Hydrogen Storage and Transportation Technologies to Enable the Hydrogen Economy: Liquid Organic Hydrogen Carriers

Overview and perspectives on liquid organic hydrogen carriers technology

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Reliable storage and transportation of hydrogen at scale is a challenge which needs to be tackled to allow a robust and on-demand hydrogen supply when moving towards a global low carbon hydrogen economy with the aim of meeting net-zero climate goals. Numerous technologies and options are currently being explored for effective hydrogen storage and transportation to facilitate a smooth transition to the hydrogen economy. This paper provides an overview of different hydrogen storage and transportation technologies, focusing in more detail on liquid organic hydrogen carriers (LOHCs), its advantages and disadvantages and future considerations for the optimisation of the LOHC technology.

1. Introduction

In recent years there has been great interest in reducing fossil fuel reliance. This comes in an attempt for countries to deliver on pledges outlined in the Paris Agreement of 2016, which was compiled to tackle climate change by lowering greenhouse gas emissions (GHG) (1, 2). Individual nationally determined contributions (NDCs) are central to this agreement, detailing the collective efforts required to achieve longer-term global aims. Within these NDCs, several countries made specific references to the increased use of renewable energy resources, given their widely recognised environmental advantages over more traditional fossil fuel equivalents. Now, atmospheric CO_2 levels are higher than any recorded in the previous 800,000 years, with a rise from 300 ppm to 400 ppm being recorded over the last 70 years (1950–2020) (3). These continually rising levels are commonly attributed to the increased consumption of fossil fuels, which are conveniently employed to satisfy ever-changing energy demands. Yet the consequences are serious: during the 20th century a 1°C increase in average global temperature accompanied the growth of CO_2 emissions, causing drastic changes in weather patterns and rising sea-levels (4, 5).

Fossil fuels are extremely widely used because of convenience, availability and the economic advantage of a lower initial capital expenditure. Developing a 'greener' system with a comparable energy density and transport efficiency is a challenge (6). Despite several years of research into alternatives, there is still a significant way to go before achieving the goals proposed in the Paris Agreement by 2050. In 2016 just 19.5% of the global energy demand was fulfilled by renewable sources (7). Germany, however, has pledged that by 2050, 80% of its energy will be produced from renewable sources, whereas other countries have implemented strategies to increase collaborative research to achieve net-zero emissions (7, 8). As

an example, Portugal and The Netherlands signed a memorandum of understanding to develop a strategic export-import value chain to ensure production and transport of green hydrogen from Portugal to The Netherlands and its hinterland *via* the ports of Sines and Rotterdam (9).

Hydrogen is a well-studied alternative to fossil fuels. With its combustion producing only water as a byproduct, the environmental advantages of employing hydrogen as an energy carrier are obvious. However, at present, around 96% of the annual global hydrogen production is generated from fossil fuels (grey or brown hydrogen) (**Table I**). This comprises steam reforming of methane (48%), reforming of oil/naphtha (30%) and coal gasification (18%) (11). Thus, in order to completely remove reliance on the non-renewable, finite, fossil fuel resources, an alternative method of hydrogen production is required. This can be achieved with the electrolysis of water. Provided the energy for this process is obtained from renewable sources, sustainable, greenhouse gas emission-free hydrogen production is possible. Hence, hydrogen produced in this manner is termed green hydrogen.

The European Union (EU) has pledged billions of Euros to develop the so-called European Green Deal in the coming years. Here, hydrogen is considered 'a key' to fulfilling the ambitious target of halving carbon emissions by 2030 (8). To achieve this, the European Green Deal acknowledges the need to increase green hydrogen production capacity, setting targets for around 10 million tonnes of hydrogen to be produced annually by 2030 (8). Currently, the hydrogen supplied from electrolysers stands at just 4% of demand (8).

A third colour-coded category of hydrogen refers to blue hydrogen (**Table I**). Blue hydrogen is often considered a vital tool in transitioning from grey to green hydrogen production and, like grey hydrogen, uses a fossil fuel feedstock. However, carbon capture and storage (CCS) technologies are also employed to capture CO_2, reducing the greenhouse gas emissions (12). Given the increase in carbon-tax expected over the coming decades, blue hydrogen is an important improvement upon grey hydrogen, despite the currently higher initial capital expenditure (12–14). Brown, grey, blue and green hydrogen (**Table I**) are the most discussed colour-coded categories of hydrogen within the energy industry. Nevertheless, countless other hydrogen colours (i.e. the hydrogen colour spectrum), such as yellow, pink and turquoise hydrogen, also exist with each colour code describing the different type of source or process used to produce hydrogen (15, 16). For instance: pink hydrogen is generated by electrolysis of water using electricity from a nuclear power plant; yellow hydrogen is produced *via* electrolysis using solar power; turquoise hydrogen is generated *via* methane pyrolysis through direct splitting of methane into hydrogen and solid carbon (15, 16).

Some countries are well-positioned to the transition to blue hydrogen production, with a potential access to large, offshore CCS facilities (17). In contrast, many landlocked countries in Europe have a greater focus on the transition to green, rather than blue, hydrogen due to their limited access to offshore facilities (18). In addition, with blue hydrogen still requiring a finite resource, the demand of one country may eventually be pushed onto another, where resources are more available (12, 19). For example, an exhaustion of natural gas supplies in one location would require a country to source this elsewhere, resulting in the production of hydrogen and its utilisation at different locations. This dependence (expected to be governed by

Table I A Comparative Summary of Hydrogen Production Processes and Hydrogen Colour Codes (10)[a]				
	Brown	**Grey**	**Blue**	**Green**
Feedstock	Coal	Natural gas	Natural gas	Renewable electricity
Carbon capture	Gasification, no CCS	Steam methane reforming, no CCS	Advanced gas reforming + CCS	Electrolysis
Emissions	Highest GHG emissions ($19\ t_{CO_2}\ t_{H_2}^{-1}$)	High GHG emissions ($11\ t_{CO_2}\ t_{H_2}^{-1}$)	Low GHG emissions ($0.2\ t_{CO_2}\ t_{H_2}^{-1}$)	Potential for zero GHG emissions
Cost	US\$1.2–2.1 $kg_{H_2}^{-1}$	US\$1–2.1 $kg_{H_2}^{-1}$	US\$1.5–2.9 $kg_{H_2}^{-1}$	US\$3–7.5 $kg_{H_2}^{-1}$

[a] CCS = carbon capture and storage; GHG = greenhouse gas; $t_{CO_2}\ t_{H_2}^{-1}$ = tonne of CO_2 per tonne of hydrogen

maintaining amicable international relations) is another factor causing several countries to seriously consider the favourability of blue over green hydrogen, or *vice versa* (12).

Producing hydrogen from renewable sources and development of technologies for this purpose have huge environmental benefits and supports the implementation of the Paris Agreement and the United Nations Sustainable Development Goals (SDG) (20). It contributes to multiple SDGs, such as SDG 7 (Affordable and Clean Energy), SDG 9 (Industry, Innovation and Infrastructure), SDG 11 (Sustainable Cities and Communities) and SDG 13 (Climate Action) (20). According to SDG 7: Affordable and Clean Energy, a substantial increase in the share of renewable energy in the global energy mix is required by 2030 (i.e. Target 7.2 of SDG 7) (21). However, the energy output from renewable sources is intermittent and dependent on geographic, seasonal and temporal factors. Furthermore, sites of highest energy potential for renewable hydrogen production (such as a desert, offshore wind and tidal farms) are rarely located in areas of highest energy demand, such as densely populated cities in central and southern Europe (1, 22). When moving towards a global low carbon hydrogen economy with the aim of meeting net-zero climate goals, a reliable storage and transportation of hydrogen at scale is a challenge which needs to be tackled to achieve a widespread usage of renewable hydrogen. The possibility to store and transport hydrogen is essential for the integration of high shares of renewable energy source with positive effects on SDGs (23).

Numerous technologies and options are currently being explored for effective hydrogen storage and transportation to facilitate a smooth transition to the hydrogen economy (24). LOHC is one such technology which has gained considerable attention in recent years (1, 6, 7, 25–27). In our work, which consists of the present paper and two accompanying papers (28, 29), we provide an overview and new perspectives on the LOHC technology among different hydrogen storage and transportation technologies. We analyse the advantages and disadvantages of the LOHC technology and future considerations for its optimisation which might accelerate its commercial deployment. Furthermore, in our following second paper we describe the potential deployment and integration of LOHCs within different industries: the transportation sector (automobiles, ships, trains); steel and cement industries; the use of stored hydrogen to produce fuels and chemicals from flue gases; and system integration of fuel cells and LOHCs for energy storage (28). Due to numerous possibilities for the commercial deployment and integration of LOHCs within different industries, the use of different LOHC systems might be considered to accommodate specific requirements. A review of the most prominent LOHC systems, focusing on properties of LOHCs and catalytic materials used for hydrogenation and dehydrogenation of LOHCs, is presented in our third paper dedicated to the analysis of LOHC systems (29).

2. Hydrogen Storage and Transportation Technologies

Despite the attractively high gravimetric energy density of hydrogen (120 MJ kg^{-1}), the low volumetric energy density at ambient conditions necessitates the use of pressurised or liquified hydrogen to ensure economic viability (30). On a large-scale, the use of stored, highly pressurised hydrogen in transport systems presents serious safety concerns, such as an explosion. The technology is also costly, much like that of liquified hydrogen storage, which requires low temperatures (−252°C). In addition, such liquified hydrogen technologies can result in losses of between 0.3% and 3% of the hydrogen due to boil-off from the storage system (1).

Compressed hydrogen is typically transported through pipelines. As a result, long-distance transport is significantly more challenging when compared to the infrastructure, such as ships or railroads, currently available to transport liquid fossil fuels. Although attempts have been made to inject hydrogen into the natural gas grid and numerous countries are exploring blending hydrogen with natural gas, it can be argued that the intercontinental transport of hydrogen would require innovative solutions (31–33). These solutions are predicted to resemble current methods, relying on tanker vessels, trucks and railroads.

To overcome the challenges raised with the transportation and storage of hydrogen as an energy vector, more sophisticated concepts have been developed (**Figure 1**) (24). One such concept involves the use of low- and high-temperature metal hydride systems, where reversible adsorption and desorption of hydrogen is permitted through formation and breakage of chemical bonds with the storage material (1, 11, 34). Here, the terms low- and high-temperature systems refer to the dehydrogenation reaction temperature. These methods of solid-state hydrogen storage, therefore,
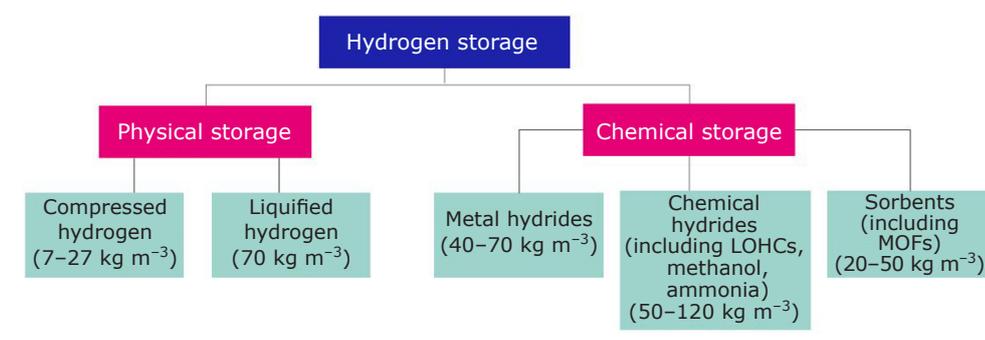
Fig. 1. Categorisation of hydrogen storage methods. Reprinted from (24) under a Creative Commons Attribution 4.0 International Licence (CCBY 4.0)

do not require the demanding pressures associated with storing compressed hydrogen.

Low temperature metal hydrides are capable of releasing hydrogen at ambient temperatures and pressures but are typically limited to a maximum hydrogen capacity of 2.15 wt% (for example, $LaNi_5H_6$) (35). On the contrary, high temperature hydrides are attractive for hydrogen storage because of their high hydrogen storage capacities (6.5 hydrogen atoms per cm^3 (7.6 wt%) for the metal hydride MgH_2, compared to a hydrogen storage density of 0.99 hydrogen atoms per cm^3 for hydrogen gas and 4.2 hydrogen atoms per cm^3 for liquified hydrogen). However, disadvantages of high temperature metal hydride systems include slow reaction kinetics of the adsorption-desorption process. Moreover, the high desorption enthalpies of these systems require high temperatures (300°C for MgH_2) for hydrogen release at atmospheric pressure, raising questions around the economic viability of the technology (34–36). The reversibility of the process is also limited by the decomposition of the metal hydride, making a regular replacement of this storage material necessary.

A different concept for solid-state hydrogen storage is the use of metal-organic frameworks (MOFs). Here, hydrogen is stored in the pores of the MOF framework, where the rate of hydrogen adsorption is dependent on its diffusivity in the particular MOF chosen (37). MOFs can be tailored to specific applications, including supercapacitors, fuel storage and batteries and have been noted for their short refuelling times (37). However, this technology typically requires low temperatures (*ca.* –196°C) and high pressures (100 bar) to achieve a reasonable energy density (7.2 MJ l^{-1}, 4.5 wt%). To illustrate this, the MOF displaying the highest hydrogen storage capacity to date (MOF-210: total hydrogen gravimetric uptake of 17.6 wt%) must be operated at 80 bar and –196°C (38). It is therefore possible that a low system efficiency in terms of energy consumption, and

thus cost, will be observed. It has been predicted that the hydrogen storage capacity of MOFs can be improved by increasing MOF surface area, but there are experimental limitations in synthesising such structures (38). Moreover, as with using compressed hydrogen, the requirement of a higher-pressure system implicates explosion risks (37).

Borohydrides have also been considered for hydrogen storage applications, given their attractively high theoretical storage capacities. For example, $LiBH_4$ has a gravimetric hydrogen storage capacity of up to 18.5 wt% (24). However, in practice this is rarely achievable as stable hydrides, such as LiH, can form during the hydrogen unloading process, for which high temperatures (typically greater than 300°C) are also required. Direct employment of borohydrides for hydrogen storage applications is therefore unfeasible. Yet, a technology combining both borohydrides and metal hydrides is now being considered. Such a system reduces the endothermicity of the dehydrogenation process, facilitating hydrogen release at lower temperatures, but the kinetics of both the hydrogenation and dehydrogenation reactions are slow and require suitable catalytic additives (24). This increases the complexity of the technology.

Chemical hydrides, both organic and inorganic, are another method available to store hydrogen, and rely on chemical reactions. Chemical hydrogen storage is used to describe storage technologies in which hydrogen is both released and restored through a chemical reaction. Like metal hydrides, chemical hydrides also form chemical bonds between the storage material and hydrogen. Yet, these two hydride classes have very different properties. Arguably the most significant of these is that chemical hydrides (such as methanol) are generally liquids at ambient conditions. This simplifies transportation and storage issues associated with either gaseous hydrogen or solid-state hydrides. Provided ammonia is in its liquid form, which can easily be achieved

by applying a pressure of 10 bar at ambient temperature, ammonia can also be considered a chemical hydride, with a very attractive storage density (17.7 wt%) (24). In addition, given both methanol and ammonia are already synthesised on a large scale, there is the possibility of using existing infrastructure and production plants (24). Both chemicals have also been reported to have potential as hydrogen-alternative energy vectors (i.e. direct use as a fuel) rather than as hydrogen storage materials (24).

Ammonia is currently of industrial interest for hydrogen storage and transportation, given its high gravimetric hydrogen density (17.7 wt%) (24, 39–42). Additionally, the high ignition temperature of ammonia increases the safety of the technology and is considered advantageous (41, 42). When green hydrogen is used for the production of ammonia, such ammonia is classified as green ammonia (43–46). Green ammonia, when liquified, facilitates the transport and storage of hydrogen, allowing existing infrastructure to be used (42). With the potential for worldwide transport of the green ammonia, for example *via* ships, the distribution of green hydrogen to growing zero-emission markets will be facilitated (42). Once transported to the site of use, ammonia can be reconverted into carbon-free hydrogen which can be used at hydrogen refuelling stations, for example (42, 47).

Within the framework of the NEOM project it was recently announced that 650 tons of carbon-free hydrogen per day will be produced using 4 GW of renewable power from solar and wind in Saudi Arabia (48). To facilitate hydrogen storage and transportation, the hydrogen will be converted into 3500 tons of green ammonia per day (or 1.2 million tons per year) which will be transported around the world and then converted back into carbon-free hydrogen at hydrogen refuelling stations (48). By supplying the fuel cells currently used within the transport sector (specifically in buses and trucks) with this hydrogen, it is predicted that over 3 million tons per year of CO_2 emission can be prevented: equivalent to all emissions from 700,000 cars (48).

Although ammonia is less flammable than hydrogen, concerns around its toxicity to both humans and the environment have been raised (49). A spillage of this feedstock (for example during transport) could therefore have serious consequences, and questions around its suitability have been raised. However, it is important to remember that suitable controls have been employed to mitigate the risks associated with

fossil fuels (in the forms of gasoline and diesel), which are also very harmful substances. Moreover, as ammonia is already synthesised on an industrial scale (Haber-Bosch process) for example, in the fertiliser industry, it can be argued that the safety concerns are known and can be managed effectively. If the ammonia were not to be dehydrogenated at its destination, but instead used as a fuel itself, the ammonia would be classified as a renewable fuel (50). As an example, using ammonia as a transportation marine fuel is currently being explored within the shipping sector to cut fossil fuel use in ocean-going vessels (51–55).

Liquid hydrocarbons and formic acid can also fall into the category of hydrogen carriers. Provided such carriers are produced using green hydrogen and atmospheric CO_2, or CO_2 from waste streams, the cycle can be labelled as carbon-neutral (11). However, as the carriers are used as liquid fuels, regeneration of the carrier material is not possible and thus new material must be purchased for every cycle, much like employing fossil fuels as energy vectors (11).

As previously discussed, renewable methanol can also be considered as a chemical hydride. Although the gravimetric energy density of methanol is lower than that of ammonia (12.5 wt% and 17.7 wt%, respectively), it is significantly higher than a typical metal hydride, such as MgH_2 (7.6 wt%, **Table II**) (24, 37). Most commonly, methanol is synthesised *via* the hydrogenation of CO_2 and carbon monoxide, whereas the release of hydrogen from methanol is done in the methanol steam reforming process, which involves the reaction of methanol with water (24). This process is generally preferred over methanol decomposition, permitting the release of three moles of hydrogen in comparison to the two moles from methanol decomposition, where the extra mole of hydrogen is provided by the water (24). Yet for the steam reforming reaction, temperatures of between 220°C and 330°C are often required to meet the thermodynamic demands of the endothermic reaction (24).

Although renewable methanol (produced *via* the hydrogenation of CO_2 waste streams) is produced on a much smaller scale than its non-renewable equivalent (in which natural gas is used to produce a mixture of carbon monoxide, CO_2 and hydrogen), similarities in the two processes exist (24). With an overlap in the technology, progress in renewable methanol production is better facilitated than other hydrogen storage technologies and as a result the first renewable methanol production plant was constructed in Iceland in 2011 by Carbon

Table II Overview of Hydrogen Storage Methods[a] (24, 37)		
Method of hydrogen storage	**Gravimetric energy density, wt%**	**Volumetric energy density, MJ l^{-1}**
Compressed	5.7	4.9
Liquid	7.5	6.4
Chemical hydride • liquid ammonia[b] • methanol	 17.7 12.5	 11.5 15.8
MOF	4.5	7.2
MgH$_2$ (metal hydride)	7.6	13.2
Metal borohydrides	14.9–18.5	9.8–17.6
LOHC	8.5	7.0

[a]Note: unless specified, the data represents typical figures, providing only an approximate comparison
[b] at 10 bar pressure

Recycling International (24). Interestingly, it has been reported that the separation of methanol and water (*via* distillation) is not required when using methanol as a hydrogen storage medium: the hydrogen can simply be released from the mixture in a steam-reforming reaction (24). This simplifies the process and eliminates costs associated with the energy intensive distillation step. However, CO_2 is also stored within the methanol-water mixture and hence is also released upon steam reforming. If a pure hydrogen output stream is required, it has been predicted that CO_2 could be separated from the hydrogen relatively easily, but this process would require additional separation technologies (24). Alternatively, the gaseous hydrogen and CO_2 mixture could be used directly within proton exchange membrane (PEM) fuel cells (56).

3. Liquid Organic Hydrogen Carriers

LOHCs, also categorised under chemical hydrides, are another option for the storage and transport of hydrogen. The first studies into this technology were completed in the 1980s by Japanese researchers, studying a benzene/cyclohexane system (1). The LOHC process comprises a two-step process, which is based on the loading of hydrogen onto the chosen LOHC in a catalytic hydrogenation reaction, followed by the unloading of hydrogen in a catalytic dehydrogenation reaction. This second step thus produces a stream of gaseous hydrogen alongside the unloaded form of the LOHC, which can then be reused in subsequent cycles (**Figure 2**). Between these two steps, the hydrogen-rich form of the LOHC can be easily stored and transported at ambient pressures, given its liquid state. The LOHC technology eliminates the expense associated with

repeatedly purchasing a feedstock (i.e. the LOHC) and hence may be considered advantageous. Yet one must also consider the expense of returning the unloaded LOHC to the hydrogenation plant. In some cases, finding an alternative use for the unloaded LOHC may be most cost-effective.

Aromatic molecules are typically used as LOHCs due to their high hydrogen loading capacities (57). In addition, the cyclic compounds hydrogenated form of aromatic compounds have relatively good thermodynamic properties for the more challenging, endothermic dehydrogenation reaction. This can be explained by the stability gained on formation of the aromatic system (58). In contrast, dehydrogenation of bonds outside of such an aromatic system is difficult (even if the double bond formed can become conjugated with the system). For instance, dehydrogenation of ethylcyclohexane would form ethylbenzene not styrene as a result of thermodynamic limitations (58).

Importantly, the high hydrogen loading capacities of LOHCs enable high hydrogen storage and transport efficiencies, increasing the economic viability of the technology. This is highlighted by previous research that identified several potential carriers which meet the objectives for storage capacity and volumetric energy density, set by the United States Department of Energy (US DoE), as 6.5 wt% and 1.7 kWh l^{-1}, respectively (7). However, it is important to consider that the respective hydrogenation and dehydrogenation reactions may not always go to 100% completion.

As noted above, catalysts are required to facilitate hydrogen loading and unloading *via* hydrogenation and dehydrogenation reactions. Despite some reports detailing advantages of homogeneous catalysts (including lower operating temperatures and improved dehydrogenation
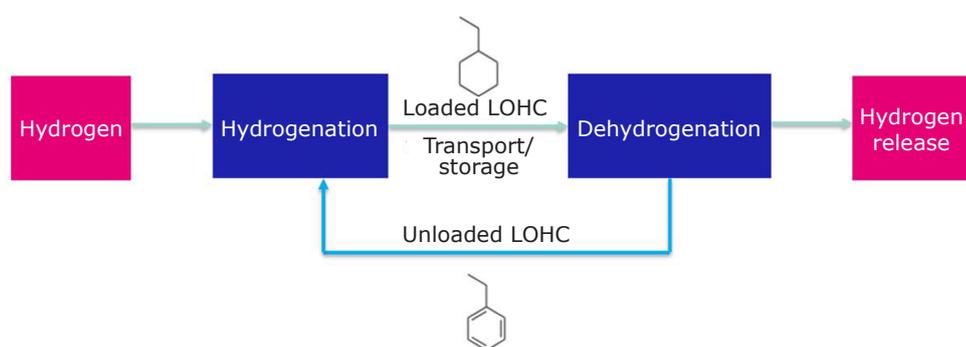
Fig. 2. Schematic representation of the LOHC concept, using ethylbenzene as a model LOHC molecule

product specificity), heterogeneous catalysts are considered preferable for both reactions in large-scale applications (26, 59).

A great majority of current studies examine the hydrogenation and dehydrogenation steps individually, often employing different catalysts to complete the two transformations. Most commonly, platinum group metal (pgm) catalysts, namely platinum, palladium or ruthenium-based, are employed (7, 30, 60, 61).

The LOHC technology is also an attractive option for stationary on-site energy storage (on-grid and off-grid), enabling long-term storage of large amounts of energy, such as seasonal storage and energy production buffering (26). In this case, a catalyst which allows both hydrogenation and dehydrogenation to be carried out in the same reactor through altering process conditions (such as temperature and pressure) can be deployed. The development of such a bifunctional catalyst would be an attractive research objective and facilitate a lower capital expenditure since a set-up in which only a single reactor and its associated pipework is necessary. From a process safety perspective, the ambient hydrogen storage pressures facilitated with the use of LOHC technology are an improvement on using a pressurised hydrogen storage tank.

Since the catalytic hydrogenation and dehydrogenation processes are exothermic and endothermic reactions, respectively, the hydrogenation step is typically performed at lower temperatures (100–240°C) and higher pressures (10–50 bar) than the dehydrogenation step (150–400°C, atmospheric pressure) (62). Thus, a higher level of heat is needed for the dehydrogenation reaction, which is often provided by an external heating source (62). To improve efficiency, system integration and intensification can be achieved, with the heat produced in the hydrogenation step being used to drive the dehydrogenation reaction when using LOHCs for on-site hydrogen storage (63). This would not be possible when the hydrogen is produced in a different location to where it is needed.

4. Advantages and Disadvantages of Liquid Organic Hydrogen Carrier Technology

As discussed, a timely migration away from fossil fuel reliance is of the utmost environmental importance, and is achievable with a combination of renewable energy, production of green hydrogen *via* electrolysis and hydrogen storage and transportation technologies. However, implementation of a LOHC hydrogen storage and transportation system also has advantages over simply using compressed hydrogen, or direct employment of renewable electricity. On the contrary to storage and transportation of compressed hydrogen, the small quantity of gas present in a LOHC system minimises the risk of explosion and facilitates the safe handling of hydrogen. Importantly, this allows for the long-term storage of large amounts of loaded LOHCs at ambient conditions, without the loss of hydrogen or negative impact upon carrier storage density, which has been reported with the use of compressed hydrogen and alternative storage technologies such as metal hydrides (64).

The elimination of pressure-related hazards also makes LOHCs suitable for long-distance transport. The liquid state of the carriers enables existing infrastructure, originally built for crude-oil transportation such as pipeline networks, to be used (1). However, unlike liquified or compressed hydrogen, the term 'infrastructure' also includes the use of ships and trucks, which enables worldwide transport of hydrogen using LOHCs. This too is often considered as one of the main advantages of the LOHC technology, meaning

the dehydrogenation plant required to release hydrogen from LOHCs does not need to be located within proximity of the hydrogen production site. Thus, the LOHC technology allows green hydrogen release (and indirect renewable energy use) in locations which are not best suited for renewable energy production. Moreover, as LOHCs are in the liquid state, they resemble current fossil fuel-based energy vectors, such as diesel and gasoline. Given societal familiarity with these systems, it is predicted that public acceptance of the LOHC technology will be increased in comparison to concepts such as metal hydrides, where public understanding is limited (7). This potential for greater acceptance of LOHC systems is considered advantageous (7).

In theory, the reversibility of the hydrogen loading and unloading processes allows LOHC to be used continually without replacement. Practically, however, this is unlikely due to LOHC material losses from side-reactions and incomplete unloading reactions (1). The choice of LOHC is also critical: for maximum efficiency, both the dehydrogenated and hydrogenated form must remain in their liquid state throughout the cycle. For instance, if the dehydrogenated form of the carrier material is a solid at ambient conditions, transport complications arise as it cannot be pumped through a pipe or into a truck or ship. To maintain the liquid state, incomplete hydrogen unloading or dilution of the LOHC would be required, reducing storage and transport efficiencies (7).

Moreover, the toxicity of the LOHCs themselves must be considered and evaluated in terms of projected applications; some LOHCs, such as benzene and toluene, have a toxicity so great that their use in practical applications is unfeasible, despite attractively high hydrogen storage capacities (65).

The choice of carrier can also influence the overall cost of the technology in other ways. Aside from the obvious cost associated with purchasing the LOHC feedstock, the released hydrogen from some carriers, like 1,2-dihydro-1,2-diazaborine, requires further hydrogen purification steps, while others (for example, dibenzyltoluene) have higher dehydrogenation heating demands (1). Both factors increase energy consumption. Moreover, the cost of transporting the unloaded LOHC *via* ships back to the site of hydrogenation (i.e. for hydrogen loading) should be taken into account. Mainly long-distance transportation of renewable hydrogen in LOHCs would be more economically viable than transportation of compressed hydrogen, which

is more suited to transport over short distances using the existing pipeline infrastructure (25). Methanol has also been reported to be economical for long-distance transport, with some studies suggesting that methanol can be a more cost-effective option than LOHCs (66). The same applies to ammonia (41). The Committee on Climate Change has reported that using ammonia as a hydrogen carrier for long-distance transport could be economically viable (25, 67). One of the key disadvantages of the LOHC technology is additional costs required for transporting of the LOHC loaded with hydrogen to end users followed by a transport of the dehydrogenated LOHC back to a chemical plant for loading with hydrogen.

5. Considerations for Process Optimisation of the Liquid Organic Hydrogen Carrier Technology

To improve economic viability of the LOHC technology, additional developments into optimising the LOHC technology might be needed. Reducing energy intensity during loading and particularly unloading of the LOHCs with hydrogen and efficient system integration can contribute to the cost reduction of the LOHC technology. In our following work, we discuss efficient system integration and potential deployment of the LOHC technology within different industries (28) and provide a detailed analysis of the most promising LOHC candidates, catalysts used for hydrogenation as well as dehydrogenation of LOHCs along with operating conditions (29). Efficient system integration of the LOHC technology as well as selection of the most suitable LOHC system, optimisation of reaction conditions and catalysts might improve economic viability and facilitate widespread commercial deployment of the LOHC technology.

Reactor configuration can also contribute significantly to the overall efficiency of the LOHC technology. The particular challenge for the LOHC technology is the hydrogen release from hydrogen-rich LOHC systems during the endothermic dehydrogenation process which is combined with the reaction mixture volume expansion. As an example, 1 ml of fully hydrogenated dibenzyltoluene can release more than 650 ml of hydrogen (68). A range of reactor types have been proposed for dehydrogenation of LOHCs, such as fixed-bed, continuous stirred tank reactor batch-type, tubular, spray-pulsed, pressure-swing and three-dimensional (3D) structured monolith reactors, among others (**Figure 3**) (68).
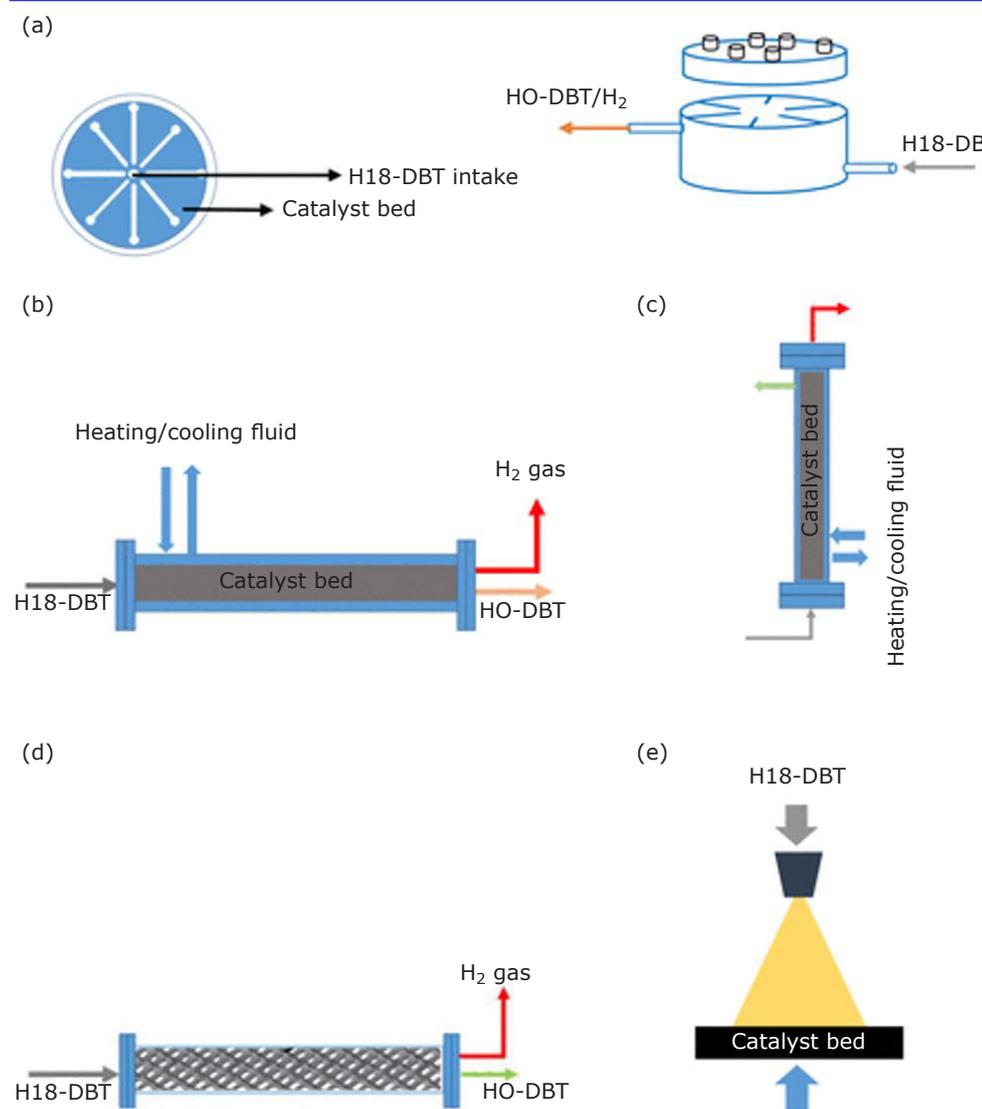
Fig. 3. Reactors used for dehydrogenation of LOHCs: (a) radial flow; (b) horizontal tubular; (c) fixed-bed; (d) 3D structured monolith (selective electron beam melting); and (e) spray-pulsed reactors. Reprinted (adapted) with permission from (68), Copyright 2019 American Chemical Society

Tubular-type reactors are often discussed for the LOHC technology. To optimise the process, different orientations of the tubular reactors have been evaluated (69). Tubular reactors can have either a horizontal or vertical orientation and have two possible operational modes: (a) LOHC flowing through the central tube and heat transfer fluid in the annulus; (b) heat transfer fluid in the central tube and the LOHC in the annulus (70). The heat transfer fluid enables external heating of the LOHC (69). In comparison to their horizontal equivalents, vertical tubular reactors have the advantage of a more even heat distribution, as a result of rising bubbles mixing the LOHC (70). Moreover, several vertical tubular reactors are suitable for both the hydrogenation and dehydrogenation reaction. Often, this is not the case for horizontal tubular reactors, where the interfacial region between the gaseous hydrogen and LOHC is often too small to achieve the mass transfer rates required for a hydrogenation process (69). Vertical dehydrogenation tubular reactors can also be constructed to produce either a co-flow or counter-flow between the LOHC and released hydrogen, offering more flexibility in a system design. In a study using *N*-ethylcarbazole as the carrier, different orientations of the reactor (horizontal/vertical) were studied, revealing that the maximum power densities are similar in both orientations, but radial heat transfer is improved compared to that in a horizontal orientation (69). Despite this, several examples of horizontal tubular

reactors can be found, with advantages including convenient removal of hydrogen from the top of the reactor and prevention of a multi-phase flow (71).

Helical reactors are more complex and comprise the LOHC flow in the central tube, with the heat transfer fluid in the surrounding shell space (70). A more effective heat transfer can be achieved with a helical reactor than a tubular reactor, as a result of a 'shear' formation, while the rate of reaction (hydrogen release) is also increased. A double helical reactor is also discussed for the LOHC technology (70). While this enables a significant saving in terms of space, the construction and assembly is typically complex and expensive. The deployment of a hot pressure-swing reactor was demonstrated for stationary hydrogen storage in which hydrogenation and dehydrogenation were performed within the same reactor using the same catalyst with dibenzyltoluene as the LOHC (72). This demonstrates the benefit of potential capital expenditure and operational expenditure savings.

Structured reactors, such as monolithic, 3D printed or foam reactors, are an attractive research area within the LOHC technology as they provide high heat conductivity, allowing for a good heat input for the endothermic dehydrogenation reaction (73, 74). Furthermore, the high porosity of such reactor systems lowers pressure drop, on the contrary to fixed-bed reactors where catalyst pellets are typically used, and facilitates an efficient hydrogen removal. This is important for dehydrogenation of hydrogen-rich LOHCs, during which significant reaction mixture volume expansions take place upon hydrogen release (for example, 1 ml of fully hydrogenated dibenzyltoluene can release more than 650 ml of hydrogen) (68, 73).

Depending on the intended application, the hydrogen purity released from LOHCs during dehydrogenation should be considered. Given that high temperatures are required for dehydrogenation of LOHCs, side products might be formed during hydrogen release, contaminating the hydrogen stream. In such cases, separation systems are required to purify the hydrogen, which increases the cost of the LOHC technology. The use of membrane reactors, which combine the benefit of shifting the equilibrium of dehydrogenation to the product side with integrated purification of the released hydrogen, have been reported in the literature for the LOHC technology (71, 75–80). Byun *et al*. performed the technoeconomic assessment of methylcyclohexane dehydrogenation in both a packed-bed reactor and a membrane reactor (78). This study demonstrates the cost effectiveness of an membrane reactor: the unit hydrogen production cost of a packed-bed reactor is US\$11.76, US\$9.50, US\$8.50 and US\$8.08 and that of an membrane reactor is US\$9.37, US\$7.43, US\$6.58 and US\$6.23 for hydrogen production capacities of 30 m^3 h^{-1}, 100 m^3 h^{-1}, 300 m^3 h^{-1} and 700 m^3 h^{-1}, respectively (78).

A lower temperature of operation for the dehydrogenation reaction, deploying a reactive distillation column under reduced pressure, could also allow for an increase in the efficiency of the LOHC system (81). This was demonstrated for perhydrobenzyl toluene dehydrogenation. A lowering of reaction temperature reduces the energy intensity of the overall process and facilitates a simpler and more effective integration of heat with waste heat sources or from subsequent hydrogen utilisation steps (81). Another recent study demonstrated that an electrochemical hydrogen compression (EHC) unit, which is connected to the LOHC dehydrogenation unit, reduces hydrogen pressure and shifts the thermodynamic equilibrium towards dehydrogenation (82). This accelerates the hydrogen release for the perhydrodibenzyltoluene LOHC and lowers dehydrogenation temperatures to 240**°C**. In addition, the EHC unit produces high value compressed hydrogen and purifies hydrogen contaminated with impurities such as traces of methane (82).

6. Summary and Perspectives

Several approaches to effective hydrogen storage technologies must be explored in parallel to facilitate a smooth transition to the hydrogen economy. LOHCs for hydrogen storage and transportation are an attractive option for storing and transporting green hydrogen. Key advantages of the LOHC technology are: high storage capacity compared to alternative hydrogen storage technologies such as MOFs; no hydrogen losses during extended storage periods; ambient storage pressures and compatibility with existing fossil fuel infrastructure (pipes, ships, trucks). LOHCs ideally have high, reversible hydrogen-loading capacities, enabling large quantities of hydrogen to be stored in the liquid carrier. Importantly, LOHCs facilitate the storage and intercontinental transport of hydrogen and can capitalise on infrastructure originally constructed for fossil fuels. Thus, over long distances, the transport of hydrogen using the LOHC technology has the potential to be economically viable in comparison to other hydrogen storage and transportation technologies.

Though costs required for transporting of the LOHC loaded with hydrogen to end users followed by a transport of the dehydrogenated LOHC back to a chemical plant for reloading with hydrogen should be considered. Furthermore, additional developments and research into optimising the technology might be needed to improve economic viability of the LOHC technology. Reducing energy intensity during loading and particularly unloading of the LOHCs and efficient system integration can contribute to cost reduction of the LOHC technology.

Acknowledgements

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