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Critical challenges towards the commercial rollouts of a LOHC-based H_2 economy

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Abstract

This short review discusses recent developments related to the storage and release of hydrogen from liquid organic hydrogen carriers (LOHCs). It focusses on three areas of recent literature: the application and development of novel, alternative LOHC systems, process development and process integration in the storage and release of hydrogen from LOHCs, and the electrochemical conversion of LOHCs. For the novel LOHC systems, we briefly focus on reaction enthalpy and storage capacity as main KPIs for the comparison of those systems and discuss the technical availability on a relevant scale. In the field of process- and reactor development our emphasis lies on the power density of the chemical conversion units. The LOHC technology still requires further development to reach the necessary energy efficiency, flexibility and overall research maturity for market competitivity and commercial impact.

Keywords: Liquid Organic Hydrogen Carrier, Hydrogen storage, Hydrogen economy, Sustainability

Nomenclature

BC	Bicyclohexyl
BP	Biphenyl
BPDM	Biphenyl (35 wt.%) and Diphenylmethane (65 wt.%) mixture
BT	Benzyltoluene
DBT	Dibenzyltoluene
DCE	Dicyclohexyl ether
DPE	Diphenyl ether
LHV	Lower heating value
LNG	Liquified natural gas
LOHC	Liquid Organic Hydrogen Carrier

MBT	Monobenzyltoluene
MCH	Methylcyclohexane
MID	1-Methylindole
MOF	Metal organic framework
MPB	2-(n-methylbenzyl)pyridine
NEC	*N*-ethylcarbazole
NPC	*N*-propylcarbazole
OMS	Ordered mesoporous silica
PCM	Phase change material

1. Introduction

The increasing effort for the development of a H_2 economy stimulated by the current push from the financial sector (240 Billion USD investments until 2030 [1]) and strong political context requires detailed attention. Especially in Europe, where the scarce resources, combined with environmental policies and the sudden switch in the energy supply chain due to political turmoil led to market volatility, energy insecurity and financial distress unseen in decades. The journey for finding a suitable solution for hydrogen storage – notoriously seen as the "game stopper" for technology development and market readiness – must now accelerate to delivering a robust alternative to fossil fuels. Liquid Organic Hydrogen Carriers (LOHCs) is undoubtedly a solution of choice, especially for long-term long-distance transportation of H_2 [2-6], offering solutions for the staggering quantities of H_2 foreseen in the 2050 horizon for Europe. The authors expect that ammonia (with the highest H_2 capacity of all carriers and plentily available worldwide), LNG, and methanol will play a key role. Nonetheless, this review focuses on the recent development of the LOHC technology. To restrict the scope of this article, we consider LOHCs as liquids that can be reversibly catalytically saturated (DBT, BT, NEC, MCH, etc.), i.e., excluding the chemical carriers leading to e.g., N_2 or CO_2. Hydrogenation is accomplished by bubbling H_2 in H_2-lean LOHC in the presence of a catalyst. In the case of (D)BT, the process is performed at pressures between 10 and 50 bar, and at temperatures ranging from 100 to 400 °C. The loaded LOHC contains has the non-negligible advantage over other storage method that is can be stored at room temperature. The LOHC research was booming in the recent years with an average of 50 articles published per year since 2020. The majority of published articles focused on the development of catalysts [7-26] (mostly for the H18-DBT/DBT [27-35], and dodecahydro-NEC/NEC systems [36-43]), followed by techno-economics and process simulation studies [2, 5, 44-56], the description of new LOHC molecules [57-68], and alternative reactor design and process integration schemes (reviewed below). In addition, major industrial demonstration projects have been completed. E.g., the "Advanced Hydrogen Energy Chain Association for Technology Development (AHEAD)", including Chiyoda Corporation; Mitsubishi Corporation, Mitsui & CO, and Nippon Yusen Kabushiki Kaisha successfully demonstrated the transportation of 210 tons of H_2 produced from steam methane reforming, from Brunei Darussalam to Japan in the form of MCH, where it was dehydrogenated, using Chiyoda's SPERA technology [69].

Since the initial report of a heat transfer fluid to be used as a LOHC by Brückner et al. [70], a panoply of materials have been proposed as LOHCs. While the available LOHC molecule employed depends on the location worldwide, there is an agreement among researchers on the superiority of cycloalkanes over MeOH, formic acid, and ammonia: the cycloalkanes are safer ("mild" toxicity, non-corrosive), and the H_2 released is not accompanied by gaseous by-products (CO_2, N_2) that should be removed/scrubbed to fulfil the promises of greener H_2-based technology. Some of these molecules (e.g., BT/DBT) are even compatible with the existing fuel infrastructure and are not considered as dangerous goods for transportation. Other molecules like toluene are already key chemicals of the chemical and petrochemical industry. H_2-rich LOHCs can also be stored in atmospheric and ambient conditions of pressure and temperature, a net advantage compared to, e.g., liquified ammonia or LNG.

However, the portrait would not be complete without considering some of their drawbacks. The most notorious ones being the relative high temperature level of the heat required (circa 300 °C) for the dehydrogenation reaction, as well as the high dehydrogenation enthalpy, i.e., amounting to up to 27% of the H_2's LHV stored for DBT. At the reactor level, the multiphase nature of the dehydrogenation reactor leads to unique heat and mass transfer challenges: the considerable release of H_2 increases heat transfer due to increased turbulence, but only up to a certain point where flooding of the reactor and de-wetting of the catalyst can occur. In addition, efficient heat transfer to the catalytic reaction site is made more challenging due to the endothermic nature of the dehydrogenation reaction, contributing to the cooling of the catalyst particles. With respect to the catalyst, the current dehydrogenation catalysts require wetted conditions, but lead to the release of a considerable amount of H_2 gas. The catalysts are also subject to liquid product deactivation. Finally, the power density of dehydrogenation reactors has to be considerably increased to compete with other H_2 storage technologies [71]. In this review, we highlight the most recent efforts deployed to tackle these challenges.

2. Alternative LOHC molecules

Recent technoeconomic feasibility study showed that the pair system H18-DBT/DBT stores more H_2 and at a lower cost than the systems 12H-NEC/NEC, toluene/MCH and CO_2/methanol [47]. However, the development of alternative LOHC molecules is still critical in order to decrease the heat demand and the temperature levels during dehydrogenation, especially if the dehydrogenation enthalpy can be lowered, while maintaining the benefits of low toxicity, adequate abundancy, as well as thermophysical properties (e.g., melting and flash points) and H_2 storage capacity. DBT and BT are already commercially available as heat transfer fluids, though not to a scale comparable with the emerging hydrogen economy. On the contrary, MCH and toluene are key components of the chemical industry, thus plentily available, just like cyclohexane and benzene. However, benzene is a known carcinogenic compound, and alongside with toluene are showing severe toxicity and are highly flammable.

2.1 N-heterocyclic aromatic compounds

It is known that heterocyclic aromatic compounds possess favourable thermodynamics and lower dehydrogenation enthalpies, however at the expense of their chemical stability. For that purpose, several nitrogen-containing systems, e.g., the dodecahydro-6,7–benzindole (hydrogenated form)/6,7-benzindole LOHC system have recently been studied, because of its lower reaction enthalpy compared to DBT (54 versus 65 kJ mol^{-1} H_2) [72]. Other examples are mono and dimethyl-quinolines [65, 68], as well as substituted quinolines and pyridines [58], which were also proposed due to their lower dehydrogenation enthalpy (56-62 kJ $mol^{-}1$ H_2, but over 65 kJ/mol for some substituted quinolines and pyridines). One of the lowest reaction enthalpies is shown by the H12-NEC/NEC or H12-NPC/NPC LOHC (50.5 kJ mol^{-1} H_2), which drives the catalyst development for this molecule [24]. Most of these molecules have already been proposed earlier and the research focuses on developing suitable catalysts for efficient and selective dehydrogenation [10, 12, 73]. To the knowledge of the authors of this review, none of the compounds are technically available in a notable scale.

2.2 Homocyclic aromatic compounds

Park et al. [66] showed that light cycle oil (LCO) from fluid catalytic cracking could store 5.3 wt. % H_2 and thus can be envisioned as a potential low cost LOHC. Using a model aromatic mixture consisting of n-decane, indane and tetralin (1 aromatic ring), as well as naphthalene and 1-methylnaphthalene (2 ring aromatic model compounds), they obtained almost full hydrogenation at 200 °C and 30 bar, and at 150 °C and 50 bar. Researchers from Korea University and Korean Institute of Science and Technology proposed biphenyl eutectic mixtures (biphenyl/diphenyl methane) to store almost 7 wt. % H_2 [74], with less than 1% loss after nine hydrogenation (Ru/Al2O3)-dehydrogenation (Pd/C) cycles [75]. Other researchers focus on decalin as possible LOHC [22].

Within the homocyclic aromatic compounds, DBT and BT have been the focus of different research groups. However, BT is gradually replacing DBT due to its equivalent hydrogen storage capacity, but with a decreased viscosity, higher reaction rates, and low side product formation. BT has a higher vapor pressure compared to the H18-DBT/H0-DBT system. This seems like a drawback on the first view, because it increases the complexity on the hydrogen purification on the downstream of the LOHC process. However, the higher vapor pressure is beneficial during dehydrogenation because of the resulting hydrogen partial pressure reduction. This reduction increases the driving force for the dehydrogenation allowing for lower dehydrogenation temperatures [76-78].

2.3 Oxygen-containing compounds

Oxygen-containing compounds can benefit from the advantage of lowered dehydrogenation enthalpy, but the C-O bond cleavage has to be avoided. Jang et al. [67] reported 6.8 wt. % H_2 capacity using an eutectic mixture of biphenyl and diphenyl ether (another commercial heat transfer fluid known as Dowtherm A) with claimed favourable dehydrogenation enthalpy. The dehydrogenation enthalpies for the ether are in the same range as that of BT and other homocyclic aromatic compounds. Depending on catalyst and reaction temperatures, significant amounts of cleavage products could be observed. However, they were able to demonstrate a reversible cycle.

In an attempt to increase the sustainability of LOHC, furfuryl alcohol was proposed with unfortunately, a dehydrogenation enthalpy reaching 77 kJ mol^{-1} H_2 [57], trisphaeridine (Amaryllidaceae alkaloids) with a 5.9 wt. % H_2 capacity and a 54 kJ mol^{-1} H_2 [60], as well as ethylene glycol/ethanol, with a 5 wt. % H_2 storage capacity [61].

An interesting approach is the acceptorless dehydrogenative ester formation. This approach was demonstrated by Zhou et al. [61] for the LOHC system ethylene glycol/ethanol. Tran et al. [53] use a similar system based on ethanol and ethyl acetate. The resulting reaction enthalpy for dehydrogenative ester formation is in the range of 36-40 kJ mol^{-1} H_2 at significantly lower temperature levels. The reaction enthalpy is about half that of homocyclic systems such as MCH/toluene or H12-BT/BT. Additionally, these system show a rather interesting hydrogen storage capacity of up to 5 wt. % H_2 [53, 61]. Ethanol and ethylene glycol have established production routes in the petrochemical industry and can be considered as available on a relevant scale.

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To summarize, Figure 1 shows the dehydrogenation enthalpy as a function of H_2 capacity for various LOHCs systems. The majority of the LOHCs pairs are showing values for the dehydrogenation enthalpy between approx. 62 – 70 kJ/mol H_2 corresponding to H_2 capacities ranging from approx. 6.1 – 7.3 wt. %. Interestingly, large difference in the dehydrogenation enthalpy is seen between LOHCs systems with similar H_2 capacities.

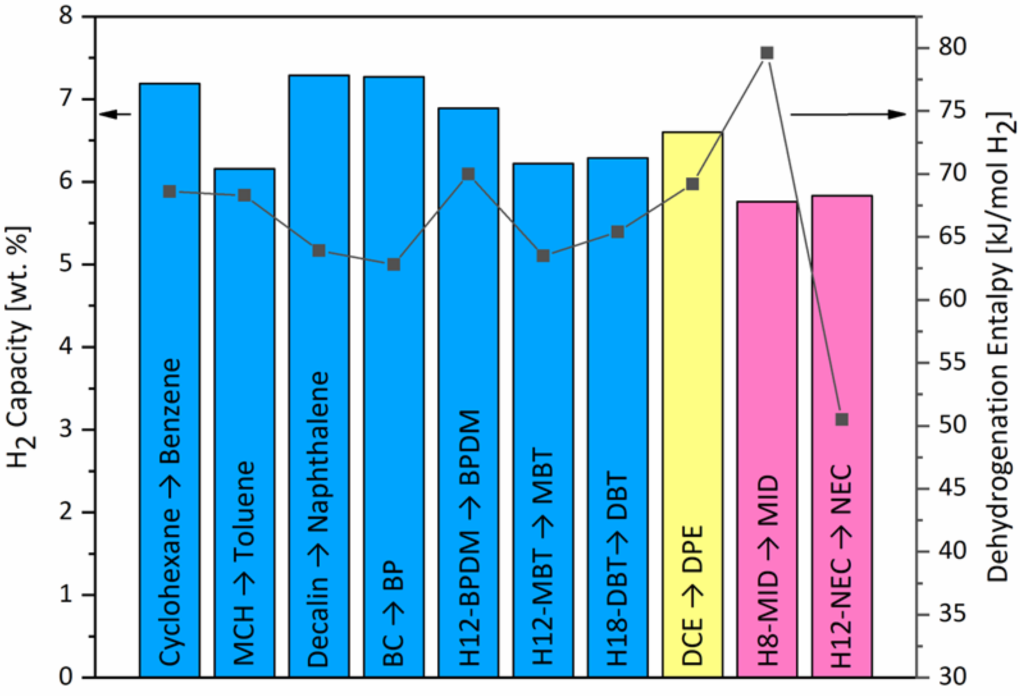

Figure 1: H_2 capacities (bars) and the corresponding standard dehydrogenation enthalpies (line and symbol) for various LOHCs systems. Colours are used to emphasize the LOHC category: blue – homocyclic aromatic compounds; yellow – oxygen-containing compounds; red – heterocyclic aromatic compounds (taken from [79])

3. Dehydrogenation reactors and process integration

3.1 Dehydrogenation reactor concepts

The integration of gas burners in dehydrogenation units for the direct heat supply has recently been explored. This technology could allow for the dynamic operations, and potentially open the door for the use of LOHC for mobile applications. However, care must be provided to minimize the risk of hot spots that could lead to LOHC decomposition (as well as cold spots limiting the dehydrogenation kinetics [80]). To do so, Badakhsh et al. [81] proposed a H_2 burner supplying the heat to a liquid-gas PCM (benzyl toluene in this case). Using the reported value, they reached a 0.94 kW_{therm} L^{-1} power density. Previously, they had proposed the use of heat conduction throughout a copper-hexahedral boron nitride composite to transfer the high level heat from a H_2 burner and an ammonia cracking dehydrogenation section, but this led to hot spots [82]. As thermal integration has to be performed by improving the driving force, i.e., either the temperature difference or the area for heat transfer, Bollmann et al. [80], for their DBT-based unit, proposed a porous media methane burner (eventually biomethane). They reached 1.5 g_{H2} g_{Pt}^{-1} min^{-1} productivity and a 3.6 kW_{therm} L^{-1} power density, without observing the formation of hot spots.

Solymosi et al. [83] described the coating of platinum catalysts on stainless steel plates for the increased heat transport to the catalytically active sites for the thermal integration with high temperature fuel cell stacks. Geiling et al. [84] described the dynamic operation of a continuous multitubular dehydrogenation reactor coupled to a PEM fuel cell for its use in the mobility sector. They showed that the fastest response (almost synchronous) was obtained via temperature and pressure modifications, however only if the strategy was to decrease the H_2 rate (by decreasing the operating temperature and increasing its pressure). They reached values of 0.26 kg H_2 h^{-1}, generating 6.6 kW of power. Jang et al. [75] coupled a packed bed biphenyl eutectic mixtures dehydrogenation reactor to a 1 kW PEM fuel cell, producing more than 0.04 kg H_2 h^{-1}, generating 500 W of electrical power.

Geiβelbrecht et al. [77] recently described a low temperature batch reactive distillation H12-BT dehydrogenation unit, providing a simple solution to the observed liquid product inhibition of the catalyst, by placing the catalyst after the H12-BT enrichment zone. They also opened the way for the use of low value low grade waste heat by describing dehydrogenation temperature as low as 200 °C. Rüde et al. [85] took it further and demonstrated the possibility of reactive distillation in a continuous mode. They also showed that the H_2 release rate was increased when compared to liquid phase dehydrogenation. Based on the productivity of 0.35 g_{H2} g_{Pt}^{-1} min^{-1}, it is possible to calculate a power density of 1,75 kW_{therm} L^{-1}. However, neither Geiβelbrecht et al. [77] nor Rüde et al. [85] (from the same research group) discussed the difficult separation of perhydro-BT/DBT and BT/DBT due to their almost identical boiling points.

To the contrary, in an attempt to keep the H_2-rich MCH during its dehydrogenation, and therefore keeping the H_2 production rate high, Macreadie et al. [86] successfully separated benzene from MCH in the vapor phase using multicomponent MOFs with a cubane linker, taking advantage of the spatial orientation-based physisorption selectivity of MOFs, i.e., without relying on energy intensive phase change as in distillation. Unfortunately, considering the carcinogenic nature of benzene, the MHC/benzene is less interesting as LOHC candidates. The authors obtained similar adsorption for MCH and toluene, excluding the adsorptive separation of the H_2-rich MCH to keep the H_2 production rate maximal during dehydrogenation. Still, this result is key as it opens the door for selective contact between H_2-rich LOHC and the catalyst, without the need for partial poisoning of the active phase to avoid liquid product deactivation.

Wunsch et al. [87] used a microstructured radial flow reactor coupled to a thin PdAg membrane, both heated using heat cartridges. They measured a 1.15 g_{H2} g^{-1}Pt min^{-1} productivity, and impurities in the H_2 stream below 7 ppm, yielding 5.0 quality hydrogen. Comparable purity levels were obtained from a continuously operated packed bed dehydrogenation reactor, but only when pre-dried and pre-purified (removal of low boiling hydrocarbons, water and permanent gases via vacuum degassing and nitrogen stripping) technical DBT was used [88].

As pointed by Heublein et al. [71], even though a lot of dehydrogenation reactors have been proposed, only the tubular one has been tested for technical operation. The authors then experimentally characterized the dehydrogenation kinetics and required approach temperature (between the heating fluid and the catalytic bed) in the case of horizontal and vertical operations, for various flow configurations (co- vs counter-current flows, i.e., with respect to the reactant versus the liquid and H_2 gas products). They showed that for tubular reactor operated in the co-current regime, a vertical orientation required a 30-40% reduced approach temperature to achieve the same power density (around 1.8 kW_{therm} L^{-1}) as in the horizontal configuration, until of course the point of catalyst de-wetting. However, they observed that increasing the pressure from atmospheric to 2.4 bar, and by allowing the generated H_2 to leave via side outlets, the “productivity drop” due to extensive catalyst de-wetting was shifted to higher temperatures and allow H_2 production to increase by 50 %.

A recent patent from Hydrogenious LOHC Technologies describes an autothermal strategy involving the selective partial oxidation of the LOHC molecule itself, where it is regenerated at the hydrogenation stage [89]. This interesting concept has the consequence of shifting the energy-demanding step on the hydrogen storage side.

3.2 Electrochemical conversion and transfer hydrogenation

The electrochemical dehydrogenation coupled with a transfer hydrogenation represents a promising process consisting of a direct alcohol fuel cell, where a secondary alcohol is electrochemically converted to the corresponding ketone as well as a transfer hydrogenation of a ketone with the charged LOHC carrier that yields the secondary alcohol at milder reaction conditions, without any release of molecular H_2. Sievi et al. [90] demonstrated the possibility of coupling the endothermal H_2 release from H18-DBT to the exothermic operation of a 2-propanol PEM fuel cell. Zakgeym et al. [34] recently successfully demonstrated the use of a Pt/SiO2 transfer hydrogenation catalyst, where the almost inert SiO_2 support minimizes the undesired acetone aldol condensation, while ensuring high Pt dispersion and large pore size necessary to avoid mass diffusion limitations. Shiraz et al. [91] proposed the direct electrochemical hydrogenation of LOHCs via a proton-coupled electron transfer, thus avoiding the current two-step process (green hydrogen production, then storage in LOHC), and allowing the advantageous room temperature and atmospheric pressure conditions. As of now, a proof of concept has been demonstrated, along with a detailed analysis of the reaction mechanism. LOHC-based H_2 deNOx at low temperature in oxygen-rich exhaust gases from both mobile and stationary combustion engines is another (non-electrochemical) transfer hydrogenation applications recently investigated [92].

4. Conclusions and outlook

The use of LOHCs for hydrogen storage is generally considered a promising solution for the future development of a hydrogen-based economy. In particular the possibility of using the existing infrastructure, their long-term stability, ease of manipulation and transportability over long distances are seen as key advantages. However, in order to contribute to a hydrogen-based economy, there are several criteria that the LOHCs should meet such as: a) unexpensive organic liquids; b) the materials should be readily and abundantly available; c) high boiling point for easy separation, long liquid range and high thermal stability for sustainable catalytic cycles and low viscosity to facilitate pumping; d) low toxicity and environmental friendly by-products; and e) H_2 storage capacity. Decreasing the dehydrogenation enthalpy via the synthesis of new molecules would only make sense if the newly identified molecules would comply with those criteria. As a consequence, there are still some major challenges. For example, the reaction enthalpy of the dehydrogenation must be provided at an elevated temperature level. This challenge has been addressed in quite different ways. One approach is to reduce the enthalpy of the dehydrogenation via alternative LOHCs such as nitrogen-containing systems, if however, the stability of the LOHCs is not affected, or by using the dehydrogenative ester formation as hydrogen release reaction. Other approaches include the direct coupling of methane/hydrogen combustion and/or partial oxidation of the LOHC with the dehydrogenation reactor, the electrochemical conversion of the LOHC-bound hydrogen directly in a fuel cell or lowering the total pressure via reactive distillation. Besides these important achievements and elaborated strategies, the future efforts should be directed more strongly on innovative reactor design. The recent findings on the importance of mechanical agitation for the enhancement of mass transfer and to trigger nucleation at the surface and in the pores of the catalyst [93] are pointing towards fluidized beds and slurry bubble columns as the most promising potential technological solutions. The urgency to provide a fast solution to the current energy crisis may overestimate the level of readiness of the LOHC technology for imposing a H_2 based economy, although it still requires multidimensional and cross disciplinary research, as well as additional industrial demonstration projects to increase the TRL of the LOHC towards the commercial rollouts of a LOHC-based H_2 economy. After several years of research, it is the time to show the promises of the LOHC technology.

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