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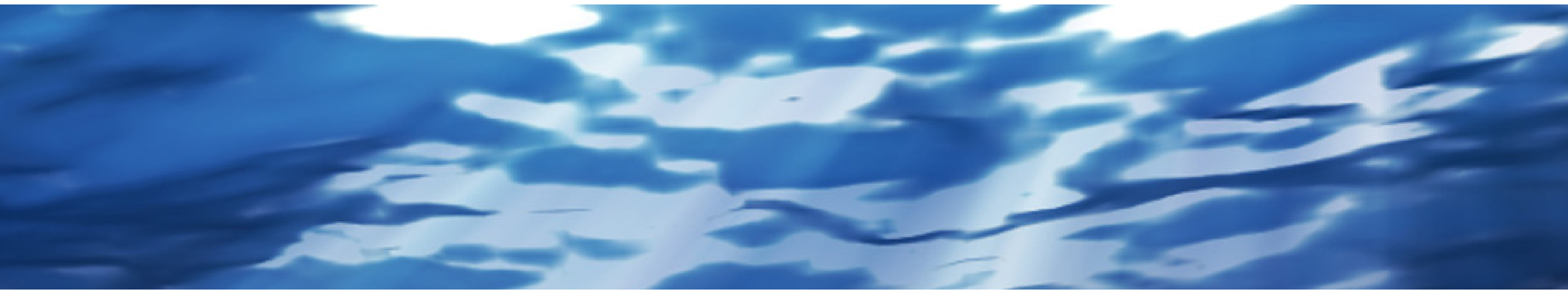
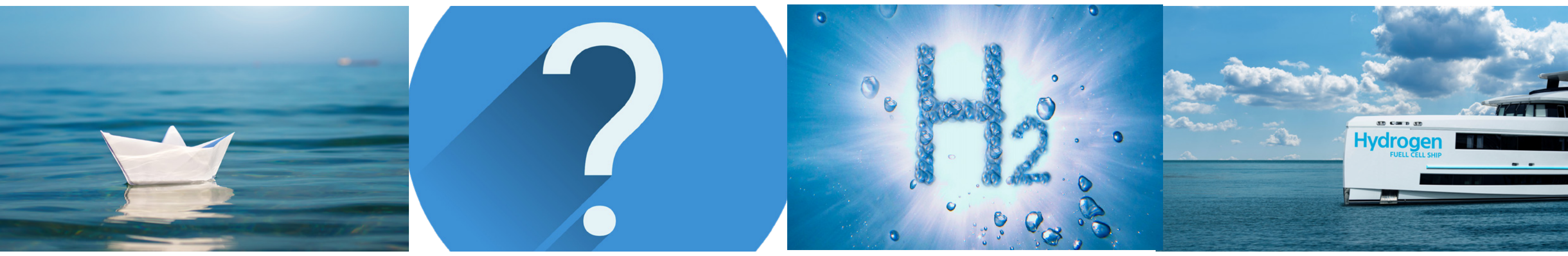


LIGHTHOUSE REPORTS

Handling of hydrogen in liquid form as LOHC from a shipping perspective – a pre-study



En förstudie utförd inom Trafikverkets branschprogram Hållbar sjöfart som drivs av Lighthouse. Publicerad mars 2023

TRAFIKVERKET

LIGHTHOUSE
SWEDISH MARITIME COMPETENCE CENTRE

HÅLLBAR
SJÖFART

Handling of hydrogen in liquid form as LOHC from a shipping perspective – a pre-study

A synthesis of knowledge

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A pre-study carried out within the Swedish Transport Administration’s industry program Sustainable Shipping, operated by Lighthouse

Summary

Hydrogen is increasingly being singled out as one of the solutions needed to achieve future climate goals in various sectors. This also applies to shipping and there is a large need for knowledge about various hydrogen-based solutions. This report summarizes existing information related to the storage and use of hydrogen when hydrogen is handled in liquid form as so-called Liquid Organic Hydrogen Carriers (LOHC). This with the aim of contributing to an initial understanding of the potential for handling LOHCs on board ships and at ports as well as a carrier of hydrogen used as fuel onboard (i.e., its potential from a maritime perspective). The concept of LOHC is that hydrogen is bound to a liquid chemical and later released while the liquid returns to its original liquid form. The report describes and compares possible technical solutions linked to LOHC and briefly describes identified ongoing initiatives in the area.

There are several different LOHC options being assessed with different properties. Relatively high hydrogen storage capacity, and low safety and environmental impacts are important for the prerequisites for a LOHC to be feasible. Several physical properties and the reversibility and durability of the LOHC are also important as they influence for example the dehydrogenation temperature, possibility to use the LOHC in existing infrastructure and the cost. The leading LOHC companies seem mainly to be exploring H0-BT/H12-BT, Benzyltoluene/perhydrobenzyltoluene (Hydrogenious maritime) and TOL/MCH, Toluene/methylcyclohexane (Chiyoda Corporation), respectively. However, these are not the only interesting options according to the literature. The main initiatives identified for testing LOHC for shipping are described in the report.

Several challenges for using LOHC as a carrier for hydrogen which is used as fuel onboard remains to be further explored. These include for example: (i) the LOHC concepts have not been tested in large-scale yet and thus need to be demonstrated and scaled up, (ii) the influence on the space onboard and lost cargo through the space needed for the LOHC (loaded and unloaded) and for the onboard dehydrogenation unit, (iii) the supply of the heat that is required to recover the hydrogen from the carrier on-board, (iv) the safety and environmental impact of the various LOHC and finally (iv) the cost for using LOHC as marine fuel.

In terms of cost, there are a few comparative studies of selected marine fuel options including LOHC. These indicate that other fuel options might be more interesting for the specific shipping segments assessed. However, LOHC might be an interesting option for certain shipping applications. Though, more similar assessments are needed before any firm conclusion about the potential for LOHC versus other hydrogen-based energy carriers (as marine fuel and for transport) can be drawn. The actual potential is also affected by the development of other hydrogen-based alternatives. Finally, more assessments and testing of LOHC for shipping is needed.

Sammanfattning

Vätgas pekas allt oftare ut som en av de lösningar som behövs för att uppnå framtida klimatmål inom olika sektorer. Detta gäller även sjöfarten och kunskapsbehovet kring olika vätgasbaserade lösningar är stort. Denna rapport sammanställer kortfattat befintlig information kopplat till lagring och användning av väte när väte hanteras i flytande form som så kallade Liquid Organic Hydrogen Carriers (LOHC). Syftet är att bidra med en inledande förståelse kring dess potential för hantering ombord på fartyg och vid hamnar och för att användas som marint bränsle (dvs dess potential ur ett sjöfartsperspektiv). Konceptet med LOHC går ut på att väte binds till en vätska (kemikalie) där väte sedan kan lossas och vätskan då återgår till sin ursprungliga flytande form. Rapporten beskriver och jämför möjliga tekniska lösningar kopplat till LOHC och beskriver kort identifierade pågående initiativ inom området.

Det finns flera olika LOHC-alternativ som utvärderas med olika egenskaper. Relativt hög vätgaslagringskapacitet samt låga säkerhetsrisker och miljöpåverkan är viktiga förutsättningarna för att en LOHC-lösning ska vara intressant. Flera fysikaliska egenskaper och reversibiliteten och hållbarheten hos LOHC är också viktig eftersom det påverkar till exempel dehydreringstemperaturen, möjligheten att använda LOHC i befintlig infrastruktur och kostnaden. De ledande LOHC-företagen utforskar främst H0-BT/H12-BT, Bensyltoluen/ perhydrobensyltoluen (Hydrogenious Maritime) respektive TOL/MCH, Toluen/methylcyclohexan (Chiyoda Corporation). Dessa är dock inte de enda intressanta alternativen enligt litteraturen. De viktigaste initiativen som identifierats för att testa LOHC för sjöfart beskrivs i rapporten.

Flera utmaningar kopplat till användning av LOHC som bränsle för sjöfart kvarstår att utreda vidare. Dessa inkluderar till exempel: (i) LOHC-koncepten har inte testats i stor skala ännu och måste därför demonstreras och skalas upp, (ii) påverkan på utrymmet ombord och förlorad last genom det utrymme som behövs för LOHC och för dehydreringsenheten ombord, (iii) tillförseln av den värme som krävs för att frigöra vätgasen från bäraren ombord, (iv) säkerhets- och miljöpåverkan från de olika LOHC och slutligen (iv) kostnaden för att använda LOHC som marint bränsle.

När det gäller kostnader finns det ett antal studier som jämför vissa utvalda alternativ för sjöfartssektorn, däribland LOHC. Dessa indikerar att andra bränslealternativ kan vara mer intressanta för de specifika sjöfartssegmenten som bedömts. LOHC kan emellertid vara ett intressant alternativ för vissa sjöfartsapplikationer. Det behövs dock fler liknande jämförelser och analyser innan några definitiva slutsatser kan dras kring potentialen för LOHC jämfört med andra vätgasalternativ. Detta gäller både för marina bränslen och för transport. Potentialen påverkas även av utvecklingen av andra vätgasbaserade alternativ. Fler analyser och testning av LOHC för sjöfart behövs.

Contents

Glossary/Definitions

Abbreviation	**Definition**
bp	Boiling point
BZ/CHE	Benzene/cyclohexane (LOHC)
CGH2	Compressed hydrogen
DBT/H18-DBT	Dibenzyl toluene/perhydro-dibenzyl toluene (LOHC)
DHQ	Decahydroquinoline (LOHC)
H0-BT/H12-BT	Benzyltoluene/perhydrobenzyltoluene (LOHC)
H12-BPDM	Eutectic mix of biphenyl and diphenylmethane (LOHC)
H_2	Hydrogen
ICE	Internal Combustion Engine
LH2	Liquid hydrogen
LNG	Liquid Natural Gas
LOHC	Liquid Organic Hydrogen Carrier
MeOH	Methanol
MGO	Marine Gas Oil
mp	Melting point
NEC/H12-NEC	N-ethyl carbazole/dodecahydro-N-ethylcarbazole (LOHC)
NH_3	Ammonia
PEM FC	Polymer Electrolyte Membrane Fuel Cell
SOFC	Solid Oxide Fuel Cell
THQ	Tetrahydroquinoline (LOHC)
TOL/MCH	Toluene/methylcyclohexane (LOHC)
wt.%	Weight percent

1 Introduction and background

Hydrogen is increasingly being singled out as one of the solutions needed to achieve future climate goals in various sectors. There is a large need for knowledge about various hydrogen-based solutions. This also applies to the shipping sector, which may use both hydrogen-based energy carriers for propulsion and transport different hydrogen-based energy carriers for various applications. For the shipping sector to substantially reduce their emissions and reach climate targets, alternative marine fuels need to be introduced.

Besides hydrogen in compressed and liquified form, hydrogen can for example be used as a basis for different electrofuels (power-to-x) produced from water and carbon dioxide or nitrogen using electricity e.g., electro-methanol, electro-methane, electro-diesel, and ammonia. As a marine fuel, hydrogen and other hydrogen carriers can be used in several propulsion systems including internal combustion engines (ICE), fuel cells (FC), and gas turbines.

As fossil fuel infrastructure will be available and used for a foreseeable future, liquid renewable fuels that can be handled in existing infrastructure can be expected to have an advantage. The purpose of this study is to review the concept of Liquid Organic Hydrogen Carriers (LOHC), explained in Section 1.1, and provide an initial basic understanding of their potential from a shipping perspective. This report briefly covers both transport of LOCH by ship and the use of LOHC as marine fuel.

The report summarizes the findings from a knowledge synthesis on LOHC. For shipping, LOHC can facilitate the transport and storage of hydrogen either as fuel to be used for propulsion of the ship or for transport of hydrogen by ships for any area of use covering (i) a mapping of relevant scientific literature, (ii) properties of various LOHC systems, (iii) a brief description of identified LOHC projects and initiatives primarily for the shipping sector and (iv) a comparison of LOHC and other selected options. The study is mainly based on a literature review.

1.1 Liquid Organic Hydrogen Carrier/s (LOHC)

Liquid Organic Hydrogen Carriers (LOHC) are liquid or low-melting organic compounds that can be reversibly hydrogenated and dehydrogenated in the presence of a suitable catalytic system. The benefits of using LOHC are their potential of being cheap, safe, and relatively easy to handle. LOHC presents advantages as they provide a high gravimetric and volumetric hydrogen storage, they can also be stored long-term without hydrogen losses, and transported overseas under ambient conditions. Moreover, they are also regarded potentially compatible with existing transport and refuelling infrastructure such as storage tanks, (Aako-Saksa et al, 2018, Abdin et al, 2021, Niermann et al, 2019, Rao et al, 2020, Yadav et al, 2021, Markiewicz et al, 2015).

The LOHC system consists of a pair of hydrogen-rich (H_2-rich) and hydrogen-lean (H_2-lean) organic compounds. The H_2-rich compound is typically an alicyclic or heterocyclic compound, whereas the H_2-lean compound is typically an aromatic or hetero-aromatic compound. In a catalytic hydrogenation reaction (exothermic i.e., process that releases energy/heat), hydrogen is stored by converting H_2-lean to H_2-rich compounds, the reaction typically occurs at elevated temperatures (about 100-250°C) and pressures (1-5 MPa). Hydrogen is then released through the reverse catalytic dehydrogenation reaction (endothermic which absorbs energy/heat) of H_2-rich to H_2-lean compounds, which takes place at close to atmospheric pressure (0.5-1 MPa) and elevated temperatures (about 150-400°C) (**Error! Reference source not found.**) (Aako-Saksa et al, 2018, Addin et al, 2021, Niermann et al, 2019, Rao et al, 2020, Yadav et al, 2021, Markiewicz et al, 2015). In the (de)hydrogenation process, the carrier is not spent but can be re-used and undergo multiple rounds of (de)hydrogenation (Markiewicz et al, 2019). Furthermore, storing hydrogen in LOHC systems is achieved without releasing or binding other substances to or from the atmosphere (Preuster et al, 2017).

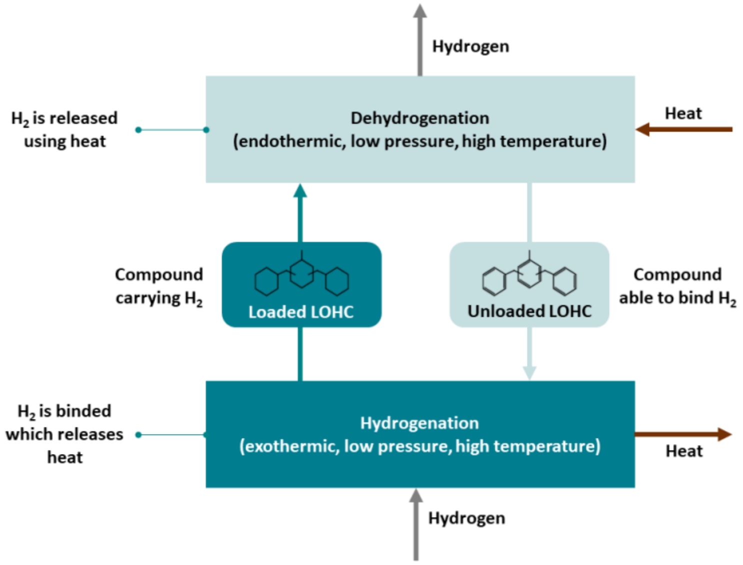

Figure 1. Schematic representation of the LOHC concept. Modified from (Hurskainen, 2019).

In principle, any molecule with an unsaturated bond could be used as an LOHC system, however limitations exist in terms of technological and safety aspects Markiewicz et al, 2019). For a LOHC system to be a promising solution, the literature emphasize that certain requirements and criteria should be considered. Criteria and requirements for a promising LOHC systems include (Niermann et al, 2019, Rao, 2020, Markiewicz et al, 2019):

- Physical properties including (i) **melting point** (mp) – for easy storage and transportation in an existing fuel infrastructure, H_2-rich/-lean LOHC should exist in a liquid state, (ii) **boiling point** (bp) – a high boiling point (>300°C) simplifies hydrogen purification after dehydrogenation, (iii) **thermal stability** – to ensure sustainable catalytic cycles which is important for LOHCs to have a high thermal stability and (iv) **viscosity** – a lower viscosity makes LOHCs useful for pumping into existing tanks and pipelines,

- **Reversibility and durability** – LOHC systems that are reversible, and durable are beneficial as they can be used for several cycles of (de)hydrogenation,
- **High storage capacity** – Volumetric (>56 kg of H_2/m^3) and gravimetric (>6 weight percent (wt%)) H_2 storage capacity,
- **Safety and environmental properties** – Safe and non-toxic LOHCs, with high toxicological and eco-toxicological profiles during transportation and usage, are important to minimize environmental and avoid health damages.

2 Mapping of LOHC literature and properties

2.1 Literature review

The possibilities for LOHC as a hydrogen carrier for shipping is assessed based on a literature review on LOHC systems. The relevant existing LOHC literature (including scientific articles and reports) was identified based on specific search phrases used in the database Scopus (for title, abstract and keywords) and from so-called snowballing using the reference lists in the identified papers and other publications found to identify additional publications.

The information from the literature review is compiled in an excel file. Collected information include (i) overall description of the content of the identified papers/reports, (ii) general properties for the LOHC systems (and some other hydrogen carriers (usage areas, energy density, boiling and melting point etc.), (iii) process conditions for hydrogenation and dehydrogenation of LOHC systems, and (iv) selected techno-economic details (to be used in subsequent studies). The identified literature is listed in Table 1.

The literature review revealed that several organic carrier molecules have been investigated and reported as potential LOHC systems, covering various aspects such as the physical properties of the system, operating conditions for the hydrogenation and dehydrogenation processes, as well as the techno-economic performance of LOHC systems compared to other hydrogen carriers. In the following sections the knowledge gathered from the literature study is summarized.

Table 1. LOHC literature identified in the literature review.

Reference	**Title**	**Brief description of content**
Aakko-Saksa et al (2018)	Liquid organic hydrogen carriers for transportation and storing of renewable energy – Review and discussion	- Properties of LOHC, solid hydrogen carriers and circular hydrogen carriers - (De)hydrogenation, catalysts
Abdin, Z. et al (2021)	Large-scale stationary hydrogen storage via liquid organic hydrogen carriers	- Properties of LOHC and circular hydrogen carriers, - Storage systems and hydrogen carriers - Comparison of LOHC, CGH2 and LH2, ammonia and methanol, - Techno-economic details
Akhtar et al (2021)	Life Cycle Assessment of Inland Green Hydrogen Supply Chain Networks with Current Challenges and Future Prospects	- LCA of LOHC, CGH2, LH2, LNH3
Cho et al (2021)	Recent Advances in Homogeneous /Heterogeneous Catalytic Hydrogenation and Dehydrogenation for Potential Liquid Organic Hydrogen Carrier (LOHC) Systems	- Properties of LOHC, circular hydrogen carriers - Reactor-types for LOHC system
EU HySTOC WP6 – D4.1	WP4 – LOHC logistics infrastructures: D4.1 Decision on LOHC storage and logistics concept	- Logistics concept of LOHC - Techno-economic details on logistics
EU HySTOC WP4 – D6.4	WP6 – Hydrogen Purification: D6.4 Report and techno-economic data of alternative aromatic removal	- Techno-economic details – purification
EU HySTOC WP8 - D8.1	WP8 - Business Development and LCA: D8.1 Potential environmental implications of LOHC concepts	- LCA of LOHC
EU HySTOC WP8 - D8.5	WP8 Business Development and sustainability – Concept Studies, Economic Analysis, Life Cycle Assessment: D8.5 A market analysis study	- Market analysis of hydrogen - Techno-economic comparison LOHC, CGH2, LH2

Han et al (2019)	A Novel Eutectic Mixture of Biphenyl and Diphenylmethane as a Potential Liquid Organic Hydrogen Carrier: Catalytic Hydrogenation	Assessment of the potential for a novel mixture of biphenyl and diphenylmethane as a LOHC.
Hurskainen (2019)	Liquid organic hydrogen carriers (LOHC)	- Properties of LOHC, - Case study on feasibility of LOHC concept - Techno-economic details, - Comparison LOHC, CH2, LH2, LNG and on-site hydrogen
Hurskainen and Ihonen (2020)	Techno-economic feasibility of road transport of hydrogen using liquid organic hydrogen carriers	- Techno-economic details of LOHC concept
IEA Baumann et al (2021)	Task 39 -Final Report	- Properties of hydrogen carriers (i.e. LOHC) - Information on H2 infrastructure, safety, barriers and challenges, new concepts + opportunities, review of hydrogen-propelled vessels
IRENA, (2022)	Global hydrogen trade to meet the 1.5C climate goal - Part II Technology review of hydrogen carriers	Comparison of the transport of hydrogen by pipeline as compressed gaseous hydrogen with three shipping pathways: ammonia, liquid hydrogen and LOHC.
Jander et al (2022)	Viscosity, surface tension, and density of the liquid organic hydrogen carrier system based on diphenylmethane, biphenyl, and benzophenone	Investigation of the viscosity, surface tension, and density of the LOHC-system based on diphenylmethane, biphenyl, and benzophenone.
Jo et al. (2022)	Recent progress in dehydrogenation catalysts for heterocyclic and homocyclic liquidorganic hydrogen carriers	- Properties of LOHC and catalyst details for dehydrogenation
Kim et al (2021)a	Comprehensive analysis of overall H2 supply for different H2 carriers from overseas production to inland distribution with respect to economic, environmental, and technological aspects	- Techno-economic details and comparison of LOHC, LH2 and NH3, production and supply
Kim et al (2021)b	Thorough economic and carbon footprint analysis of overall hydrogen supply for different	- Techno-economic and environmental comparison of LOHC, LH2, NH3

	hydrogen carriers from overseas production to inland distribution	
Kwak et al (2021)	Hydrogen production from homocyclic liquid organic hydrogen carriers (LOHCs): Benchmarking studies and energy-economic analyses	- Properties of LOHC - Dehydrogenation details, reactor, catalyst, performance evaluation - Economic assessment
Lee et al (2021)	Comparative energetic studies on liquid organic hydrogen carrier: A net energy analysis	- Modeling of RHFC system, - Hydrogenation and dehydrogenation details (modeling of LOHC system), - Comparison (energy req.) with CHG, LH2, metal hydrides and ammonia
Makaryan and Sedoc (2021)	Catalytic Reactors for Dehydrogenation of Liquid Organic Hydrogen Carriers	- Dehydrogenation reactors, comparison of performance
Markiewicz et al (2015)	Environmental and health impact assessment of Liquid Organic Hydrogen Carrier (LOHC) systems – challenges and preliminary results	- Hazard assessment
Markiewicz et al (2019)	Hazard assessment of quinaldine-, alkylcarbazole-, benzene- and toluene-based liquid organic hydrogen carrier (LOHCs) systems	- Hazard assessment on categories such as AChE inhibition, cytotoxicity, mutagenicity, aquatic toxicity (details in supplementary materials)
Meille and Pitault (2021)	Liquid Organic Hydrogen Carriers or Organic Liquid Hydrides: 40 Years of History	Brief overview of historic and current literature on LOHC-pairs, catalysts, reactors and economic studies.
Müller et al (2021)	Strategies for Low-Temperature Liquid Organic Hydrogen Carrier Dehydrogenation	- Strategies to lower temp. at dehydrogenation process
Niermann et al (2021)	Liquid Organic Hydrogen Carriers and alternatives for international transport of renewable hydrogen	- Detailed techno-economic performance assessment, supply chain - Comparison of LOHC (NEC, DBT, MET, TOL) with CH2, LH2 and on-site hydrogen prod.
Pawelec (2020)	System-Based Solutions for H2-Fuelled Water Transport in North-West Europe - Comparative report on alternative fuels for ship propulsion	- Comparison of H2 production, logistics and onboard usage on ships - LOHC, LH2, CH2, e-LNG, e-ammonia, e-methanol, e-diesel

Popp and Müller (2021)	Technical reliability of shipboard technologies for the application of alternative fuels	- Comparison of reliability LNG (gas turbine, ICE), Methanol (ICE), Ammonia (FC), LOHC (FC), - Failure rates and severity of failures for the pathways and propulsion technology
Preuster et al (2016)	Liquid Organic Hydrogen Carriers (LOHCs): Toward a Hydrogen-free Hydrogen Economy	State-of-the-art in hydrogen storage using LOHC systems.
Raab et al (2021)	Comparative techno-economic assessment of a large-scale hydrogen transport via liquid transport media	- Comparison of transport with LH2, LOHC (TOL/MCH, H00/H18-DBT), - Detailed techno-economic assessment, - Large-scale point-to-point long-distance overseas hydrogen transport
Sekine and Higo (2021)	Recent Trends on the Dehydrogenation Catalysis of Liquid Organic Hydrogen Carrier (LOHC): A Review	- Catalysts for dehydrogenation of LOHCs (MCH, DBT, NECZ)
Verevkin et al (2021)	Paving the way to the sustainable hydrogen storage: Thermochemistry of amino-alcohols as precursors for liquid organic hydrogen carriers	- Studying amino-alcohols as precursors for LOHC such as alkylpyrazines
Wulf et al (2018)	Life Cycle Assessment of hydrogen transport and distribution options	- Comparison, Life cycle assessment on different hydrogen supply chains GH2 and LOHC
Ydav et al (2021)	Recent Advances in Liquid Organic Hydrogen Carriers: An Alcohol-Based Hydrogen Economy	Alcohol-based LOHC such as methanol
Zheng et al (2021)	Current research progress and perspectives on liquid hydrogen rich molecules in sustainable hydrogen storage	- Summarizes the latest development of hydrogen generation from liquid H2-rich molecules and their regeneration - Catalysts for dehydrogenation of LOHCs

2.2 Properties of different LOHCs

Any molecule with an unsaturated bond could in principle be used as an LOHC system. However, there are limits in terms of technological and safety aspects. Thus, there are certain requirements and criteria that should be considered for LOHCs to be considered promising (see Section 1.1).

In the literature, some commonly reoccurring LOHCs are for example the cyclic hydrocarbons including:

- benzene/cyclohexane (BZ/CHE),
- toluene/methylcyclohexane (TOL/MCH),
- dibenzyl toluene/perhydro-dibenzyl toluene (DBT/H18-DBT),
- (mono)benzyltoluene/perhydrobenzyltoluene (H0-BT/H12-BT), and
- n-ethyl carbazole/dodecahydro-N-ethylcarbazole (NEC/H12-NEC) (Aako-Saksa et al, 2018, Abdin et al, 2021, Markiewicz et al, 2019, Hurskainen, 2019, Cho et al, 2021, Kwak et al, 2021, Schjølberg et al, 2021, Muller et al, 2021, Jo et al, 2022, Lee et al, 2022).

In addition to these compounds, the potential of other organic compounds to act as an LOHC system have also been studied in the literature. Some examples of these include:

- quinoline to tetrahydroquinoline (THQ) or decahydroquinoline (DHQ) and
- the eutectic mix of biphenyl and diphenylmethane (H12-BPDM) to bicyclohexyl and dicyclohexylmethane (Aakko-Saksa et al, 2018, Markiewicz, 2019, Cho et al, 2021, Kwak et al, 2021).

In Table 2, an overview of properties of the commonly mentioned LOHC systems is presented (including hydrogen storage capacity, temperature for hydrogenation and dehydrogenation as well as safety and environmental properties). Some more details including melting and boiling point as well as common area of usage is presented in Table A-1 in Appendix A. Information for the different options are also given in the text below. In Table B-1 and Table Error**! No text of specified style in document.**-1 in 0 and C some hydrogenation and dehydrogenation conditions, as reported in the literature, are also summarized.

2.2.1 BZ/CHE and TOL/MCH

Benzene (BZ) and toluene (TOL) are aromatic hydrocarbons which are well-studied in the literature as potential LOHC systems. Both are widely used as industrial chemicals, with an annual global production of approximately 50 Mt at a price below 1 EUR/kg (Aakko-Saksa et al, 2018). However, some uses of benzene and toluene are restricted under the European Union regulation REACH (EC 1907/2006)[1] (Markiewicz et al, 2019).

BZ/CHE was first studied as an LOHC-pair in the 1980s (Niermann et al, 2021) and has the advantage of a high gravimetric hydrogen storage capacity of ~7.2 weight percent (wt.%). However, BZ is classified as a known human carcinogenic and is highly toxic, while CHE is highly flammable. On an industrial scale, BZ is hydrogenated to CHE using a Raney-Ni catalyst. With a commercial Ni catalyst BZ has been hydrogenated at 95-125°C and 20-40 bar, and with a Ru-catalyst at 90°C and 60 bar. CHE has been dehydrogenated using various catalysts, in which Aakko-Saksa et al, (2018) has reported conditions of 350°C with a Pt/AC catalyst and 375°C with Pt/alumite. Jo et al (2022) reported dehydrogenation conditions for CHE using several catalysts on various supports, in which the temperature ranged from 147 to 550°C with a Pt-catalyst and 300 to 350°C with a Ni-catalyst.

By adding a methyl radical to the BZ/CHE system, the toxicity can be lowered by turning it into TOL/MCH, however this reduces the hydrogen storage capacity to approximately 6.2 wt.% (Aakko-Saksa et al, 2018, Abdin et al, 2021). TOL is a stable liquid in room temperature (melting point (mp): -95°C, boiling point (bp): 111°C) but has a low flashpoint which makes it highly flammable. Although TOL has a lower toxicity than BZ, it has a classification of presumed reproductive toxicity. MCH can also be directly harmful if inhaled during possible leakages (Aakko-Saksa et al, 2018, Markiewicz et al, 2019, Kwak et al, 2021). TOL has been hydrogenated with Ni and Pd-catalysts at 50-100°C and 10-50 bar. MCH has been dehydrogenated with a Pt-catalyst with various supports at 150 to ~350°C, with an Ir-catalyst at 250°C, Ni-catalyst at 350-440°C and Mo-catalyst at 400°C (Aakko-Saksa et al, 2018, Abdin et al, 2021, Kwak et al, 2021, Jo et al, 2022).

2.2.2 DBT/H18-DBT and H0-BT/H12-BT

Benzyl toluene (BT) and dibenzyl toluene (DBT) are cyclic hydrocarbons, commonly used as heat transfer fluids and can be found at a price range of 4-5 USD/kg. The DBT/H18-DBT and H0-BT/H12-BT systems both have a hydrogen storage capacity of 6.2 wt.% and presents advantages for LOHC applications such as low toxicity, high flash point and good thermal stability. DBT is more commonly mentioned in the literature as it has the benefit of a lower vapor pressure and higher boiling point (H_2-lean: 390°C) than BT (H_2-lean: 280°C). The boiling point of DBT is also higher than its dehydrogenation temperature, therefore no further separation of gases is required (Abdin et al, 2021, Hurskainen, 2019, Schjølberg et al, 2021). Drawbacks of the DBT-system includes the risk for degrading the hydrogenation capacity of the system, according to Abdin et al (2021) it has been reported that after several cycles of

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[1] Chemicals produced or imported into the European Union in quantities higher than 1 ton/year are subject to REACH (EC 1907/2006). The regulation aims to protect human health and the environment, and covers different criteria for risk assessment of chemicals, in which two important factors are hazard and release/exposure

(de)hydrogenation the capacity is reduced to approximately 23% of its theoretical value. BT has the advantage over DBT with its lower viscosity, making it easier to handle. The H0-BT/H12-BT systems is also the system selected by Hydrogenious LOHC Maritime AS which is developing a marine LOHC system (see Section 3.2).

Using a Pt-catalyst with various supports DBT has been hydrogenated into H18-DBT at approximately 140°C (Abdin et al, 2021) and 290-310°C (Aakko-Saksa et al, 2018), while a Ru-catalyst enables hydrogenation at 150°C and 50 bar. Due to a relatively high enthalpy exchange (65 kJ/mol H_2), catalytic dehydrogenation must occur at >250°C. Dehydrogenation of H18-DBT into DBT has been performed with Pt-catalysts at 270-310°C and 1-1.5 bar (Niermann et al, 2019, Preuster et al, 2017, Cho et al, 2021, Kwak et al, 2021, Jo et al, 2022, Lee et al, 2021). BT has been hydrogenated into H12-BT using a Ru-catalyst at 150°C and 50 bar. H12-BT has been dehydrogenation at 270-340°C at 1 bar with a Pt-catalyst (Aakko-Saksa et al, 2018, Cho et al, 2021).

2.2.3 NEC/H12-NEC

N-ethyl carbazole (NEC) is a heterocyclic compound that can be found at a price of >40 USD/kg (Hurskainen, 2019). The hydrogen storage capacity of the NEC/H12-NEC system is 5.8 wt.%, it has a low flammability and NEC biodegrades fast. However, there are potential concerns for bioaccumulation of H8-NEC, which is the main intermediate formed during hydrogenation of NEC to H12-NEC. Due to its relatively high melting point (68-69°C), the system is solid at room temperature which presents limitations for usage in the existing infrastructure for fossil fuels (Aakko-Saksa et al, 2018, Abdin et al, 2021, Markiewicz et al, 2015, Cho et al, 2021). Hydrogenation of NEC has been reported at 110-180°C and ~20 bar with a Pd-catalyst and 140°C and 60 bar with a Ru-catalyst. The dehydrogenation temperatures of the NEC system are quite low due to its low enthalpy exchange (about 50-53 kJ/mol H_2). Dehydrogenation of H12-NEC has been reported for Ni-catalysts at 250°C, Pd-catalysts at 170-260°C and with a Pt-catalyst at 180-260°C (Aakko-Saksa et al, 2018, Jo et al, 2022).

Table 2. Overview of commonly mentioned LOHC systems and their properties. See also Table A-1, B-1 and C-1 in appendix for more information on e.g., hydrogenation and dehydrogenation conditions.

LOHC system	Hydrogen storage capacity [wt.%]	Hydrogenation	Dehydrogenation	Safety and environmental properties	Example of references including the LOHC system
		Temperature [°C]			
Benzene/ cyclohexane (BZ/CHE)	7.2 (Aakko-Saksa et al, 2018, Abdin et al, 2021)	90-125 (Aakko-Saksa et al, 2018)	300-550 (Jo et al, 2022)	High toxicity (BZ), high flammability (CHE). Restricted used under Regulation (EC) No. 1907/2006 (Aakko-Saksa et al, 2018, Markiewicz et al, 2015).	Aakko-Saksa et al, 2018 Abdin et al, 2021, Jo et al, 2022 Markiewicz et al 2019
Toluene/ methylcyclohexane (TOL/MCH)	6.2 (Kwak et al, 2021)	50-100 (Aakko-Saksa et al, 2018)	150-440 (Jo et al, 2022)	High flammability, explosive mixture could form at room temperature. Restricted used under Regulation (EC) No. 1907/2006 (Aakko-Saksa et al, 2018, Markiewicz et al, 2015, Kwak et al, 2021).	Aakko-Saksa et al, 2018, Abdin, Z. et.al, 2021, Hurskainen, 2019, IEA Baumann et al, 2021, Jo et al, 2022, Kwak et al, 2021, Markiewicz et al 2019 Niermann et al, 2021
Dibenzyl toluene/ perhydrodibenzyl toluene (DBT/H18-DBT)	6.2-6.29 (Aakko-Saksa et al, 2018, Abdin et al, 2021, Kwak et al, 2021)	50-100 (Aakko-Saksa et al, 2018)	140-440 (Cho et al, 2021, Jo et al, 2022, Kwak et al, 2021)	Low toxicity and thermal stability. Not classified as dangerous goods. (Aakko-Saksa et al, 2018, Abdin et al, 2021, HyStoc, 2018).	Aakko-Saksa et al, 2018, Abdin et al, 2021, Cho et al, 2021, EU HySTOC WP8 - D8.1 Hurskainen, 2019 IEA Baumann et al, 2021, Jo et al, 2022, Kwak et al, 2021, Lee et al, 2021, Markiewicz et al, 2019

Benzyltoluene /perhydro-benzyltoluene (H0-BT /H12-BT)	6.2 (Jander et al, 2022, Aakko-Saksa et al, 2018)	About 250 (Hydrogenous LOHC Maritime, 2023), 150 (Aakko-Saksa et al, 2018, Cho et al, 2021)	270-340 (Aakko-Saksa et al, 2018, Cho et al, 2021), 300 (Hydrogenous LOHC Maritime, 2023)	Low toxicity and eco-toxicity (Aakko-Saksa et al, 2018)	Aakko-Saksa et al, 2018, Cho et al, 2021, Hydrogenous LOHC Maritime, 2023 Kwak et al, 2021
N-ethyl carbazole/ perhydro-N-ethyl carbazole (NEC/H12-NEC)	5.8 (Aakko-Saksa et al, 2018, Abdin et al, 2021)	110-180 (Aakko-Saksa et al, 2018)	170-260 (Aakko-Saksa et al, 2018, Kwak et al, 2021)	Low flammability. NEC biodegrades fast while there are potential concerns for bioaccumulation for H8-NEC which is not biodegradable (Aakko-Saksa et al, 2018, Markiewicz et al, 2015).	Aakko-Saksa et al, 2018, Abdin et al, 2021, Cho et al, 2021, Hurskainen, 2019, Jo et al, 2022, Kwak et al, 2021 Markiewicz et al, 2015 Müller et al, 2021, Niermann et al, 2021, Dong et al, 2018

2.2.4 Other LOHC

H12-BPDM and quinoline have not been as widely investigated, thus detailed information regarding their properties is more difficult to obtain. The information that was found have also been included in the tables in the appendix.

Both biphenyl (H0-BP) and diphenylmethane (H0-DPM) have been investigated as LOHC-system due to their relatively high hydrogen storage capacity of 6.9-7.1 and 6.66 wt.%, respectively. However, as H0-BP is a solid in room temperature and H0-DPM has a high toxicity and high melting point (22-25°C), a eutectic mixture (H12-BPDM) of both has been investigated and presented by the Yoon group. H12-BPDM with a mass fraction of 0.35 H0-BP and 0.65 H0-DPM, has a hydrogen storage capacity of 6.9 wt.%, a melting point (13.1°C) below that of the pure compounds and thereby exist in a liquid-state at room temperature (Cho et al, 2021, Jander et al, 2022). The mixture has been hydrogenated at 120°C and 50 bar with a Ru/Al_2O_3-catalyst with 99% conversion. Dehydrogenation to a mixture of bicylohexyl (BC) and dicyclohexylmethane (DCM) has been performed at 340°C with a Pd/C-catalyst (Cho et al, 2021).

Quinoline and its derivatives has been mentioned as promising LOHCs due to their high boiling point. Quinoline can be hydrogenated into decahydroquinoline (DHQ) and tetrahydroquinoline (THQ), with DHQ at an advantage due to its hydrogen storage capacity of 7.2 wt.%, compared to 2.9 wt.% for THQ. Quinoline has been hydrogenated to DHQ at 125°C and 8 bar with a Rh/AlO(OH)-catalyst at a yield of 99.3%. Dehydrogenation has been performed at 350°C with a Ni-NiCrO-catalyst, yielding 42-47% of quinoline from DHQ in 5 h (Aakko-Saksa et al, 2018).

2.2.5 Most promising LOHC?

In terms of most promising LOHC, BZ/CHE, Quinoline/THQ and potentially H0-BP/BC have the highest hydrogen storage capacity according to the literature (followed by H0-BT/H12-BT, DBT/H18-DBT and TOL/MCH). However, in terms of boiling point H0-BT/H12-BT, DBT/H18-DBT, NEC/H12-NEC followed by TOL/MCH has the highest reported value. Finally, in terms of safety and environmental performance, DBT/H18-DBT and H0-BT/H12-BT seem to have low toxicity and can likely be stored and transported in the existing infrastructure for fossil fuels. As will be described in Section 3 the leading LOHC companies seem mainly to be exploring H0-BT/H12-BT (Hydrogenious maritime) and TOL/MCH (Chiyoda Corporation), respectively. However, these are not the only interesting options.

2.3 Costs

Literature that includes comparisons of the costs for different storage alternatives for hydrogen take several costs into consideration in their analysis. In Pawelec (2020) for example the following costs are included: production costs for hydrogen, transformation and conditioning costs (where in the case of LOHC hydrogenation costs are included), fuel logistics costs, storage costs, onboard reforming costs and energy conversion costs. The costs estimated in Pawelec (2020) are presented in Section 4.1. The mapping of costs linked to transport of hydrogen as LOHC and other hydrogen-based carriers based on IRENA (2022) are presented in Section 4.2.

3 Status of existing and planned projects

A few projects are currently in operation or planned with various LOHC applications. The identified projects that include shipping are presented in this section as well as a short summary of other more general LOHC initiatives/projects. The leading companies for LOHC in general include Hydrogenious LOHC Technologies and Chiyoda Corporation. For shipping it is Hydrogenious LOHC Maritime AS.

3.1 Chiyoda Corporation and others: LOHC supply and oversea transport chain

In 2020, the world's first end-to-end global hydrogen supply chain was demonstrated by the Japanese company Chiyoda Corporation, in collaboration with Mitsubishi Corporation, Mitsui & Co., Ltd. and NYK Line. The demonstration project was launched in 2015 and conducted by "Advanced Hydrogen Energy Chain Association for Technology Development (AHEAD)", which was established together by all the partners involved (Chiyoda Corporation, 2022).

The project successfully demonstrated the use of the LOHC-system TOL/MCH for overseas transportation of hydrogen in this form. The hydrogen supply chain includes hydrogen procurement in Brunei Darussalam, conversion to MCH, followed by overseas transportation of MCH to the consumer country, Japan (Chiyoda Corporation, 2022) and then distributed through Chiyoda's SPERA Hydrogen™ technology. The hydrogenation plant is thus located in Spark, Brunei Darussalam to produce hydrogen, followed by LOHC and the dehydrogenation plant in Kawasaki City, Japan (Chiyoda Corporation, 2022-A, AHEAD, 2022). The SPERA Hydrogen™ technology enables the hydrogen to be handled, stored and transported as a liquid in ambient temperature and pressure (Chiyoda Corporation, 2022-A, Chiyoda Corporation, 2022-B). Figure 2 provides a schematic figure of the hydrogen supply chain by Chiyoda.

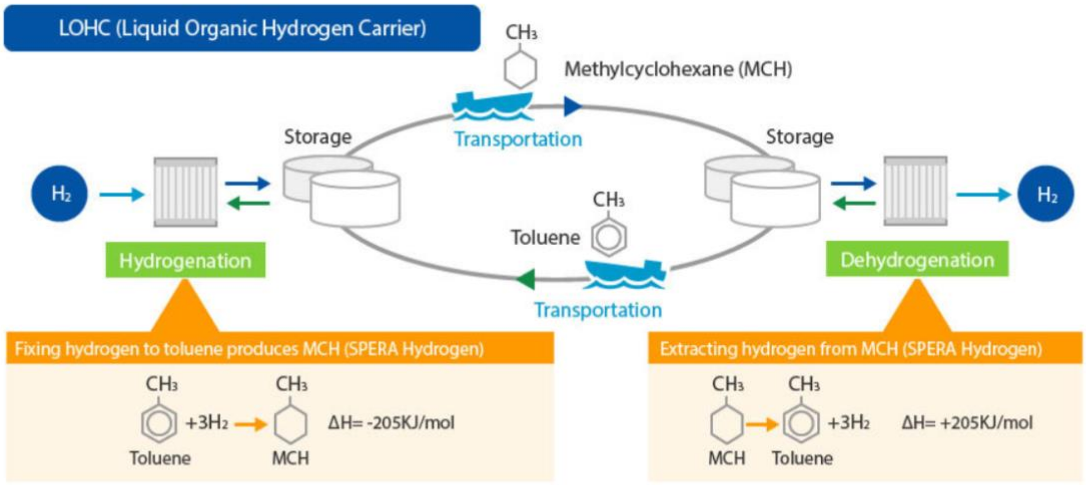

Figure 2. Flow chart of Chiyoda's hydrogen-LOHC supply chain using TOL/MCH. Figure from Chiyoda corporation (2022-B)[2].

3.2 Hydrogenious LOHC Maritime AS: on-Board LOHC powertrain

The German company Hydrogenious LOHC Technologies GmBH (hereafter Hydrogenious) was founded in 2013 and provides hydrogen infrastructure solutions by implementing LOHC technology. Hydrogenious offers LOHC solutions to store and release hydrogen and utilises benzyltoluene (BT) as hydrogen carrier (Hydrogenious LOHC Technologies GmBH, 2022-A). The Storage systems store hydrogen in the LOHC system and are designed with a hydrogen storage capacity starting from 5 tonnes/day. The Storage systems can be applied to different applications such as for industries, sectoral integration and hydrogen refuelling infrastructures (Hydrogenious LOHC Technologies GmBH, 2022-B, Hydrogenious LOHC Technologies GmBH, 2022-C). The Release systems release hydrogen from the LOHC and has a hydrogen release capacity starting from 1.5 tonnes/day, which can be applied to industrial supplies and refuelling stations (Hydrogenious LOHC Technologies GmBH, 2022-D).

In 2021, Hydrogenious and Johannes Østensjø dy AS announced a partnership, founding the joint venture company Hydrogenious LOHC Maritime AS, aiming to develop LOHC-based applications for shipping, i.e., for the development of LOHC driven ships. More specifically they mainly focus on the LOHC system H0-BT/H12-BT. The goal is to develop an on-board LOHC solution for shipping using a hydrogen driven fuel cell propulsion system, that is planned to be commercially available to operate from 2025. The initial project, HyNjord, of the joint venture received funding from the Norwegian governmental agency Enova with approximately 2.5 million EUR (Enova, 2022, Hydrogenious LOHC

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[2] Chiyoda provides a virtual reality tour of the hydrogenation and dehydrogenation plants [Plant VR Tour (chiyodacorp.com)](chiyodacorp.com) including photos of the hydrogenation and dehydrogenation plants.

Technologies GmBH, 2022-E). The focus of HyNjord is to develop a 200 kW pilot utilising LOHC onboard with a fuel cell propulsion system. A schematic figure of the HyNjord project is shown in Figure 3 (Hydrogenious LOHC Maritime, 2022). Proton-exchange membrane (PEM) fuel cells (FC) but also solid oxide fuel cells (SOFC) will be tested by Hydrogenious LOHC Maritime, the latter to assess the possibility for the high-temperature heat to be integrated into the dehydrogenation process onboard (Hydrogenious LOHC Maritime, 2023).

Together with Edda Wind, seven newbuilt service offshore vessels (service for offshore wind turbines) prepared for implementing LOHC in the future (i.e., LOHC ready) is in the order pipeline. The vessels will initially have a capacity of 200 kW LOHC-BT-fuel cell system to power the vessel's auxiliary power but with the vision of a possible upgrade to megawatt (MW)-size system powering (Hydrogenious LOHC Maritime, 2023). The first vessel was delivered in 2022 (more info: https://splash247.com/edda-winds-hydrogen-ready-csovs-to-be-built-to-dnv-class/). Hydrogenious LOHC Maritime reports that about 10 kWh of heat/kg is created in hydrogenation and 11 kWh of heat/kg is needed for the dehydrogenation for their LOHC case

Hydrogenious LOHC Maritime identifies (Hydrogenious LOHC Maritime, 2023) offshore service vessels, bulk carriers, and medium range ferries as promising candidates for first LOHC demonstration projects.

Thus, currently Hydrogenious LOHC Maritime is in the phase of testing small-scale LOHC for shipping but with the plan to scale it up to 1 MW prototype from 2023 with a potential commercial roll out from 2024-2025 (Hydrogenious LOHC Maritime, 2023).

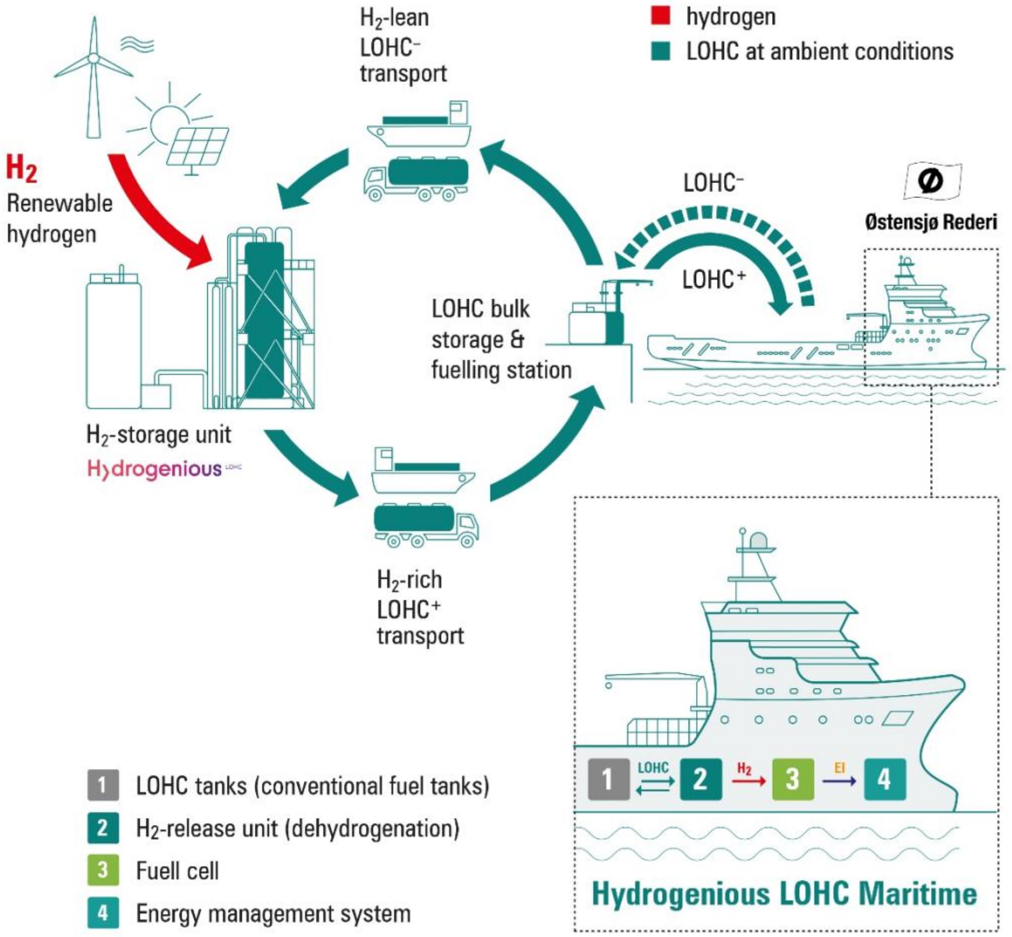


Figure 3. Schematic of the HyNjord-project with an on-board LOHC-solution (Figure from Hydrogenious LOHC Maritime, 2023).

3.3 Pilot project linked to Green shipping programme Norway: infrastructure for LOHC

Siemens has, together with a number of other partners, and as part of the Green shipping programme in Norway led by DNV, a pilot which aims to present a concept and business case for a project that will provide hydrogen oil (LOHC) to ships in the Norwegian shipping industry. The pilot project started in January 2021. Through the development of the concept, the project hopes to form a basis for an engineering project which in the longer run can become an established facility for hydrogen oil (LOHC).

3.4 Summary of other more general LOHC initiatives/projects

Hydrogenious has several other projects with establishments of sites in Spain, the Netherlands and Germany with funding from for example the Important Projects of Common European Interest (IPCEI) and the EU. The Green Crane project aims to establish a route for hydrogen transport from southern to northern

Europe. The Blue Danube project wishes to establish a pan-European supply chain in the Danube region. The project Hector in Chempark Dormagen is supposed to be the start of a wide LOHC based hydrogen infrastructure in Europe. The largest plant for LOHC in the world is being established by Hydrogenious in Chempark Dormagen (Germany) with a capacity of 5 tonnes/day to be followed by another plant with a capacity of 24 tonnes/day which has received funding.

Chiyoda also has several projects and studies including feasibility studies on importing hydrogen into Singapore, on the economic viability of large-scale import and distribution of hydrogen in the Chubu region, for importing hydrogen into the Netherlands (in collaboration with Mitsubishi) and for a 300 MW electrolyser project in Canada. Together with Eneos, Chiyoda has a joint project for development of technology combining electrolysis and hydrogenation steps.

H2-industries and Framatome/Covalion (owned by EDF) have projects focusing on using dibenzyltoluene (DBT) as a carrier. H2-industries has for instance an integrated electrolysis and conversion technology, which takes electricity and produces the loaded LOHC. Framatome/Covalion is a licensee of Hydrogenious and builds LOHC plants with DBT.

Worth mentioning is also the Chinese company Hynertech, who is supplying 1-50 kW high-purity hydrogen supply systems for mobile and stationary applications. During 2021 Petronas and Eneos presented a feasibility study to export hydrogen from Malaysia to Japan. This will be the first commercial-based international hydrogen trade, supported by funding from the Japanese green innovation fund.

The project AquaVentus in Germany, with members Hydrogenious and H2-industries, aims to deploy 10 GW of offshore wind in the NorthSea by 2035. Some of the electricity will be used to produce hydrogen, which will be transported to shore using pipelines. AquaVentus has connections to the TransHyDE-project which includes a project to test the LOHC-route.

4 LOHC in comparison with other selected options

As indicated in the introduction, LOHC can facilitate the transport and storage of hydrogen either as fuel to be used for propulsion of the ship (including onboard dehydrogenation where hydrogen is released and used as fuel) or for transport by ships of hydrogen for any area of use.

In the following sections, a comparison of the LOHC concept with other alternative hydrogen carriers is presented, first focusing on using LOHC as marine fuel and then focusing on using LOHC primarily for transporting hydrogen. The main sources for the comparisons are Pawelec (2020) and IRENA (2022) which include comparative assessments.

Pawelec (2020) includes a techno-economic analysis and comparison of different fuel and propulsion options for shipping suitable for north-western Europe. The assessment covers LOHC, liquified hydrogen (LH2), compressed hydrogen (CGH2), liquefied natural gas (LNG), ammonia (NH3), methanol (MeOH) and marine gas oil (MGO), all renewable, as well as fossil MGO. The analysis focuses on regional shipping and does not cover deep-sea shipping and the international infrastructure that would be necessary for the possibility of using LOHC in these applications. The analysis is a total cost of ownership (TCO) analysis and covers all the relevant vessel types for the area in focus.

The report by IRENA from 2022 compares LOHC with two other hydrogen pathways, ammonia, and liquid hydrogen, as well as transport via pipeline. The report focuses on transport of hydrogen and hydrogen-based energy carriers. The report covers gaseous hydrogen, the transformation into a suitable form for transport, the transport of the hydrogen medium and the transformation back to pure hydrogen. The storage of hydrogen, which is a key factor for infrastructure in ports is also covered. The study also includes a review of the capital costs and the energy use in each step and defines in which span these values are and could be in the future. The review includes several different LOHC.

Hydrogen can be transferred to LOHC either close to the production site or at the port (if the production site is elsewhere). In the case the hydrogen should be used as fuel, the LOHC can then be loaded on the ship and the hydrogen released onboard to be used as marine fuel (which require heat). Since heat is generated in the forming of LOHC and is needed in the release of the hydrogen there is also the possibility to produce and use LOHC at the same location. For shipping, this case (including also on-board hydrogenation i.e., production of LOHC) does not represent a very interesting option as the advantages for shipping of using LOHC instead of hydrogen is lost for this case (as the reason for using LOHC for shipping is to avoid the need for storing large amount of hydrogen onboard).

When hydrogen (and other energy carriers) are to be transported by or used as fuels for propulsion of a ship, the energy density of the energy carrier/fuel is an important factor when determining the viability of the alternatives. In Figure 4 energy density (volumetric and gravimetric) for the different alternatives energy carriers as presented by Pawelec (2020) is shown.

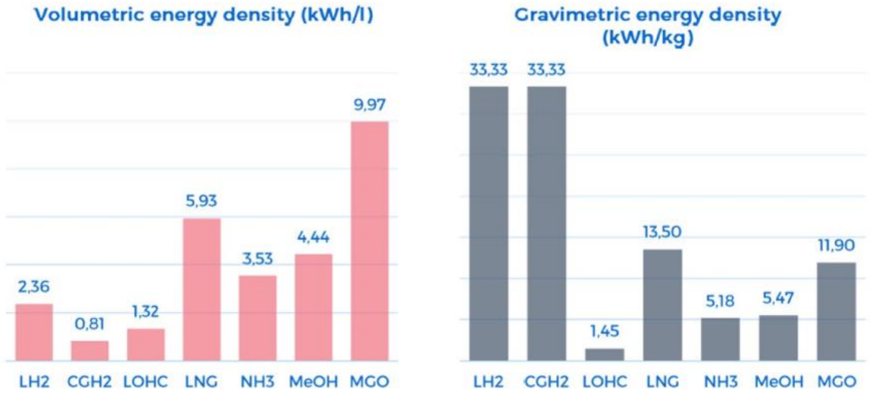


Figure 4. Comparison of density for selected energy carriers. Figure collected from Pawelec (2020).

Compared to MGO and LNG, all the hydrogen-based options have lower volumetric energy density. While LOHC have higher volumetric energy density than compressed hydrogen, it has lower than liquid hydrogen, ammonia, and methanol.

4.1 LOHC as marine fuel in comparison to other hydrogen-based options for the case of regional shipping

As indicated above Pawelec (2020) compares the use of LOHC as marine fuel with other hydrogen-based marine fuel options. To use LOHC as fuel for a ship requires an onboard dehydrogenation unit and extra storage tanks for unloaded LOHC (after release of hydrogen). On a ship hydrogen can be used in fuel cells (SOFC and PEM) and different types of engines (internal combustion engines, and gas turbines). It is not fully specified which specific type of LOHC that is considered in Pawelec (2020).

For LOHC (like hydrogen) to be used as marine fuel, the space required for on board fuel storage and in the case of LOHC also dehydrogenation unit and for extra tanks for storing the unloaded LOHC is interesting. In some cases (PEM FC) also hydrogen purification equipment is needed. Pawelec (2020) has made an estimate of the total space requirements for the included fuels including also tank and engine room, for a container ship using several general assumptions, see Figure 5. LOHC and compressed hydrogen is estimated to have the highest total space requirement.

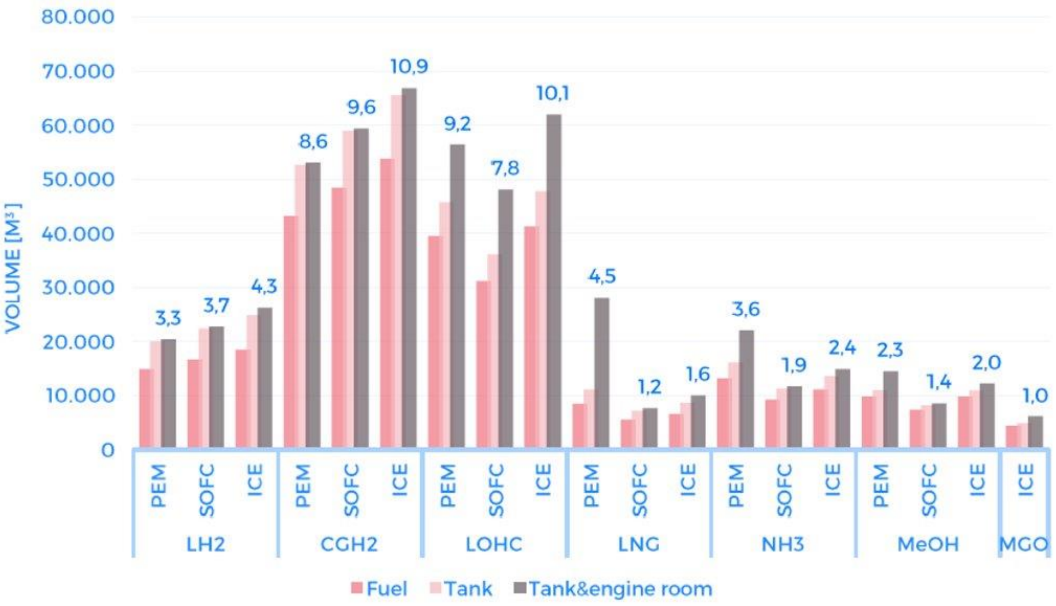


Figure 5. General estimate of total space requirements for fuel in m3 and relative to MGO and ICE for a 8000–1200 TEU Containership and different fuel and propulsion combinations. Figure collected from Pawelec (2020).

The amount of heat produced, temperature of the heat, possibilities for waste heat recovery (which could potentially be integrated into the dehydrogenation process on board), estimated efficiency for different propulsion options for hydrogen and LOHC (based on IRENA, 2022) is presented in Table 3. The table also includes a preliminary assessment of the estimated technical compatibility of the propulsion concept with LOHC.

While gas turbines produce more heat per kg hydrogen than the other propulsion options, the table indicates that they have a lower efficiency (around 36 %). All propulsion options, except for the PEM FC, have heat temperature levels above the heat level needed for most dehydrogenation processes and seems to produce enough waste heat to cover the dehydrogenation process (unless used for other purposes). As an example, SOFC requires a high heat level of 900 °C (which could potentially be integrated into the dehydrogenation process on board) (IRENA, 2022). If the heat should come from additional fuel, then there is an increased fuel demand. Dehydrogenation is carried out at atmospheric pressure whilst some of the technologies mentioned need pressurized hydrogen. This requires an additional compressor on board, taking up more space.

Table 3. Conditions for selected propulsion options possible for LOHC (Based on: IRENA 2022) and estimated preliminary technical compatibility.

Technology	**Heat produced (kWh/kgH_2)**	**Heat level (°C)**	**Relevant waste heat recovery potential**	**Efficiency (%)**	**Preliminary compatibility with LOHC (high, low, moderate)**
SOFC	13	900	Heat transfer for dehydrogenation or combined cycle	68	Moderate to high
PEMFC	9	90	None	42[a]	Low to moderate
ICE	8	400	Heat transfer for dehydrogenation	46	Moderate to high
Gas turbine	20	600	Heat transfer for dehydrogenation	36	Moderate to high

[a] Estimations of PEMFC efficiency vary in literature and 42% can be considered a conservative value, efficiency of 55% is not uncommon see for example Batelle (2016).

The idea with using LOHC as a marine fuel is based on the possibility for low-cost onboard storage and storage in ports using existing fossil fuel storage tanks (standard steel tanks) at ambient conditions (i.e., no need for pressurization or low temperature) which according to the literature might be possible (e.g., Pawelec, 2020). In addition, there are no losses of hydrogen during storage as it is bound to the carrier. A storage plant for LOHC from Hydrogenious LOHC Maritime is illustrated in Figure 6.

The idea is also to facilitate refuelling. In the case of LOHC refuelling takes place by pumping a liquid. It seems possible to use conventional pumps and existing bunkering terminals. Compared to refuelling with some other hydrogen-based carriers the refuelling is fast, and it is possible to load and unload while refuelling (at least for some LOHC) (Hydrogenious LOHC Maritime, 2023).

Figure 6. The LOHC storage plant developed by Hydrogenious LOHC Maritime (Figure from Hydrogenious LOHC Maritime, 2023).

4.1.1 Cost estimate

The fuel production cost estimates in Pawelec (2020), presented in Figure 7, include the costs for renewable hydrogen production as well as the transformation and conditioning required for the fuel to reach its final form. Based on the cost of renewable electricity production in several European countries as well as a future positive development for CAPEX for hydrogen production units, the cost of hydrogen production was set to 2.4 EUR/kg (for more information on the assumptions made in the calculations see Pawelec, 2020).

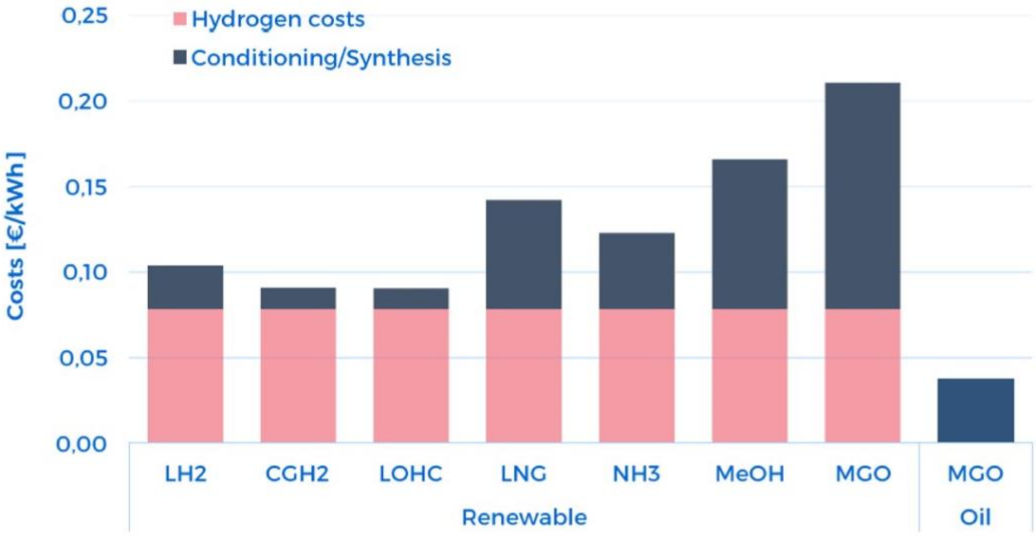


Figure 7. Fuel production cost estimates in Pawelec, 2020. Figure collected from Pawelec (2020).

The lowest fuel production costs of the studied options are compressed hydrogen (CGH2) and LOHC, where the production cost is around 91 EUR per MWh. In comparison to the MGO value used, this represents the double cost. However, given that proposed policies are implemented (such as the inclusion of shipping in the EU emission trading system) the MGO cost within EU waters will increase which will reduce the cost gap.

The cost of logistics for the different options, presented in Figure 8, depends largely on if the alternative can use existing infrastructure or if novel infrastructure will be needed. LOHC is assumed to be able to mainly use existing infrastructure (Pawelec, 2020). For the pure hydrogen alternatives, the low volumetric energy density creates a need for large volumes but in addition neither compressed nor liquefied hydrogen can use existing infrastructure to the same extent as the other options, resulting in a higher logistic cost compared to LOHC and other options (Pawelec, 2020). Compressed hydrogen is in the estimate by Pawelec (2020) found to be the most costly option from the perspective of transportation and storage, Figure 8.

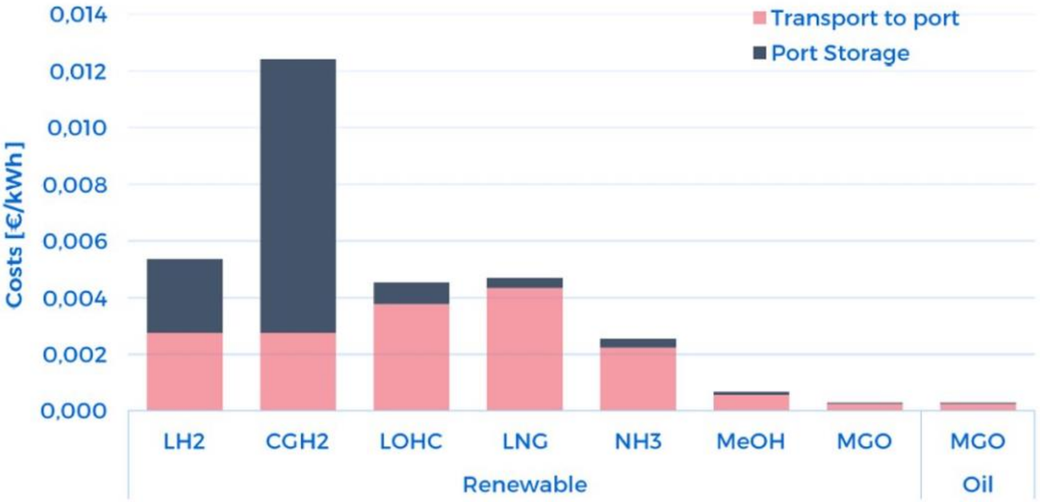


Figure 8. Fuel logistics cost estimates in Pawelec, 2020. Figure collected from Pawelec (2020).

Pawelec (2020) also makes a comparison of the total cost of ownership (TCO) for different categories of shipping. Figure 9 presents the TCO comparison for an inland passenger ferry (with low power requirements and many bunkering opportunities). Compressed hydrogen turns out as the lowest cost option (especially when combined with PEM FC) while LOHC, renewable methanol (electro-methanol) and renewable MGO plus for PEM FC also renewable LNG represent the most costly options.

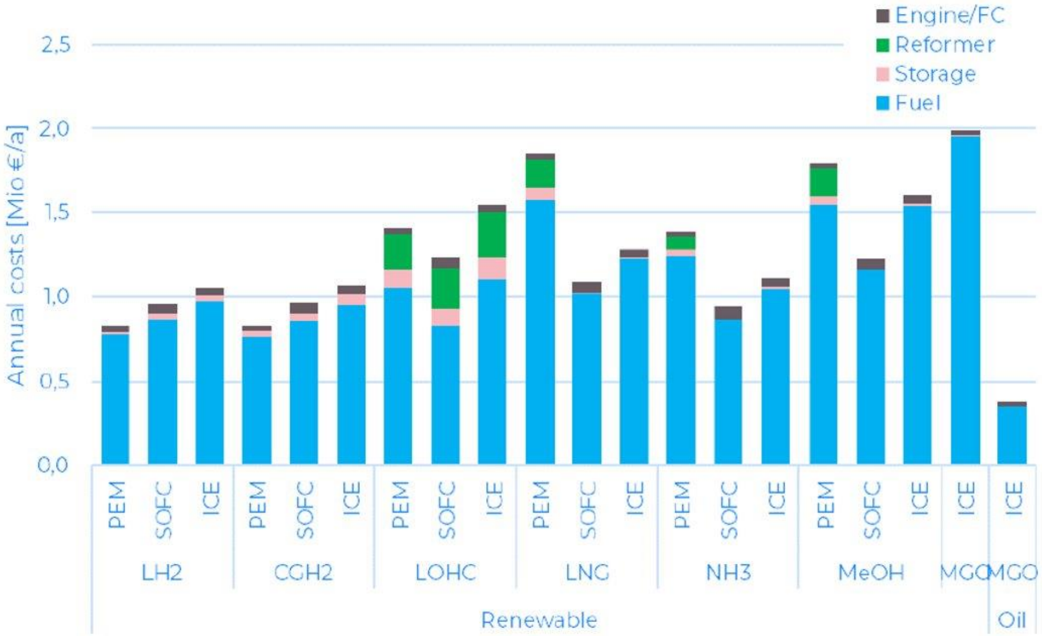


Figure 9. Total costs of ownership comparison for an inland passenger ferry. Figure collected from Pawelec (2020).

Figure 10 presents the same TCO comparison for a Ro-pax vessel (which have a larger power requirement and operates on short routes with frequent refuelling possibilities). In this case the liquified hydrogen cases represent the least costly cases while LOHC together with renewable LNG in PEM FC represent the most costly options.

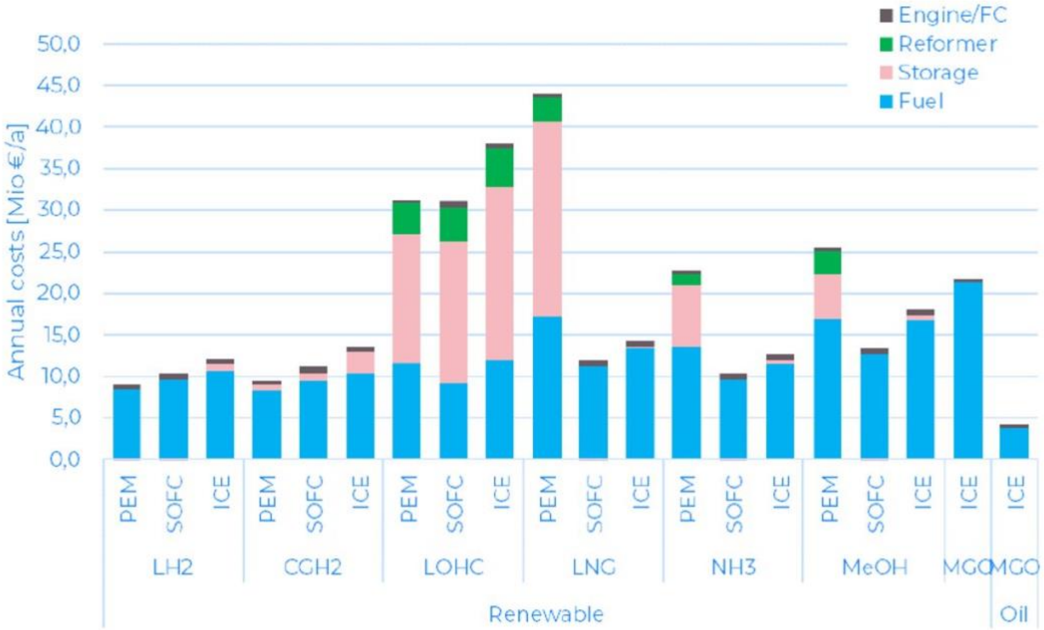
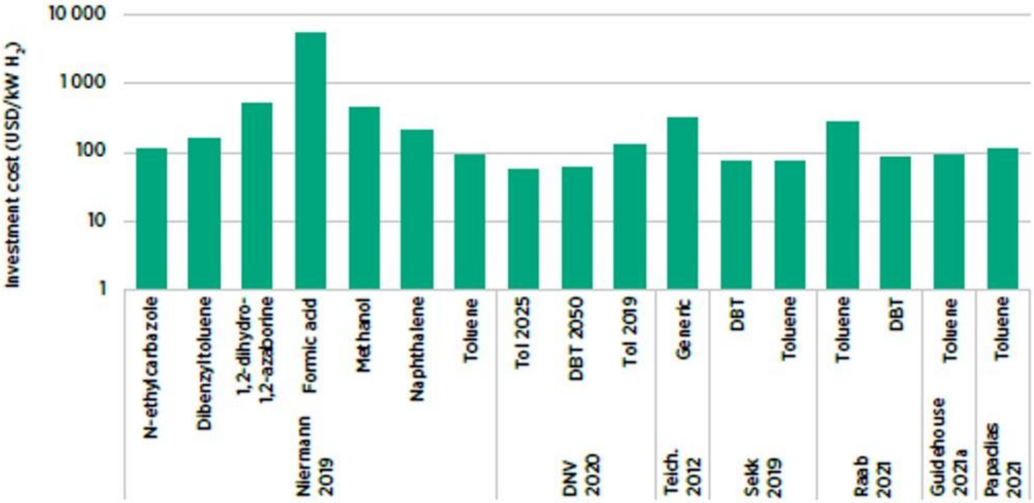


Figure 10. Total costs of ownership comparison for a Ro-pax vessel. Figure collected from Pawelec (2020).

4.2 LOHC for transport of hydrogen with ships in comparison to transport of other hydrogen-based options

IRENA (2022) includes a comparison of different systems for transport of hydrogen and includes some cost estimates linked to LOHC and shipping based on a literature review.

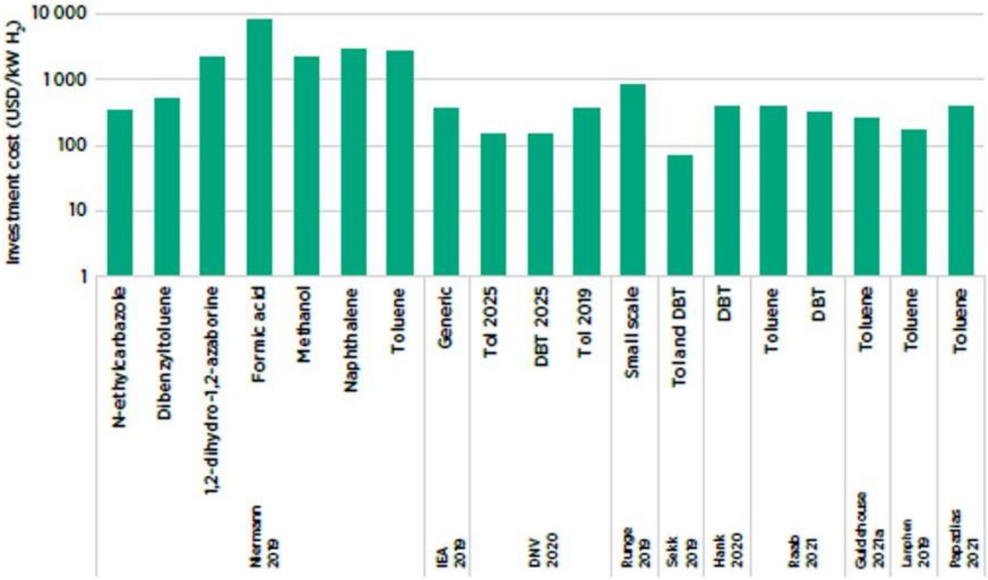
The comparison of cost for LOHC hydrogenation for various LOHC technologies (expressed in specific investment cost) based on the literature review presented in IRENA (2022) is shown in Figure 11. The hydrogenation process, i.e., the process of binding hydrogen to the LOHC is considered to be fairly simple (IRENA, 2022). The cost depends on the productivity of the process which influences the scale of the hydrogenation. Toluene and dibenzyltoluene is included in most of the reviewed studies and end up in the lower cost range when there are other LOHC included. According to IRENA (2022) it can be expected that large-scale LOHC hydrogenation plants would cost about 60-120 USD/kW hydrogen.



Source: DNV (2020); Guidehouse (2021a); Niermann et al. (2019); Papadias, Peng and Ahluwalia (2021); Raab et al. (2021); Sekkesæter (2019); Teichmann, Arlt and Wasserscheid (2012).

Figure 11. Investment cost for hydrogenation for different LOHC. Figure collected from IRENA (2022). Note the scale on the y-axis.

Figure 12 present the comparison of cost for LOHC dehydrogenation for various LOHC technologies (expressed in specific investment cost) based on the literature review presented in IRENA (2022). The cost for dehydrogenation also depends largely on the productivity. The range 100-250 USD/kW hydrogen is mentioned by IRENA (2022) with potentially even lower cost for large-scale plants (which however is not completely in line with the costs presented in the figure).

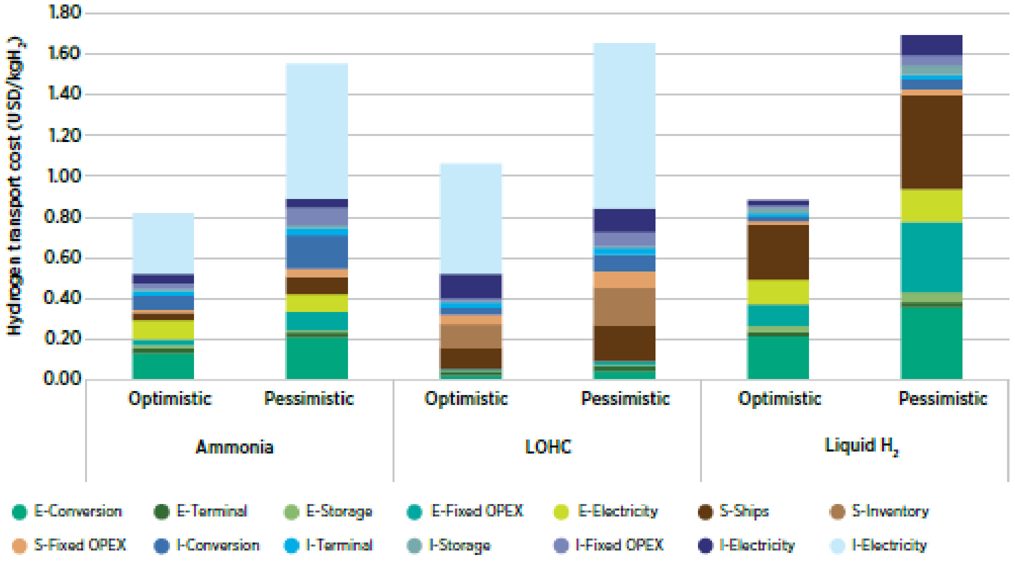


Sources: DNV (2020); Guidehouse (2021a); Hank et al. (2020); IEA (2019a); Lanphen (2019); Niermann et al. (2019); Papadias (2021); Raab et al. (2021); Runge et al. (2019); Sekkesæter (2019).

Figure 12. Investment cost for dehydrogenation for different LOHC. Figure collected from IRENA (2022). Note the scale on the y-axis.

In terms of cost for a LOHC vessel, the review by IRENA (2022) indicates a ship cost of about 800 USD/ton LOHC for capacity above 60 000 deadweight tonnage (the cost decreases with ship size). When transporting hydrogen in the form of LOHC, the carrier represents a relatively large share of the weight (potentially up to 93-95%, according to IRENA, 2022). In hydrogen terms, cryogenic liquid hydrogen ships are estimated to be three times more expensive than LOHC ships and seven to ten times more expensive than ammonia ships (IRENA, 2022)

The total transport cost for LOHC, ammonia and liquid hydrogen by 2050 estimated by IRENA (2022) is presented in Figure 13 (for a yearly flow of 1 MtH2and a distance between ports of 10 000 km). In the optimistic scenario, LOHC represent the most costly option and in the pessimistic scenario LOHC is somewhat less costly than transport of liquified hydrogen but somewhat more costly than ammonia. For LOHC, the cost for the energy needed to recover pure hydrogen from the carrier represents the largest share. The cost of producing hydrogen is not included. There are also sensitivity assessments made in IRENA (2022) where the yearly hydrogen flow and the transport distance are varied. Ammonia represents the lowest cost option for almost all cases. LOHC is only the lowest cost option in the pessimistic scenario in case of low transport distance or low hydrogen flows.



Notes: Costs are for a 1 MtH$_2$/yr export flow and a distance between ports of 10 000 km. Cost components are divided by part of the value chain: E = exporting country; S = ships; I = importing country. Refer to Figure 1.3 for the scope of these costs.

Figure 13. Comparison of total transport cost for hydrogen carriers by 2050. Figure collected from IRENA (2022).

5 Conclusions and further research need

There are several different options for LOHC being assessed with different properties. This partly makes it difficult to draw conclusions about the potential for different LOHC and risks to lead to unfocused research endeavours. Relatively high hydrogen storage capacity, and low safety and environmental impacts are important prerequisites for a LOHC to be feasible. Several physical properties and the reversibility and durability of the LOHC are also important as they influence for example the dehydrogenation temperature, the possibility to use the LOHC in existing infrastructure and the cost. The leading LOHC companies seem mainly to be exploring H0-BT/H12-BT (Hydrogenious Maritime) and TOL/MCH (Chiyoda Corporation) for shipping, respectively. However, these are not the only interesting options. The main initiatives identified for testing LOHC for shipping are described in this report.

Several challenges for using LOHC for shipping remain. These include:

- The LOHC concepts have not been tested in large-scale yet. Thus, they need to be demonstrated and scaled up.
- The influence of the space onboard and lost cargo through the space needed for the LOHC (loaded and unloaded) and for the onboard dehydration unit. The relatively low hydrogen storage capacity of the LOHC implies that considerable amounts of LOHC need to be transported and the carrier also remain when the hydrogen has been unloaded.
- The supply of the heat that is required to recover the hydrogen from the carrier (estimated by IRENA (2022) at about 30-40% of the energy contained).
- The cost for using LOHC as marine fuel. Potential losses when the carrier is recycled also need to be considered although relatively low (about 0.1% per cycle) (IRENA, 2022)
- The safety and environmental impacts of the various LOHC need to be confirmed (there is more knowledge on some than on others). For example, the sustainability of the pathways for the carriers needs to be proven, some may currently partly rely on fossil oil. Toxicity (and associated regulations) is an important factor for the prospects for a LOHC.
- In general, a scale up multiple times of the current production volumes of the chemical used is needed for LOHC to be used in large-scale.

In terms of cost, the comparative study of selected marine fuel options by Pawelec (2020) concludes that for regional shipping compressed hydrogen with PEM fuel cells (for small ships that can be refuelled often or for ships that can accommodate the larger volume) and liquefied hydrogen with PEM fuel cells (for ships with more energy storage requirements) are most interesting from the total cost of ownership assessment performed while LOHC is less interesting. However, cost estimates linked to hydrogen-based options are uncertain and more similar assessments are needed before any firm conclusions about the potential for LOHC versus other hydrogen-based fuel options can be drawn.

Hydrogenious LOHC Maritime identifies offshore service vessels, bulk carriers, and medium ferries as promising candidates for first LOHC demonstration projects (Hydrogenious LOHC Maritime, 2023).

In general, more studies on and testing, and then later potentially also demonstration of LOHC for shipping, is needed before any firm conclusions about the potential for LOHC for shipping (as fuel and for transport) can be drawn. This includes how the heat needed for the dehydrogenation unit should be supplied. For example, it could be interesting to map the possibility to use excess heat at various relevant locations for dehydrogenation of LOHC.

The comparisons of LOHC as marine fuel made in literature indicate that other fuel options might be more interesting for the shipping segments assessed. However, LOHC might be an interesting option for certain shipping applications. In addition, the potential for LOHC as marine fuel depend on which fuels that are included in the comparison. LOHC have larger potential if compared to compressed and liquefied hydrogen but more limited if compared to e.g., methanol and ammonia. As for all hydrogen-based options there are challenges that need to be addressed. The actual potential is of course also affected by the development of other hydrogen-based alternatives.

As indicated for example, studies comparing the environmental impact of LOHC compared to other hydrogen-based options (including e.g., toxicity), but also other alternative marine fuels are needed. In general, more research on different LOHC and their possibilities and how to integrate the concept onboard are needed. More detailed assessment of the possibility to use existing infrastructure in ports and terminals and for onboard storage is also needed. For example, case studies for the potential to produce and/or store and handle LOHC in specific ports. How policies handle and are proposed to handle different hydrogen-based energy carriers is also an interesting issue.

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Appendix A LOHC properties

Table ***Error! No text of specified style in document.****-1. Examples of currently in use and/or promising LOHCs and their properties.*

LOHC system	Common areas of usage	Hydrogen storage capacity [wt.%]	Melting point [°C]		Boiling point [°C]		Safety and environmental properties
			H_2-rich	H_2-lean	H_2-rich	H_2-lean	
BZ/CHE	BZ is used to make other chemicals to make plastics, resins, nylons and synthetic fibers (Aakko-Saksa, et al, 2018).	7.2 (Aakko-Saksa, et al, 2018, Abdin et al 2021)	7 (Aakko-Saksa, et al, 2018)	5.5 (Aakko-Saksa, et al, 2018)	81 (Aakko-Saksa, et al, 2018)	80 (Aakko-Saksa, et al, 2018)	High toxicity (BZ), high flammability (CHE). Known human carcinogen, presumed to cause germ cell mutagenicity. Restricted used under Regulation (EC) No. 1907/2006 (Aakko-Saksa, et al, 2018, Markiewicz et al, 2019).
TOL/MCH	TOL is used in oil refining, manufacturing of paints, lacquers, explosives, and glues (US EPA, 1992).	6.2 (Kwak et al, 2021) [1]	-127 (Aakko-Saksa, et al, 2018, Kwak et al, 2021)	-95 (Aakko-Saksa, et al, 2018, Kwak et al, 2021)	101 (Aakko-Saksa, et al, 2018, Kwak et al, 2021)	111 (Aakko-Saksa, et al, 2018, Kwak et al, 2021)	High flammability, explosive mixture can be formed at room temperature. Possible leakage of MCH can be directly harmful if inhaled. Classified as presumed to cause reproductive toxicity. Restricted used under Regulation (EC) No. 1907/2006 (Aakko-Saksa, et al, 2018, Markiewicz et al, 2019, Kwak et al, 2021).
DBT/H18-DBT	DBT – industrial applications, mainly used as a heat transfer oil (Abdin et al, 2021).	6.2-6.29 (Aakko-Saksa, et al, 2018, Abdin et al, 2021, Kwak et al, 2021)	58 to -50 (Aakko-Saksa, et al, 2018, Kwak et al, 2021)	-39 to -34 (Aakko-Saksa, et al, 2018)	371 (Kwak et al, 2021)	390 (Cho et al, 2021, Aakko-Saksa, et al, 2018, Kwak	Low toxicity and thermal stability. Not classified as dangerous goods, can be stored, and transported in the existing infrastructure for fossil fuels (Aakko-Saksa, et al, 2018, Abdin et al, 2021, HyStoc, 2018).

						et al, 2021)	
H0-BT/H12-BT	BT – industrial applications, mainly used as a heat transfer oil (Abdin et al, 2021) [2].BT – industrial applications, mainly used as a heat transfer oil (Abdin et al, 2021).	6.2 (Cho et al, 2021, Markiewicz et al, 2019)		-30 (Cho et al, 2021, Markiewicz et al, 2019)	270 (Rao et al, 2020)	280 (Cho et al, 2021, Markiewicz et al, 2019)	Low toxicity and eco-toxicity (Markiewicz et al, 2019).
NEC/H12-NEC	NEC - used as an additive/modifier in photorefractive composite (Chemical Book, 2022).	5.8 (Aakko-Saksa, et al, 2018, Abdin et al, 2021)	85 (Aakko-Saksa, et al, 2018)	68-69 (Aakko-Saksa, et al, 2018, Abdin et al, 2021)	281 (Aakko-Saksa, et al, 2018)	378 (Aakko-Saksa, et al, 2018)	Low flammability. NEC biodegrades fast. Potential concerns for bioaccumulation for H8-NEC and it is not biodegradable (Aakko-Saksa, et al, 2018, Markiewicz et al, 2015).
H0-BP/BC	Biphenyl - organic syntheses, heat transfer fluids, food preservatives (US EPA, 1999)	6.9-7.3 (Cho et al, 2021, Aakko-Saksa, et al, 2018, Han et al, 2019)	4 (Aakko-Saksa, et al, 2018)	68-70 (Cho et al, 2021, Aakko-Saksa, et al, 2018)	228 (Aakko-Saksa, et al, 2018)	255 (Cho et al, 2021, Aakko-Saksa, et al, 2018)	High thermal stability. Solid at room temperature (Cho et al, 2021, Aakko-Saksa, et al, 2018).
H0-DPM/DCM		6.66 (Jander et al, 2022)	-19 (Han et al, 2019)	22-25 (Cho et al, 2021)	248-250 (Han et al, 2019)	264-266 (Cho et al, 2021)	Relatively low viscosity, high flash point and boiling point. High toxicity for aquatic life (Jander et al, 2022).

Quinoline/THQ or DHQ	Quinoline is mainly used as an intermediate in the manufacture of other products (US EPA, 1992) [3].	7.2 (Aakko-Saksa, et al, 2018)	48.75 (Aakko-Saksa, et al, 2018)	-15 (Aakko-Saksa, et al, 2018)	200-205 (Aakko-Saksa, et al, 2018)	237 (Aakko-Saksa, et al, 2018)	Colorless, hygroscopic and degradable liquid (Aakko-Saksa, et al, 2018) [4].Colorless, hygroscopic and degradable liquid (Aakko-Saksa, et al, 2018) [4].

Benzene/cyclohexane (BZ/CHE),
Toluene/methylcyclohexane (TOL/MCH),
Naphthalene/decalin (NAP/DEC),
N-ethyl carbazole/perhydro-N-ethylcarbazole (NEC/H12-NEC),
Dibenzyl toluene/perhydro-dibenzyl toluene (DBT/H18-DBT),
(Mono)benzyltoluene/perhydrobenzyltoluene (H0-BT/H12-BT),
Biphenyl/bicyclohexyl (H0-BP/BC),
Diphenylmethane/dicyclohexylmethane (H0-DPM/DCM)

Appendix B Hydrogenation conditions for LOHC systems

*Table **Error! No text of specified style in document.**-1. Hydrogenation conditions for LOHC systems.*

LOHC system	Enthalphy exchange [kJ/mol H2]	Catalysts	Temperature [°C]	Pressure	Ref.
BZ/CHE	68.6	Raney-Ni Ru $[Rh(5\text{-}C_5Me_5)Cl_2]_2$	95-125 90 50	20-40 atm 60 bar 50 bar	(Aakko-Saksa et al, 2018)
TOL/MCH	68.3 (Hurskainen, 2019)	Ni and Pd-catalyst supported on Si-Al	50-100	10-50 bar	(Aakko-Saksa et al, 2018)
DBT/H18-DBT	65 (Hurskainen, 2019)	0.25 mol% Ru/Al_2O_3 Pt group metals Rh and Ru	150 140 <180	50 bar - -	Aakko-Saksa et al, 2018 Abdin et al, 2021 Cho et al, 2021
H0-BT/H12-BT	63.5 (Rao et al, 2020)	0.25 mol% Ru/Al_2O_3	150 (Cho et al, 2021) about 250 (Hydrogenous LOHC Maritime, 2023)	50 bar (Cho et al, 2021) 25-50 bar (Hydrogenous LOHC Maritime, 2023)	(Aakko-Saksa et al, 2018; Hydrogenous LOHC Maritime, 2023)
NEC/H12-NEC	50-53 (Abdin et al, 2021, Hurskainen, 2019)	Pd catalyst 1.0 $gRu/g\text{-}Al_2O_3$	160 140	72 atm 60 bar	Aakko-Saksa, 2018

		Pd2Ru@SiCN	110	20 bar	
H12-BPDM/BC and DCM		Ru/Al_2O_3	80	40 bar	Cho et al, 2021
		Ru/Al_2O_3	120	50 bar	Cho et al, 2021
Quinoline/DHQ	61.9	Rh/AlO(OH)	125	8 bar	Aakko-Saksa et al, 2018
Methylquinolines/DHQ		Ru nanoparticles supported on glucose-derived carbon spheres (Ru/CSP)	120	20 bar	
Quinoline/THQ		0.5mol% Ir-3 (aq sol.)	90	5 bar	Cho et al, 2021

Appendix C Dehydrogenation conditions

*Table **Error! No text of specified style in document.**-1. Dehydrogenation conditions of LOHC systems.*

LOHC system	Enthalphy exchange [kJ/mol H2]	Catalysts	Temperature [°C]	Pressure	Refs.
BZ/CHE	68.6 (Aakko-Saksa, 2018) [4]68.6 (Aakko-Saksa, 2018) [4]	Pt, Cu promotor, SiO_2 support	147-377		(Jo et al, 2022)
		Pt, Re promotor, AC support	195		
		Pt, Sn promotor, MgAl2O4 support	550		
TOL/MCH	68.3 (Hurskainen, 2019)	Pt, CB support	300	-	(Jo et al, 2022)
		Pt, T1O2 support	175	-	
		Ni, Zn promotor, Al2O3 support	300-360	-	
DBT/H18-DBT	65 (Hurskainen, 2019)	Pt/C (1 wt%)	310	-	(Cho et al, 2021)
		Pt, Al_2O_3 support	270		(Jo et al, 2022)
		0.5Pt/γ-Al_2O_3, 10 ml	280-340	1 bar	(Kwak et al, 2021)
H0-BT/H12-BT	63.5 (Rao et al, 2020)	Pt/C with 1% metal loading	270 (Cho et al, 2021) 300 (Hydrogenous LOHC Maritime, 2023)	1-3 bar (Hydrogenous LOHC Maritime, 2023)	(Aakko-Saksa, 2018), (Hydrogenous LOHC Maritime, 2023)
NEC/H12-NEC	50-53 (Abdin et al, 2021, Hurskainen, 2019) [2, 5]	Pd on alumina (5 wt%)	180	Normal pressure	(Aakko-Saksa, 2018)
		Pd or Pt catalysts on alumina, silica or carbon	180-260	Amb. Pressure	

		Pd, SiO2 support	170		(Jo et al, 2022)
H12-BPDM/BC and DCM		Pd/C pellet catalysts	340	-	(Cho et al 2021)
		0.5Pt/γ-Al2O3, 10 ml	280-340	1 bar	(Kwak et al, 2021)
		0.5Pt/Al2O3 (γ,θ,α,SiO2-Al2O3), 2 g	280-340	1 bar	
Quinoline/DHQ	61.9	Ni-NiCrO and benzene as solvent	350	-	(Aakko-Saksa, 2018)

Lighthouse samlar industri, samhälle, akademi och institut i triple helix-samverkan för att stärka Sveriges maritima konkurrenskraft genom forskning, utveckling och innovation. Som en del i arbetet för en hållbar maritim sektor initierar och koordinerar Lighthouse relevant forskning och innovation som utgår från industrin och samhällets behov.

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