, before building a storage plant, proper modeling and optimization are essential to reduce the fixed capital cost by considering all possible constraints, including appropriately sizing the system's components according to the load demand. Typically, the fixed capital cost (or CapEx) includes the direct cost of the system's components, including the plant's balance of plant and indirect costs such as site preparation, engineering design, project contingency, and so on. As the fixed capital costs are not the focus of our current study and the cost of major components contributes to the highest share in CapEx ([Towler and Sinnott, 2012](#)), we have limited capital cost analysis only for the major components of the storage system to demonstrate which storage system is less capital intensive. Components of the storage system are typically considered for the lifetime of the plant (and/or a lifetime of the components) and sized accordingly to meet the optimum demand, but the sizing of storage units (i.e., tanks or vessels) of the product depends on daily demand and the uncertainty of the supply chain.

This study analyzed the capital cost in USD 2020 using a system storing 500 tonnes of hydrogen per day as an example based on ([Equation 1](#)) (can be found in the [method details](#) Section). Usually, stationary gaseous storage vessels have pressure ranges between 50 and 200 bar, and the capital cost for the vessels varies from \$800 to \$850 per kg of  $\text{H}_2$  in this pressure range ([Reuß et al., 2017](#); [USA Office of Energy Efficiency and Renewable Energy, 2014a](#)). However, the Department of Energy (DOE), USA, found that storage vessel cost is around \$700/kg of  $\text{H}_2$ , and it expects a possible decrease to \$635/kg of  $\text{H}_2$  in the near future ([USA Office of Energy Efficiency and Renewable Energy, 2014a](#)). For our analysis, we use a vessel pressure of 200 bar, the volumetric density of 13 kg of  $\text{H}_2$  per  $\text{m}^3$ , and vessel capital cost of \$700/kg of  $\text{H}_2$ , which translates into \$350M for 500 tonnes of  $\text{H}_2$ . Data for compressor price are scarce in the literature, especially for large scale; here, we assume the \$7.2M/system price for a reciprocating compressor with a flow rate of 4 tonne/h ([Wang et al., 2012](#)) with 6 systems for compressing 500 tonnes of  $\text{H}_2$ /day. For the liquefaction plant, extrapolation of data from Ref ([USA Office of Energy Efficiency and Renewable Energy, 2014a](#)), where the authors obtained \$70M capital cost for 30 tonnes of  $\text{H}_2$  and \$560M for 300 tonnes of  $\text{H}_2$ , gives the approximate cost \$935M for 500 tonnes of  $\text{H}_2$ . We assumed the cost of a cryogenic storage tank to be \$2250/ $\text{m}^3$ , translating into \$17.5M for 500 tonnes of  $\text{H}_2$  ([Hurskainen, 2019](#)). The LOHC (de)hydrogenation reactor is still at an emerging stage, and so there is a high degree of uncertainty in the literature on the cost of LOHC reactors for large scale. For example, [Teichmann et al. \(2012\)](#) used reactor cost \$315/kW for hydrogenation of 347MW at lower heating value (LHV) and 250 tonnes of hydrogen per day; [Reuß et al. \(2017\)](#) considered reactor cost \$115/kW for hydrogenation of 417MW at LHV and 300 tonnes of hydrogen per day. Furthermore, [Eypasch et al. \(2017\)](#) estimated the reactor cost to be \$300/kW for hydrogenation of 1MW at LHV and 0.003 tonnes of hydrogen per day. We assumed reactor cost \$97/kW for hydrogenation of 693MW at LHV based on recent literature ([Reuß et al., 2017](#)) and 500 tonnes of hydrogen per day for our calculation. The price of an example LOHC compound (DBT) is considered to be \$5/L, and the cost of a storage tank is considered to be \$150/ $\text{m}^3$  ([Hurskainen, 2019](#)).

Usually, for gaseous and liquid stationary hydrogen storage systems, a hydrogen dispensing system with a buffer tank needs to be installed based on end-user demands, but for LOHCs, a dehydrogenation system is

**Table 1. The key information for the analysis in sections ‘Current state of liquid organic hydrogen carriers for stationary storage’ and ‘Hydrogen storage by circular hydrogen carriers’**

(a) Energy consumption for different types of hydrogen storage (hydrogenation) systems

Storage systems	Consumption		Generation	Comments	Reference
	Electrical energy (kWh/kg of H <sub>2</sub> )	Thermal energy (kWh/kg of H <sub>2</sub> )	Electrical/thermal energy(kWh/kg of H <sub>2</sub> )		
CGH <sub>2</sub>	~2-7	–	–	Depends on the compressor.	(Gardiner, 2009)
LH <sub>2</sub>	~10-15	–	–	Depends on plant size, compressor, and turbine efficiencies.	(Gardiner, 2009)
LOHC	~0.016	–	~10.60	Exothermic process, usually, the storage cycle’s overall heat demand is low for stationary storage if we can use heat from the hydrogenation process. The LOHC system can be integrated with an existing heat distribution system to meet the heat demand.	(Eypasch et al., 2017)
NH <sub>3</sub>	~4.8	–	~4.5(g) ~6.8 (L)	Exothermic process, this heat can be used to generate steam to meet the energy demand for compression.	(Morgan, 2013)
CH <sub>3</sub> OH	~7.25 [DAC], ~3.17 [CCU]	~24[DAC], ~12[CCU]	~4.4 ~0.34(e)	Exothermic process, so the heat of reaction can be used to capture CO <sub>2</sub> . The electrical energy is generated in the synthesis loop due to the organic Rankine cycle.	(Van-Dal and Bouallou, 2013; Fasihi et al., 2019)

(b) Capital cost (in USD, 2020) for major system components of the hydrogenation process

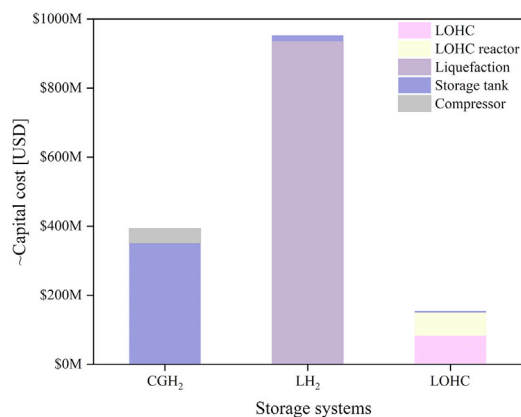
Storage systems	Major system components/materials	Approximate cost [\$M USD/tonne]	Comments	Reference
CGH <sub>2</sub>	Compressor	0.086	500 tonnes of hydrogen compress per day by reciprocating compressor with a flow rate of 4 tonnes of H <sub>2</sub> /h	(Wang et al., 2012)
	Storage tank	0.700	500 tonnes of hydrogen store @200 bar per day	(USA Office of Energy Efficiency and Renewable Energy, 2014a)
LH <sub>2</sub>	Liquefaction	1.870	Comprised series of components to liquefy 500 tonnes of hydrogen per day	(USA Office of Energy Efficiency and Renewable Energy, 2014a)
	Storage tank	0.035	500 tonnes of hydrogen store in a cryogenic tank per day	(Hurskainen, 2019)

(Continued on next page)

**Table 1. Continued**

(b) Capital cost (in USD, 2020) for major system components of the hydrogenation process

Storage systems	Major system components/materials	Approximate cost [\$M USD/tonne]	Comments	Reference
LOHC	Materials	0.005	~8700 tonnes of LOHC materials are required to store 500 tonnes of H <sub>2</sub> per day	(Hurskainen, 2019)
	Reactor	0.134	500 tonnes of H <sub>2</sub> processed per day via hydrogenation of ~8700 tonnes of LOHC	(Reuß et al., 2017)
	Storage tank	0.003	500 tonnes of hydrogen store per day	(Hurskainen, 2019)
NH <sub>3</sub>	Synthesis loop	0.219	~3200 tonnes of NH <sub>3</sub> need to be synthesized to store 500 tonnes of H <sub>2</sub> per day	(Morgan, 2013)
	Mechanical compression	0.051	The pressure of the synthesis gas (N <sub>2</sub> and H <sub>2</sub> mixture) need to increase for the synthesis of ~3200 tonnes of NH <sub>3</sub> per day	
	Air separation unit	0.094	Cryogenic air separation unit (ASU) for ~2637 tonnes of N <sub>2</sub> per day to synthesize 3200 tonnes of NH <sub>3</sub>	
	Storage tank	0.008	500 tonnes of hydrogen store per day	
CH <sub>3</sub> OH	DAC	0.267	~6750 tonnes of CO <sub>2</sub> required to synthesize ~4500 tonnes of CH <sub>3</sub> OH to store 500 tonnes of H <sub>2</sub> per day	(Fasihi et al., 2019; Keith et al., 2018)
	Synthesis loop	0.094	~4500 tonnes of CH <sub>3</sub> OH need to be synthesized to store 500 tonnes of H <sub>2</sub> per day	(Van-Dal and Bouallou, 2012, 2013; Nyári, 2018; Collodi et al., 2017)
	Storage tank	0.008	500 tonnes of hydrogen store per day	



**Figure 4. Approximate capital cost of major system components for CGH<sub>2</sub>, LH<sub>2</sub>, and LOHC storage systems with the capacity to store/hydrogenate 500 tonnes of hydrogen per day**

The costs of storage tanks and LOHC materials are considered for one-day storage.

an extra step to extract hydrogen (as shown in Figure 3C) along with the dispensing system. As our primary focus is hydrogenation, we have not considered the dehydrogenation and dispensing system. However, based on the preceding analysis and also listed in Table 1B, Figure 4 shows the capital cost of the main components of the hydrogen storage/hydrogenation systems, CGH<sub>2</sub>, LH<sub>2</sub>, and LOHC, with a storage capacity of 500-tonnes per day, calculated using (Equation 1). Among these storage systems, LOHC is the least capital intensive (even if we include the dehydrogenation system's capital cost, ~\$60M for 500 tonnes per day (Reuß et al., 2017)), and the cost of the LOHC compound governs LOHC storage costs, being almost 54% for the one-day storage system and around 91% for a 30-day storage system (details in section 'Hydrogen storage by circular hydrogen carriers'). However, the storage vessel is capital intensive in the gaseous system, whereas liquefaction is the ruling capital cost for liquid hydrogen storage. For the LOHC system, we have considered three storage tanks, two filled with LOHCs (one is reserved as a contingency) and the third one being empty to store discharged LOHCs. Usually, two storage tanks are enough for stationary application, one for charged LOHCs and one for discharged LOHCs.

### Distribution

Most hydrogen production is currently at or in the vicinity of end-use sites, e.g., petroleum refineries and ammonia plants, the primary industrial hydrogen users. The relatively small merchant hydrogen market uses cryogenic liquid hydrogen trucks or gaseous tube trailers. However, the hydrogen industry is growing, and many countries have invested in strategies to encourage large-scale hydrogen production as a sustainable energy carrier (COAG Energy Council, 2019; Germany Federal Ministry for Economic Affairs and Energy, 2020). Given the economies of the scale associated with hydrogen production, it becomes imperative to distribute hydrogen from a centralized or semi-centralized production facility to other points. There are three ways by which hydrogen is commonly transported, i.e., as a liquid by cryogenic tank trucks, as a compressed gas by tube trailers, or by pipelines (USA Office of Energy Efficiency and Renewable Energy, 2014a). Typically, each transportation option consists of a series of different process operations, and the reduction of delivery cost requires process optimization by considering geographic location, availability of operational resources, market size and type (urban, interstate, or rural), and customer needs. In the following, we discuss and compare individual options in more detail.

Pipelines are the apparent lowest cost option for hydrogen transportation at a large scale, but their installation is highly capital intensive and thus only suitable for a steady, high-volume hydrogen demand. Apart from pipeline design, having the right materials is a concern because of the hydrogen embrittlement of high strength steel. Furthermore, compressed gaseous hydrogen is limited for road transport due to strict safety regulations, depending on vessel structure, size, and transport container design. For road transport, composite pressure trailers are available in a pressure range of 200–350 bar with a net capacity of up to ~900 kg (USA Office of Energy Efficiency and Renewable Energy, 2014a). However, due to the low volumetric density of compressed gas, its transportation by steel tube trailer is only economic within ~300 km from the point of production (USA Office of Energy Efficiency and Renewable Energy, 2014a). Over 90% of merchant hydrogen is currently transported in liquid form; the US DOE reported that it is economically viable for greater than ~300 km (USA Office of Energy Efficiency and Renewable Energy, 2014a), but Reuß et al. (2017) found that it is the most cost intensive above 300 km. A LOHC tank trailer

with a capacity of 36,000 L can carry around 2000 kg of hydrogen from point to point, compared to 4300 kg of LH<sub>2</sub> (Table 2) (Teichmann et al., 2012; Hurskainen, 2019). Hydrogen transportation by sea is yet an early stage, and active research and development are going on worldwide to carry high-volume hydrogen. For sea transport of LOHCs, conventional tankers for oil and chemicals can be used, but with the maximum deadweight tonnages below 50,000 tonnes (MAN Diesel and Turbo, 2013), LOHCs are classed as chemicals. For liquid hydrogen, such carriers are not currently available at a large scale, other than Kawasaki Heavy Industry (Japan) small liquefied hydrogen carriers with a capacity of 200 tonnes (Abdin et al., 2020).

Table 2 quantitatively compares hydrogen transportation via gaseous, liquid, and LOHC forms. Among these three carriers, LOHC has an intermediate storage capacity but is the least cost intensive. For example, the trailer cost of LH<sub>2</sub> is ~6 times higher than that of LOHCs for road transport and ~10 times higher for sea transport. For road transport, if LOHC material cost is included, the LH<sub>2</sub> approach is ~3 times more expensive than LOHC, and with the same capital cost, the LOHC can carry ~1700 kg more hydrogen though it incurs extra tank trailer cost. Likewise, for sea transport, with the same capital cost of LH<sub>2</sub>, LOHCs can transport ~1.5 times more hydrogen though more energy and operation costs are incurred to conveyance.

## HYDROGEN STORAGE BY CIRCULAR HYDROGEN CARRIERS

### Ammonia synthesis and decomposition

#### Ammonia synthesis

Ammonia is typically synthesized by the Haber-Bosch process, coupled with hydrogen and nitrogen plants. As the hydrogen source, around 600 kg of natural gas is consumed to produce 1 tonne of NH<sub>3</sub> (Pfromm, 2017). Other fuels, e.g., biomass or petroleum coke, can also be used as hydrogen sources, but they are not as efficient or cheap as natural gas because of the more complex processes involved. At present, most ammonia plants are close to end use, and more than 85% of the global production, over 200 million tonnes per annum, is currently used as fertilizers, with the rest used mainly by chemical and processing industries (Giddey et al., 2017). Ammonia production is a promising trend because of the CO<sub>2</sub> emission associated with the natural gas approach and continuous price reduction of renewable energies (MacFarlane et al., 2020; Giddey et al., 2017). However, ammonia production and decomposition (to extract pure hydrogen) at end use are energy intensive. The supply chain infrastructure and regulatory framework are already in place in many countries, which are important factors for transporting ammonia as an energy vector.

The green Haber-Bosch process for ammonia synthesis (as shown in Figure 3D) uses renewable hydrogen from water electrolysis and nitrogen from an air separation unit (ASU) as the feedstock. Around 27 kW of power is required for the synthesis loop to produce 1 tonne of ammonia per day, and the ASU and mechanical compression (MC) require around 3.5 and 1.5 kW, respectively (Morgan, 2013). The ammonia synthesis process is exothermic and accompanied by a reduction of entropy, and thus, low temperatures and high pressures tend to help the reaction proceed toward the product direction. However, the Haber-Bosch process is carried out at high temperatures and pressures (~450°C and ~200 bar) because of the slow kinetics associated with the difficult dissociation of molecular nitrogen into atomic nitrogen (Rayment et al., 1985). Among many candidates, the catalyst of choice for the Haber-Bosch process is iron promoted with main group element oxides (Rayment et al., 1985), although Ru-based catalysts have also been commercialized (Appl, 1999). Recent years have seen the investigation of novel methods for ammonia synthesis, including solid-state ammonia synthesis (Garagounis et al., 2014).

**Ammonia decomposition.** Ammonia decomposition or cracking is endothermic, and active cracking depends on the catalyst. Typically, decomposition occurs at temperatures from 400 to 700°C, but for some catalysts, e.g., Ni, it needs temperatures around 1000°C (Lamb et al., 2019). A wide variety of materials are useful for ammonia decomposition, as reviewed in Ref (Lamb et al., 2019). Among single-metal catalysts, Ru is the most active. Some binary and ternary catalysts such as Ni-Pt, NiMo, MoNx, NiMoNx, and Co<sub>3</sub>Mo<sub>3</sub>N are also promising. The reactions of ammonia synthesis and decomposition follow the same fundamental principles and hence are microscopically reversible. However, Boisen et al. (2005) found that the optimal catalysts for ammonia decomposition are not the same as those for synthesis because the very different synthesis/decomposition reaction conditions (such as ammonia concentrations) result in different optimal energy ranges for the critical step, namely nitrogen binding on the catalyst surfaces.

**Table 2. Comparison of hydrogen transportation by road and sea, with the capital cost for truck and ship not considered**

Storage carrier	Road transport				Sea transport				References
	Capital cost Tanker/Trailer	Net H <sub>2</sub> capacity	Average fuel consumption	Comments	Capital cost Tanker/Carrier	Net H <sub>2</sub> capacity	Average fuel consumption for 5000 km	Comments	
CGH <sub>2</sub>	~\$630K @200 bar for 2 steel bottles ~\$500K @350 bar composite	400 kg 900 kg	~45 l/100 km at ~65–77 km/h	Other costs may be incurred, including O&M (operations and maintenance), fuel price and driver salary, etc..	-	-	-	CGH <sub>2</sub> is not viable due to its low storage capacity. Here the main dominating factor on the supply chain is storage tank cost and loading infrastructure and jetty, O&M, fuel cost, etc..	(Hurskainen, 2019, Reuß et al., 2017, Teichmann et al., 2012, Kan and Shibata, 2018)
LH <sub>2</sub>	~\$1050K	4300 kg	~\$430M [Tanker size is 160, 000 m <sup>3</sup> ]		~11,200 tonnes	~1050 tonnes for 17 days at 30km/h			
LOHC	~\$180K	2000 kg	~\$42M [Tanker size is 45 000 DWT]		~2800 tonnes	~530 tonnes for 19 days at 27 km/h			

At present, electric furnaces are commercially available to decompose ammonia at a small scale to produce forming gas ( $H_2$  and  $N_2$  mixture) for various industrial applications. Currently, there is no ammonia decomposition plant at a large scale for extracting pure hydrogen from ammonia. However, recently, [Jackson et al., 2020](#) designed and simulated a large-scale ammonia fired reformer, which is a conventional cracking system, in Aspen Suite to generate  $200 \text{ tonnes} \cdot \text{day}^{-1}$  of high purity hydrogen at 250 bar with an overall efficiency of around 69%, resulting in specific energy consumption of around 40 kWh per kg of hydrogen. For ammonia decomposition, reactor material choice is critical because of the detrimental reaction environment, which may cause thermal stress, stress corrosion cracking, and hydrogen embrittlement to the reactor. The membrane reactor for ammonia decomposition has been demonstrated at the lab scale, in which chemical reactions and the selective separation of a product co-occur. Thus, it may not need any downstream separation unit, which would help increase efficiencies at lower operating temperatures ([Zhang et al., 2019](#)). However, using tantalum tubes as the membrane support, which exhibits selective hydrogen diffusion, would be prohibitively expensive for large-scale ammonia decomposition.

## Methanol synthesis and decomposition

### Methanol synthesis

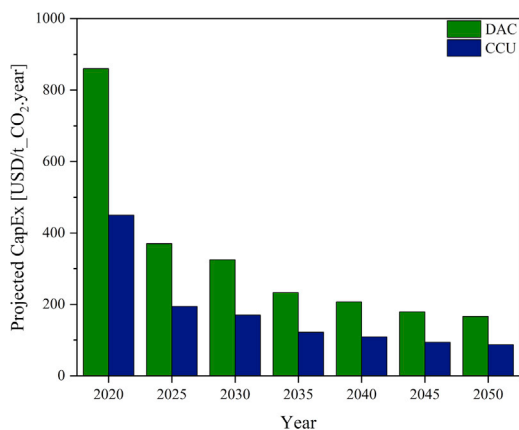
Usually, methanol is produced from pressurized syngas, as illustrated in [Figure 3E](#). Syngas can be produced by either steam reforming light hydrocarbons, such as natural gas or light naphthas, or by partial oxidation of heavy oils or solid carbonous materials ([Pérez-Fortes et al., 2016](#)). For the steam reforming process, one tonne of methanol production costs  $\sim 10$  MWh equivalent natural gas and releases  $\sim 0.5$  tonne of  $CO_2$ ; for the partial oxidation process, it costs  $\sim 10.5$  MWh equivalent oil and releases  $\sim 1.4$  tonnes of  $CO_2$  ([Pérez-Fortes et al., 2016](#)). Methanol can also be produced by  $CO_2$  hydrogenation with hydrogen produced by water electrolysis and  $CO_2$  captured from the flue gas of fossil fuel-based power plants or non-energetic sectors, e.g., cement plants. However,  $CO_2$  capture is capital and energy intensive and hinders the overall plant efficiency. For example, capturing one tonne of  $CO_2$  at a capture rate of 85% costs about  $\sim 44 \text{ kWh}_{el}$  for compressing the feed and  $\sim 890 \text{ kWh}_{th}$  for regenerating the solvent ([Van-Dal and Bouallou, 2012](#)). Methanol synthesis is exothermic. Thus, it does not require any external heat input; so, the thermal energy during the synthesis process can be used to capture  $CO_2$ , which helps increase overall efficiency. It is noted that after synthesis, distillation or purification of methanol is solely relying on the end-user demand; for example, the methanol stream ( $CH_3OH + H_2O$ ) can be stored as is to produce hydrogen via steam reforming. Therefore, it may help to save on capital cost and energy consumption for the distillation process.

However,  $CO_2$  capture from flue gas may not be sufficient and/or economically feasible for methanol synthesis at a large scale. Also, flue gas suitable for capture is only a small fraction of global emissions, and with a carbon capture unit (CCU), the flue gas capture rate is between 40% and 90% ([Pérez-Fortes et al., 2016](#); [Van-Dal and Bouallou, 2012](#); [Leung et al., 2014](#)). CCU-based methanol plants are typically installed on site at fossil fuel-based power plants and/or other industrial sites where hydrogen is produced either via steam methane reforming or sourcing from hydrogen merchants. However, the green hydrogen economy is thriving. Moreover, if we want to store green hydrogen as methanol, it is imperative to synthesize methanol at the hydrogen generation site; thus, capturing  $CO_2$  on site could be a possible alternative.  $CO_2$  purchased from a carbon capture and storage (CCS) plant (off-site) could be a possible option. However, it needs purification, incurs purchasing cost and high transportation cost, on-site storage cost, peripheral cost of a  $CO_2$  storage system, etc., substantially increasing the overall cost. The capture of  $CO_2$  from the atmosphere, commonly known as direct air capture (DAC) ([Keith et al., 2018](#)), could be another possible option to capture  $CO_2$  on site, though it is currently capital and energy intensive. In a DAC system, around  $300 \text{ kWh}_{el}$  electrical energy and  $1800 \text{ kWh}_{th}$  thermal energy are required to capture 1 tonne of  $CO_2$  ([Fasihi et al., 2019](#)). The production of 1 tonne of methanol costs around  $0.8 \text{ MWh}_{el}$  and  $3.20 \text{ MWh}_{th}$  energy as well as 1.5 tonne of  $CO_2$  and 0.2 tonne of  $H_2$  ([Fasihi et al., 2019](#)). It is expected that the cost of DAC will drop significantly in the following decades, as shown in [Figure 5](#), which compares the CapEx learning curves of DAC and CCU at a learning rate of 12.5%. These are calculated based on ([Equation 2](#)) and ([Equation 3](#)) (can be found in the [method details](#) section) with input data from Refs ([Fasihi et al., 2019](#); [Keith et al., 2018](#); [Nyári, 2018](#); [Collodi et al., 2017](#); [Wilberforce et al., 2020](#); [Rosa et al., 2020](#)), as shown in [Table 3](#).

### Methanol decomposition

Methanol dissociation is an endothermic and catalytic process; typically, around 9 to 12 tonnes of  $CO_2$  is produced to extract 1 tonne of hydrogen by steam reforming ([Collodi, 2010](#)). Thus, dynamic thermal





**Figure 5. Project CapEx learning curves for CO<sub>2</sub> capture by direct air capture (DAC) and carbon capture unit (CCU)**

Typically, for conservative scenarios, it is assumed that only 50% of CO<sub>2</sub> capture demand defined by the Paris Agreement is realized, and the CapEx for DAC and CCU has a learning rate of 10%. For the best-case scenario, 100% realization and a learning rate of 15%, which is typically exhibited by highly modular energy technologies (Schmidt et al., 2017; Caldera and Breyer, 2017), are assumed. Here, we consider an intermediate case assuming an effective execution of the Paris Agreement with 75% realization and a learning rate of 12.5%.

management and CCU are prerequisites to extract the hydrogen from methanol and avoid CO<sub>2</sub> emissions. In addition, the captured CO<sub>2</sub> can be used during the synthesis process, though this may incur extra cost and energy use. As of now, no hydrogen extraction out of methanol has been implemented in methanol plants by integrating carbon capture unit and storage because most methanol is either used as is for the transport sector or further transformed into its derivatives like formaldehyde or dimethyl ether. Thus, it is imperative to have a robust techno-economic analysis to understand the feasibility and round trip efficiency of converting methanol to hydrogen, recycling CO<sub>2</sub> and other derivatives.

### Comparison between ammonia, methanol, and LOHCs

As mentioned earlier, in this perspective article, our primary focus is the hydrogenation system and capital cost analysis of its major system components. Thus, in this section, we limit our study to the hydrogenation process that produces ammonia, methanol, and the hydrogen-rich LOHC compound H18-DBT. These carriers are currently mostly used as is or other derivatives; large-scale dehydrogenation of these carriers is not much studied because of the emerging state of hydrogen as a global energy carrier. Nevertheless, Jackson et al., 2020 estimated capital cost of around \$510M for ammonia dehydrogenation system of 200 tonnes of H<sub>2</sub> per day, and Reuß et al. (2017) estimated that approximate investment costs of \$36M for LOHC dehydrogenation plants of 300 tonnes of H<sub>2</sub> per day. Usually, additional steps are required to separate pure hydrogen from other gaseous by-products for hydrogen extraction from ammonia and methanol. Besides, ammonia and methanol (i.e., hydrogenation of N<sub>2</sub> and CO<sub>2</sub>) are more energy intensive than the hydrogenation of LOHCs. In the following, we compare the power and capital costs related to the three carriers for an example process of storing 500 tonnes of hydrogen per day, which corresponds to the production/hydrogenation of ~3200 tonnes of ammonia, ~4500 tonnes of methanol, or ~8700 tonnes of hydrogenated LOHCs (using H18-DBT as an example) per day, all including ~10% surplus. For ammonia, this requires electrical power of ~100 MW<sub>el</sub> (Morgan, 2013). The exothermic ammonia synthesis process (in the liquid phase) also produces ~153 MW<sub>th</sub> thermal power. For methanol, the required electrical and thermal power (based on DAC) is ~151 MW<sub>el</sub> and ~500 MW<sub>th</sub>, respectively, and at the same time, ~7 MW<sub>el</sub> electrical and ~92 MW<sub>th</sub> thermal power are produced, which can be used for carbon capture and to reduce the required power input (Van-Dal and Bouallou, 2013; Fasihi et al., 2019). For DBT, the required electrical power (~0.35 MW<sub>el</sub>) is negligible compared to ammonia and methanol, and the generated thermal power due to exothermal hydrogenation is ~220 MW<sub>th</sub> (Eypasch et al., 2017). These are illustrated in Figure 6A and listed in Table 1A. For ammonia and LOHCs, the produced thermal power can be stored and used later for dehydrogenation, especially for an on-site stationary plant. Ammonia and methanol are stored and transported at ambient temperatures, with ammonia at slightly elevated pressure (~10 bar). However, a recent study showed that boil-off occurs at different stages, with the total daily energetic boil-off of ammonia and methanol being 0.098% and 0.034%, respectively (Al-Breiki and Bicer, 2020). In contrast, LOHCs can be stored and transported in a standard existing fuel tank without any loss.

Next, we consider the capital costs for material storage and other major system components, computed using (Equation 1), associated with the three carriers based on the example process mentioned in the previous paragraph. Usually, chemical plants require storage in two parts of the manufacturing process: firstly,

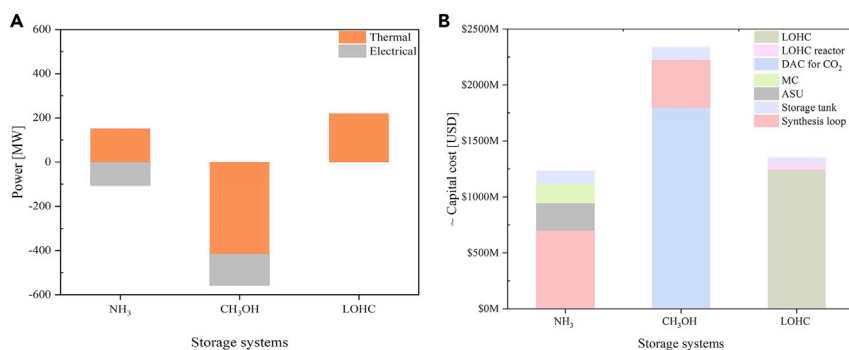
**Table 3. Projecting the future CapEx for DAC and CCU**

Particulars	CO <sub>2</sub> capture [Mt/year]						
	2020	2025	2030	2035	2040	2045	2050
Year							
Approximate cumulative capacity	3	238	473	2632	4791	10,075	15,356
@75% realization cumulative capacity	2.25	179	355	1974	3593	7555	11,517
Approximate CapEx for DAC/CCS	USD/t <sub>CO<sub>2</sub></sub> -year						
@ learning rate 12.5%	860/450	370/194	325/170	233/122	207/109	179/94	166/87

a diurnal reservoir to store about 8 hr worth of reactants so that maintenance can be done as required without shutting down the entire facility and secondly 30 days of storage for all products and reactants in case of supply chain interruptions (Ulrich, 1984; M Walas, 1990). Since the synthesis or hydrogenation process of ammonia, methanol, and LOHCs is continuous without disruptions, sufficient on-site storage space for the products is required. Therefore, this study considered only the end products' daily storage (i.e. ~3200, ~4500, and ~8700 tonnes of ammonia, methanol, and charged LOHC, respectively) plus the vessels for their 30-day storage. The approximate costs for the storage vessels, together with other major components detailed below, are shown in Figure 6B calculated by (Equation 1).

For ammonia, in addition to the storage vessels mentioned above, an ASU for N<sub>2</sub>, MC to condense the synthesis gas mixture, and synthesis loop for ammonia conversion are the main components we have considered, with the capital cost data from Ref (Morgan, 2013) being extrapolated for our study and also listed in Table 1B. The synthesis loop incurs the most capital cost, as shown in Figure 6B, which is evident because it comprises a series of compressors, heat exchangers, pumps, reactors, and flash drums. For methanol, DAC for CO<sub>2</sub>, the synthesis loop for methanol conversion, and the storage tank are the main components. The synthesis loop of methanol also consists of different components such as a reactor, boiler, series of heat exchangers, flash separators, distillation columns, and compressors. Cost information has been extracted from (Van-Dal and Bouallou, 2012, 2013; Keith et al., 2018; Collodi et al., 2017; Nyári, 2018) and listed in Table 1B. Afterward, we have calculated the capital cost of methanol's major hydrogenation system components using (Equation 1). As shown in Figure 6B, the most expensive component is DAC due to its emerging stage. However, as shown in Figure 5, if the demand for CO<sub>2</sub> capture from the atmosphere continues to increase, the cost is expected to decrease. We note that, in contrast, a previous study by Niermann et al. (2019b) predicted that methanol has a lower system cost than ammonia and LOHCs. The inconsistency results from the fact that the previous work assumed the CCS approach for methanol synthesis while our work assumed the currently more expensive DAC. We note that even in that study, the LOHC approach is only slightly more expensive than that of methanol. For the LOHC approach, the material cost is the major cost component for 30 days of operation. Overall, Figure 6B indicates that methanol could be the most expensive hydrogen storage approach, significantly higher than that of ammonia and LOHC. LOHC is slightly more expensive than ammonia due to its high material cost. For DBT, the loss per storage cycle is ~0.013%, and it can be recycled 750 times before regeneration is required (HySTOC, 2019a). If recycled LOHC is used for hydrogen storage, the material cost is in inverse proportion to recycle times and hence significantly reduced. Noted that the above analysis assumes the new LOHC material cost is \$5/L. However, for a large-scale storage system, the material price could be significantly lower due to wholesale and/or on-site synthesis of the liquid organic compounds, which could greatly enhance the competitiveness of LOHCs (HySTOC, 2019b; Raab et al., 2021).

In the analysis of Figures 4 and 6B, we did not consider the catalyst cost as the major system component capital cost for the LOHC and circular carriers because it is consumables and hence belongs to operating cost (Niermann et al., 2019b). However, it deserves discussion due to its importance. For LOHCs, an early assumption (USA Office of Energy Efficiency and Renewable Energy, 2014b) that 1 kg of catalyst, at a price of ~\$150, can hydrogenate ~500 tonnes of LOHCs is widely cited in the literature (Niermann et al., 2019a; Aakko-Saksa et al., 2018; Teichmann et al., 2012), while it lacks detailed justification. A recent study (Jorschick et al., 2017) indicates that the hydrogenation productivity for 0.3wt.% Pt/Al<sub>2</sub>O<sub>3</sub> catalyst is ~3 g<sub>hydrogen</sub>/g<sub>Pt</sub>-min or ~0.54 kg<sub>hydrogen</sub>/kg<sub>catalyst</sub>-hour. The catalyst price ranges from \$110 to \$2100 for 0.5-5wt.% Pt/Al<sub>2</sub>O<sub>3</sub> (Alibaba, 2021). Based on a conservatively estimated catalyst life span, 14,000 hr (Rüde et al., 2018), charging 15,000 tonnes of H<sub>2</sub> in 30 days needs ~1984 kg of catalyst or ~\$0.22M if \$110 per kg for 0.3wt.% Pt catalyst is assumed.



**Figure 6. Estimation of power and capital cost for NH<sub>3</sub>, CH<sub>3</sub>OH, and LOHC hydrogenation plants**

(A) Estimated power requirement for incorporating 500 tonnes of hydrogen into different storage systems per day. The required/generated power is shown as negative/positive numbers. We assumed the post-reaction cooling of the products roughly cancels the power required to heat up the reactants, and so, the generated thermal power is mainly determined by the enthalpy change of the reactions.

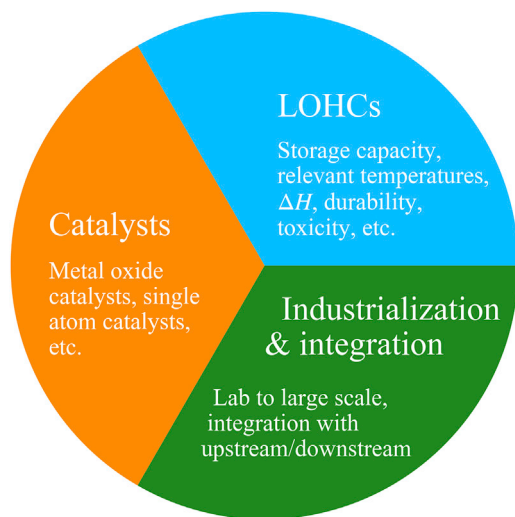
(B) Approximate capital cost of major system components for NH<sub>3</sub>, CH<sub>3</sub>OH, and LOHC hydrogenation plants to store 500 tonnes of hydrogen daily. The costs for storage tanks and LOHC material are for 30-day storage.

We note the above productivity (Jorschick et al., 2017) is for a lab-scale reactor where hydrogenation and dehydrogenation alternatively occur, with the former's temperature slightly higher than that of the latter. For large-scale operation, we assume a higher Pt loading (hence with higher efficiency), 5wt.% Pt/Al<sub>2</sub>O<sub>3</sub>, for the same productivity  $\sim 0.54$  kg<sub>hydrogen</sub>/kg<sub>catalyst</sub>-hour. Our assumption increases the corresponding catalyst cost to  $\sim \$4.17$ M at price  $\$2100$ /kg. In contrast, ammonia and methanol synthesis catalysts, not containing noble metals, are significantly cheaper than LOHCs. Nevertheless, one can see that the catalyst cost for LOHCs does not significantly change relative economic attractiveness of the different carriers shown in Figure 6B, although it becomes significantly more important for the LOHC approach if recycled LOHCs are considered. The catalyst cost for LOHCs is expected to reduce significantly as new catalysts with less or no noble elements are developed in the future.

## SUMMARY AND OUTLOOK

This perspective article has demonstrated how LOHCs could be one of the best possible options for storing hydrogen at a large scale in comparison with current dominating densified storage technologies (gaseous and liquid) and circular hydrogen carriers (mainly ammonia and methanol). Compared to LOHCs, the gaseous storage approach's major obstacles include the low volumetric density and safety concerns, and those of liquid hydrogen storage include boil-off loss and high cost. For an example case of storing 500 tonnes of hydrogen per day, our analysis of major system components indicates that the capital cost for liquid hydrogen storage is more than two times of that for the gaseous approach and four times of that for the LOHCs (DBT used as an example) approach. Although the shipping of LOHCs is not the focus of this work, analysis by Wang et al. (2016) shows that the energy efficiency for LOHC shipping without heat recycling is around 60-70%, depending on the dehydrogenation rate, which is comparable to liquid hydrogen shipping. With heat recycling, efficiency is around 80-90%. As with LOHCs, ammonia and methanol could be attractive options as hydrogen carriers at a large scale because they are compatible with the existing liquid fuel infrastructure. However, their synthesis and decomposition are energy and capital intensive compared to LOHCs. The electrical power required for storing 500 tonnes of hydrogen per day is  $\sim 100$ ,  $\sim 150$ , and  $\sim 0.35$  MW for ammonia, methanol, and DBT, respectively. The capital cost of major components for the methanol approach is roughly two times that of ammonia and LOHCs, mainly due to the expensive CO<sub>2</sub> capture from the atmosphere, which has not been commercialized yet. In addition, if the circular hydrogen carriers are not used as is, extra steps for hydrogen separation are required after their decomposition.

Based on cost and energy efficiency considerations at the current stage, the above indicates that LOHCs could be one of the best options to store hydrogen at a large scale for a long time. However, compared to densified storage and circular carriers, of which the technologies are relatively mature, the LOHC approach is still in its early stage. Therefore, as illustrated in Figure 7, three research directions are identified for its



**Figure 7. Challenges and milestones for LOHCs**

Note that these challenges and milestones are equally needed to be considered for both hydrogenation and dehydrogenation processes.

success and competitiveness in the future. First, the research on LOHC materials aims to find new molecules in terms of energy efficiency, durability, cost, safety, etc., for various applications, although a few materials have already been commercialized. Second, cheaper and more abundant catalysts, such as transition metal oxides, with comparable performance are necessary because of the scarcity of noble metals. The third milestone is about the transition from laboratory/prototype scale to industrial-scale production and the integration with other industries (Krieger et al., 2016).

### Method details

The following equation can define the capital cost for major system components of the stationary hydrogen storage system:

$$\text{Capital Cost} = \sum \text{Cost of major system components} + \text{Cost of storage unit} \times N \quad (\text{Equation 1})$$

Here, "N" is the number of storage units required for a period of storage time.

Estimating CapEx learning curves for CO<sub>2</sub> capture by DAC and CCU can be calculated based on (Caldera and Breyer, 2017) as follows:

$$C(t) = C_{in} \left( \frac{X}{X_{in}} \right)^b \quad (\text{Equation 2})$$

$$LR = 1 - 2^b \quad (\text{Equation 3})$$

Here, C(t) is the CapEx cost at a given time, t, X is the cumulative production at that time, C<sub>in</sub> is the initial CapEx at a cumulative production of X<sub>in</sub>, and b is the learning elasticity; using this learning elasticity, the price reduction for each doubling of cumulative production capacity can be calculated as learning rate, LR.

### LIMITATIONS OF THE STUDY

This perspective article primarily analyzed the hydrogenation system of LOHCs along with other hydrogen storage methods based on their technologies and the capital cost of major components. However, it has not investigated the dehydrogenation system. And also have not studied the whole of system for each technology to predict the leveled cost of hydrogen storage and the plant's overall cost (i.e. CapEx, operational expenditure (OpEx), and decommissioning cost). It is also noted that this study lightly covered hydrogen distribution and transportation as this is not the focus of this study. This manuscript illustrated how LOHCs could be one of the best possible options to store hydrogen compared to other storage methods (analyzed in this work), but to prove the viability of LOHCs compared to other methods requires robust modeling and optimization (includes different constraints) for the whole of system, which is not the focus of this study.

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## AUTHOR CONTRIBUTIONS

Conceptualization, Z.A.; methodology, Z.A.; formal analysis, Z.A.; investigation, Z.A.; visualization, Z.A. and C.T.; resources, Z.A. and C.T.; writing – original draft, Z.A. and C.T.; writing – review & editing, Z.A., C.T., Y.L., and K.C.

## DECLARATION OF INTERESTS

The authors declare no competing interests.

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