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Liquid Organic Hydrogen Carriers: comparing alternatives through H_2 equivalent analysis

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ABSTRACT

Liquid Organic Hydrogen Carriers (LOHCs) represent a promising solution for the efficient transport and storage of hydrogen, addressing critical challenges associated with its low volumetric density and safety concerns in gaseous and liquefied forms. LOHCs are oil-like substance, capable of reversibly binding and releasing hydrogen through catalytic hydrogenation and dehydrogenation. Hydrogenation is performed where renewable energy is extensively available: at the loading terminal, green H_2 is produced and is chemically bonded to the LOHC molecule. In this way, the hydrogenated molecule is transported safely under ambient conditions using existing liquid fuels infrastructures. At the delivery site, the dehydrogenation process releases high-purity hydrogen for industrial or mobility applications, with the regenerated LOHC carrier being recycled back to the H_2 production site for reuse. In view of highlighting critical issues associated to LOHCs implementation at large scale, this paper explores green H_2 transport through toluene and dibenzyltoluene. Considering the overall H_2 transport value chain, the performances of these two alternatives are assessed by means of equivalent H_2 methodology. As a result, insights are provided on their role in enabling a sustainable and efficient hydrogen economy.

Keywords: green H2 transport, LOHC, clean energy, toluene, dibenzyltoluene.

INTRODUCTION

In the transition towards sustainable energy, green hydrogen has gained attention as a low-emission alternative. However, its transport is hindered by its low volumetric density. To address this challenge, various hydrogen carriers have been proposed as a more practical solution. These hydrogen-bearing compounds can be transported more easily at milder conditions and dehydrogenated upon arrival to release hydrogen. Among all the possible options, liquid organic hydrogen carriers (LOHCs) are considered promising due to their compatibility with existing infrastructures [1]. Various LOHCs have been explored in the literature. While some compounds are more suitable for hydrogenation and dehydrogenation, certain criteria help in identifying optimal candidates. The ideal LOHC should have a low melting point and high boiling point to avoid solidification and volatility issues, respectively, a high hydrogen storage capacity, low dehydrogenation enthalpy, low toxicity and be cost-effective at the same time [2].

Once the hydrogen carrier is selected, a detailed techno-economic assessment of the entire H_2 value chain is essential to compare alternatives and demonstrate their feasibility. The H_2 value chain typically includes: hydrogenation of the organic molecule exploiting green H_2, produced where renewable energy sources are extensively available, transport of the hydrogenated compound to its final destination and, upon arrival, dehydrogenation to release hydrogen.

In this framework, the aim of this work is to present a systematic methodology for comparing different H_2 value chains. Toluene (TOL) and dibenzyltoluene (DBT) are selected as representative carriers due to their promising characteristics. A harbor-to harbor scenario is discussed, to study long distance H_2 transport. The hydrogenation and dehydrogenation stages were designed in Aspen Plus V11®. Based on process simulations, a detailed technical assessment is provided. Each stage of the value chain (*i.e.*, hydrogenation, seaborne transport, dehydrogenation) is technically discussed. Energy consumptions are expressed in terms of equivalent H_2,

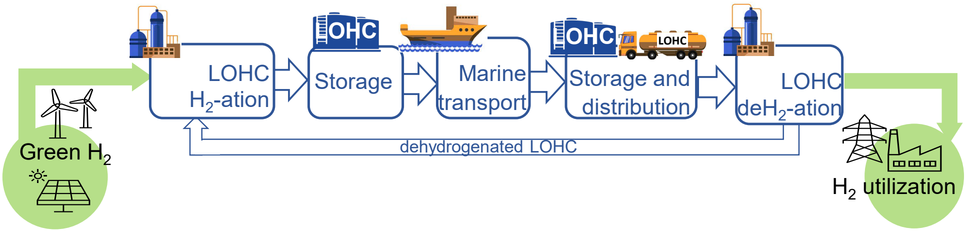

Figure 1: Hydrogen value chain exploiting LOHCs as H_2 carriers.

which, in the end, lowers the amount of hydrogen delivered at the utilization hub. In this way, the efficiency of each stage can be easily quantified. Weaknesses and drawbacks are pointed out, to pave the way for future process intensification.

H_2 TRANSPORT SCENARIO: BASIS OF DESIGN

The H_2 value chain considering LOHCs as H_2 carriers is reported in Figure 1.

A harbor-to-harbor H_2 transport scenario is assumed. At the loading terminal, a flat H_2 production by 100 MW alkaline electrolysers is considered. These electrolysers, operating at 20 bar, are responsible for delivering 20000 Nm^3/h of H_2. The assumed production scale of the alkaline electrolysers results in significantly lower H_2 production compared to conventional steam reforming plants. This limitation arises because renewable energy-driven industrial sites must align their scale with the land requirements of renewable energy installations.

At the loading terminal, H_2 is reacted with an organic carrier through an exothermic hydrogenation process and the resulting hydrogenated compound stored before seaborne transport.

The maritime distance between harbours is 2500 km, with the ship powered by traditional fossil-based fuels (IFO 380 1%S).

Upon arrival at the unloading terminal, the hydrogenated carrier is transported to a H_2 valley located 100 km inland via truck.

At the H_2 valley, the carrier undergoes a dehydrogenation reaction to release hydrogen. The released hydrogen meets industrial application standards, being produced at 30 bar with a purity exceeding 99.9 mol%.

The conversion and reconversion stages are the core of the whole hydrogen value chain: for this reason, a detailed technical assessment is performed by means of Aspen Plus V11® process simulations, discussed in the following section. Details about the thermodynamic property package are provided elsewhere [4]. On the other hand, for storage, maritime and road transport, reference is made to the available literature [3]. As the organic carriers are oil-like substances, they are compatible with existing oil-handling infrastructure, making their integration seamless.

SIMULATION OF THE COST-DRIVING PROCESSES

Hydrogenation section for toluene and dibenzyltoluene are reported in Figure 2.

Referring to toluene hydrogenation section, reported in Figure 2a, toluene, both from the unloading terminal and from make-up stream, enters the process unit's battery limits. It is pressurized and heated to the reaction conditions of 20 bar and 210°C [4]. Reactants pre-heating is performed into a process-to-process heat exchanger (PREHEAT in Figure 2a) to recover the high enthalpy of the reaction products. The hydrogenation reaction (1) is highly exothermic: N_2 acts as a thermal diluent. Its flowrate is such that its concentration in the reactor inlet stream (REAC-IN in Figure 2a) is approximately 17 mol% [5]. Alongside nitrogen and toluene, green hydrogen produced via water electrolysis (stream H_2 in Figure 2a) is also supplied to the battery limits.

$$C_7H_8 + 3H_2 \rightarrow C_7H_{14} \qquad (1)$$

The reactor outlet stream (REAC-OUT in Figure 2a), consisting of unreacted hydrogen, nitrogen, and methylcyclohexane, is cooled in the PREHEAT exchanger before proceeding to the separation stages. The separation section, comprising two flash drums in series (FLASH 1 and FLASH 2 in Figure 2a), purifies the reactor output from heavy ends, before and, then, from light ends. The resulting methylcyclohexane (MCH in Figure 2a) is stored and transported by ship to the unloading terminal. Unconverted hydrogen (stream LIGHTEST in Figure 2a) is compressed in COMP and recycled back to the reaction section.

On the other hand, Figure 2b shows the dibenzyltoluene (DBT) hydrogenation process. The organic carrier, H0-DBT in Figure 2b, is sourced from the unloading terminal. Along with a minimal make-up stream, it is routed to the reactor after being pressurized and heated. The reactor (B2 in Figure 2b) is fed with dibenzyltoluene, hydrogen, and nitrogen, with N_2 flow rate set identically to that used in the toluene hydrogenation process.

The reactor, operated at 35 bar and 210°C [6], performs DBT hydrogenation as in reaction (2).

$$C_{21}H_{20} + 9H_2 \rightarrow C_{21}H_{38} \tag{2}$$

The reaction products, primarily the hydrogenated species, are cooled and stored for transportation to the unloading terminal. In this case, the separation section downstream of the reactor is simplified, as hydrogen conversion is complete and by-product formation during the reaction is negligible. This characteristic is widely recognized in the literature as a key advantage of dibenzyltoluene as a hydrogen carrier [7]. Additionally, DBT's higher molecular weight compared to toluene enables more effective separation based on vapor-liquid equilibrium, as the larger difference in relative volatilities enhances separation efficiency for lighter compounds.

For the sake of comparison between toluene and dibenzyltoluene hydrogenation, Table 1 reports the thermal energy consumptions and Table 2 provides the electric energy consumptions, retrieved from process simulations.

The dehydrogenation process for both methylcyclohexane and perhydro-dibenzyltoluene (H18-DBT) is shown in Figure 3. As for methylcyclohexane (Figure 3a), it enters the process, it is pressurized and directed to the reaction section. The reactor (REACTOR in Figure 3a) operates at 350°C and is responsible for producing toluene and hydrogen according to reaction (3).

$$C_7H_{14} \rightarrow C_7H_8 + 3H_2 \tag{3}$$

Table 1: Thermal energy consumption for hydrogenation sections of Figure 2. Duty is assumed positive when entering the system.

equipment	***T_{IN}* *[°C]***	***T_{OUT}* *[°C]***	***Q* [kW]**
toluene hydrogenation			
REACTOR	146	210	-14557.1
COOLER	82	50	-3378.5
dibenzyltoluene dehydrogenation			
COOLER	82.08	50	-482.3
REACTOR	175.11	210	-16462.3

Table 2: Electric energy consumption for hydrogenation sections of Figure 2.

equipment	***P_{IN}* *[°C]***	***P_{OUT}* *[°C]***	***W* [kW]**
toluene hydrogenation			
PUMP	1.01	20	22.05
COMP	1.01	20	1271
dibenzyltoluene dehydrogenation			
PUMP	1.01	35	47.17
COMPR	20	35	550.6

The reactor's outlet mixture, composed of minor undesired byproducts (primarily benzene), together with

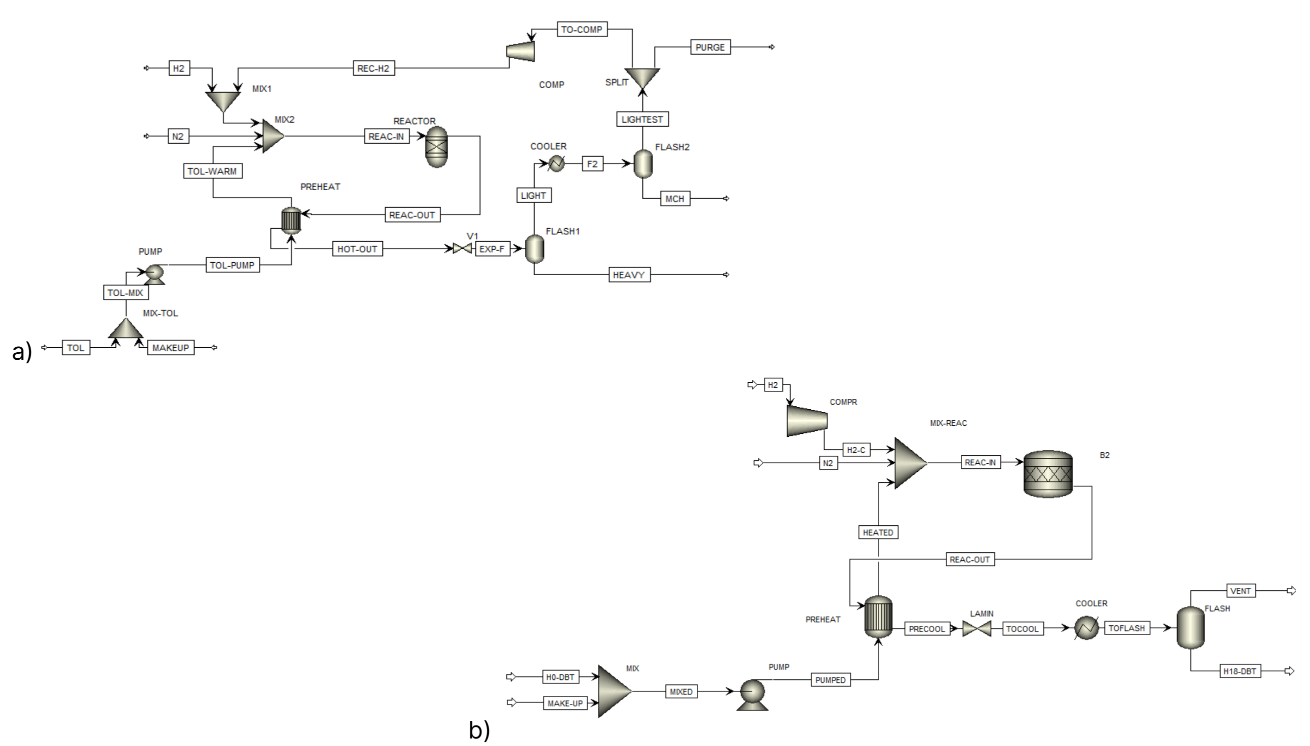

Figure 2: Hydrogenation section for: a) toluene and b) dibenzyltoluene. Simulation in Aspen Plus V11®.

toluene and hydrogen, is sent to the downstream separation train. The separated toluene stream (OUT-TOL in Figure 3a) is stored and subsequently routed back to the loading terminal. Hydrogen is purified via pressure swing adsorption (PSA) to achieve the necessary purity specifications for its intended applications.

The dehydrogenation reaction is highly endothermic, requiring a significant heat supply. This heat is provided by burning a portion of the hydrogen produced, along with waste streams (V and VENT in Figure 3a). As a result of this arrangement, the high endothermicity of the dehydrogenation reaction reduces the net amount of hydrogen available for utilization.

In a similar fashion, Figure 3b shows the process simulation performed for the H18-DBT dehydrogenation. The H18-DBT entering the system is pressurized and directed to the reaction section. The reactor (REACTOR in Figure 3b) operates at 320°C and 1.1 bar. In this unit, H_2 is obtained according to reaction (4).

$$C_{21}H_{38} \rightarrow C_{21}H_{20} + 9H_2 \tag{4}$$

The reactor's output mixture, consisting of DBT and hydrogen, is processed through a series of separation stages downstream of the reaction section. The recovered DBT (DBT-OUT in Figure 3b) is stored and transported back to the loading terminal, while the hydrogen, which is nearly pure, is compressed and sent to the hydrogen valley for utilization.

Table 3 and Table 4, provide, respectively, the thermal energy consumptions and the electric energy consumptions of the processes depicted in Figure 3.

Table 3: Thermal energy consumption for dehydrogenation sections of Figure 3. Duty is assumed positive when entering the system.

equipment	***T_{IN}* [°C]**	***T_{OUT}* [°C]**	***Q* [kW]**
methylcyclohexane dehydrogenation			
REACTOR	210	350	20093
COOL1	100	50	-3344.6
COOL2	198	80	-996.1
COOL3	240	50	-1943.6
perhydro-dibenzyltoluene dehydrogenation			
REACTOR	306.8	320	19887.3
COOL1	184.8	60	-1002.3
COOL2	235.9	50	-1347.0
COOL3	220.8	50	-1238.5
COOL4	219.9	50	-1234.2

Table 4: Electric energy consumption for dehydrogenation sections of Figure 3.

equipment	***P_{IN}* [°C]**	***P_{OUT}* [°C]**	***W* [kW]**
methylcyclohexane dehydrogenation			
PUMP	1.01	3	2.62
COMP-1	2.9	9.3	1113.3
COMP-2	9.3	30	1231.2
REC-COM	2.9	3	2.17
dibenzyltoluene dehydrogenation			
PUMP	1.01	1.1	0.14
COMP1	1.01	3.15	1148
COMP2	3.15	9.74	1081.5
COMP3	9.74	30	1080.2
COMP-R	1.01	1.1	5.75

To assess the viability of toluene and dibenzyltoluene as H_2 carriers and compare their performances, the equivalent H_2 methodology is applied, which is described in the following section.

TECHNICAL ASSESSMENT: EQUIVALENT H_2 METHDOLOGY

The Equivalent Hydrogen Methodology (EHM) provides a common metric for evaluating the energy content and efficiency of H_2 production, storage and transportation. By calculating the net equivalent hydrogen consumption (*NEHC*) of each energy-consuming process, the Equivalent Hydrogen Methodology enables a more accurate assessment of the total energy required for the full hydrogen cycle, from production to utilization. Then, by subtracting the *NEHC* to the H_2 entering the process battery limits, the net equivalent H_2 delivered (*NEHD*) to the utilization hub is evaluated, as shown in equation (5).

$$NEHD = F_{H_2,in} - NEHC \tag{5}$$

In this way, this methodology allows to standardize and simplify the comparison of different H_2 carriers, in view of identifying the most cost-effective hydrogen solution.

For the evaluation of *NEHC*, heating above the ambient temperature ($NEHC_{h,i}$), cooling below ambient temperature ($NEHC_{c,i}$) and electric power supply ($NEHC_{e,i}$) are accounted for, thus neglecting heating below ambient temperature (< 25°C) and cooling above ambient temperature (> 25°C) [8] (equation (6)).

$$NEHC = \sum_i NEHC_{h,i} + NEHC_{c,i} + NEHC_{e,i} \tag{6}$$

$$NEHC_{e,i} = \frac{W_i}{\eta_{FC} \cdot LHV} \tag{7}$$

In the present case-study, heating above ambient temperature is achieved by process-process heat exchange, when feasible. Otherwise, heating is provided by either burning part of the hydrogen produced, as in the

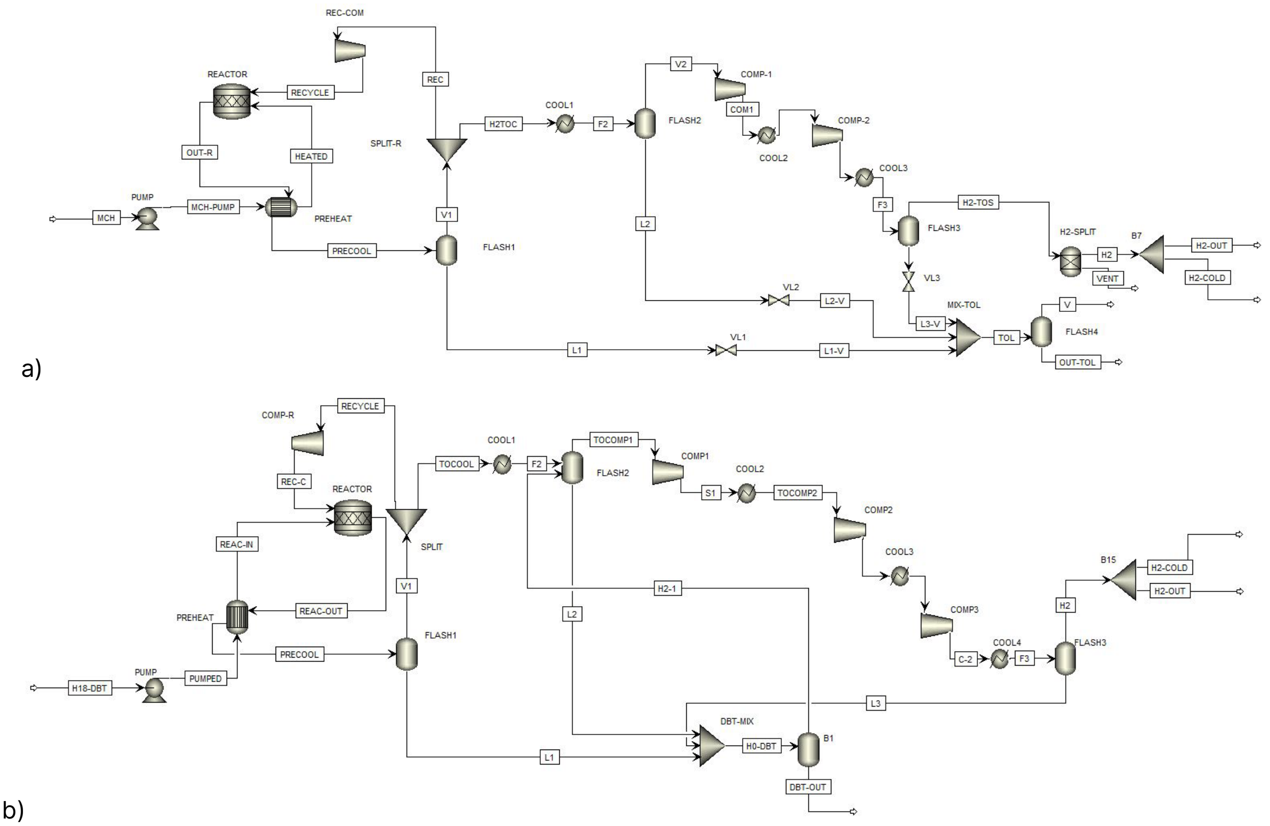

Figure 3: Dehydrogenation section for: a) methylcyclohexane and b) H18-DBT. Simulation in Aspen Plus V11®.

dehydrogenation section. In this case, the term $NEHC_{h,i}$ of equation (6) is retrieved from process simulation [3]. In addition, cooling below the ambient temperature is not required considering the value chain of Figure 1. Finally, the Net Equivalent Hydrogen Consumed for supplying electric power ($NEHC_{e,i}$), used for driving compressors and pumps, is calculated according to equation (7), assuming H_2 utilization in fuel cells with an efficiency (η_{FC}) of 60%. In equation (7), W_i is the electric power consumption retrieved from Aspen Plus V11® simulations, while *LHV* is the H_2 lower heating value, assumed equal to 120 MJ/kg.

CONCLUSION

Figure 4 summarizes the results of the equivalent H_2 methodology, considering both toluene and dibenzyltoluene as H_2 carriers.

As can be observed from Figure 4, dibenzyltoluene is more effective for H_2 transport than toluene, allowing for a higher H_2 flow rate delivered at the unloading terminal.

In both cases, part of the green hydrogen entering the battery limits is lost in the hydrogenation stage. The toluene hydrogenation stage is more energy-intensive than the dibenzyltoluene one: this is due to the higher electric consumption of the hydrogenation stage, because of the H_2 recycle compressor.

As opposite to other H_2 carriers (*i.e.*, liquefied hydrogen or ammonia), no H_2 losses because of the carrier boil off occur during storage and seaborne transport. One of the main advantages of LOHCs is their capability of storing hydrogen without significant degradation or loss over time, making them ideal for balancing seasonal variations in renewable energy supply. In addition, they are stable under ambient temperature and pressure, reducing the risks associated with hydrogen's volatile and explosive nature.

Regarding the dehydrogenation process, the perhydro-dibenzyltoluene dehydrogenation turns out to be less efficient than the methylcyclohexane one. However, for both of the instances analysed, dehydrogenation processes require significant energy input, which reduces the overall efficiency. A non-negligible amount of the H_2 delivered to the unloading terminal is burnt to cope for the endothermicity of the reaction. Moreover, the use of precious metal catalysts (e.g., Pt-based) in hydrogenation and dehydrogenation reactions increases operational costs and catalyst deactivation over time adds to maintenance expenses.

As a result, this assessment confirms that the LOHCs can store significant amounts of hydrogen by

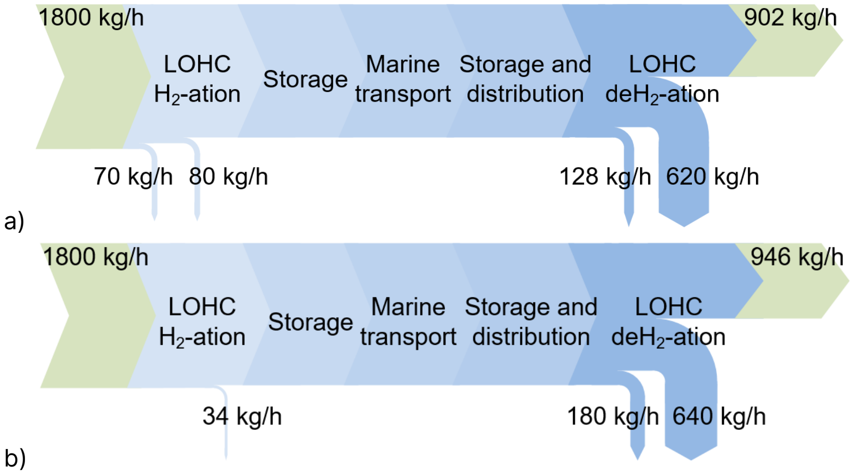

Figure 4. Results of the equivalent H_2 methodology for: a) toluene and b) dibenzyltoluene as H_2 carrier.

chemically binding it, offering high volumetric hydrogen storage density compared to gaseous or cryogenic hydrogen. The liquid-like nature of LOHCs allows them to be transported using existing fuel distribution and storage infrastructure, including pipelines, tanks, and ships.

The carrier molecules can be regenerated and reused for multiple cycles of hydrogenation and dehydrogenation, making LOHC systems sustainable over the long term.

On the other hand, their dehydrogenation is highly energy intensive. For this reason, it is essential to identify species with a lower dehydrogenation enthalpy to enhance the dehydrogenation section energy balance. Also, more active and selective catalysts are needed to enable the dehydrogenation at milder operating conditions.

Finally, it must be noted that both of the LOHC molecules involve fossil-derived feedstocks, raising concerns about the overall environmental footprint if not sustainably sourced, despite the closed cycle realised. Future research should be focus on finding suitable carriers derived from renewable feedstocks, improving the life cycle assessment of the whole value chain.

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