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Meeting Hydrogen Dynamic Demand for on Board Applications Through a Liquid Organic Hydrogen Carrier

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Abstract. The need to drastically reduce CO_2 emissions is leading to the transformation of current carbon-based energy system into a more sustainable renewables-based one. Along this path, Hydrogen is a promising carbon-free energy vector when produced from renewable sources, but its storage and transport are challenging due to low volumetric energy density and safety concerns. Recent scientific advancements in handling hydrogen chemically bound to a Liquid Organic Hydrogen Carrier (LOHC) support the prospect of establishing a hydrogen economy, potentially avoiding to deal with large amounts of elemental hydrogen, in its liquid cryogenic or compressed gaseous forms. Indeed, hydrogen is stored in the dibenzyltoluene/perhydrodibenzyltoluene system through chemisorption and can be released as needed via a catalytic reaction. This paper describes the development of an innovative system setup that allows the generation of hydrogen on-demand to follow dynamically the power supply required by the electric system of a cruise ship. Indeed, the LOHC system has been designed to meet the power demand for a short transit, maneuvering and berthing, ensuring that the hotel load is fully powered by fuel cells, thereby achieving zero emissions while in port. This prevents the hydrogen and energy losses associated with traditional storage methods, allowing for a safer and more efficient utilization of hydrogen in the maritime sector.

Keywords. Dynamic, LOHC, Maritime, Hydrogen, Cruise

1. Introduction

The maritime industry is increasingly focusing on sustainability and renewable energy solutions to address the pressing global issue of climate change. While the former goal is commonly met by using well-established methodologies, such as life cycle assessment (1,2), the latter has been investigated using various approaches, including low-carbon fuels(3) and hybrid solutions.(4) Among the various sustainable energy vectors, elemental hydrogen (H_2) has emerged as a particularly promising candidate due to its high gravimetric energy density and potential for zero-emission operations.

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However, significant technical challenges related to the storage, transport, and safe handling of elemental hydrogen have hindered its widespread adoption. In fact, hydrogen is highly flammable, possesses a low volumetric density, and requires high-pressure or cryogenic conditions to be stored effectively, making its integration into existing maritime infrastructure complex and expensive.(5)

In response to these challenges, Liquid Organic Hydrogen Carriers (LOHC) technology has recently gained increasing attention. LOHC systems offer a practical and efficient method for hydrogen storage and transportation by chemically bonding hydrogen within stable organic liquid compounds.(6) These compounds undergo reversible catalytic reactions, where hydrogenation is employed for storing hydrogen and dehydrogenation is used for releasing hydrogen on demand. These subsequent processes enable a safe transportation and storage of hydrogen under ambient temperature and pressure conditions. The compatibility of LOHC with current liquid fuel infrastructure provides a distinct advantage, facilitating rapid deployment and integration within existing logistics and operational frameworks.

Among various LOHC materials studied, dibenzyltoluene (DBT) and its hydrogenated counterpart perhydro dibenzyltoluene (DBTH) stand out thanks to their chemical stability, high hydrogen storage capacity (up to 6.2 wt%), low toxicity, and compatibility with standard marine vessel materials. These properties make DBT-based LOHC systems particularly suitable for maritime applications, including dynamic hydrogen generation onboard vessels.(7)

This work specifically investigates the technical and operational feasibility of DBT-based LOHC systems for dynamic onboard hydrogen generation, addressing several critical aspects, including process optimization, reactor design and sizing, thermal management, and overall system integration with Proton Exchange Membrane (PEM) fuel cells. The comparison between LOHCs and other storage technologies, such as liquefied or compressed hydrogen, has been widely addressed in the literature, with several studies focusing specifically on their use in maritime applications and port infrastructure.(8)

Ultimately, this research aims to support the maritime industry's transition toward sustainable operations by demonstrating the technical viability, safety, and economic feasibility of LOHC-based hydrogen systems. Through this comprehensive evaluation, this work contributes significantly to overcoming existing barriers to hydrogen adoption in marine environments, paving the way for more widespread implementation of clean energy solutions within the maritime sector.

2. Materials and methods

This section outlines the selection criteria for identifying the most suitable LOHC and the simulation framework used to evaluate reactor performance and system integration in a maritime context.

2.1. Selection of LOHC for Maritime Applications

The criteria for selecting suitable LOHCs for marine applications include safety, environmental compatibility, energy efficiency, transported energy density (kWh/m^3), operating conditions for hydrogen release, quality of hydrogen produced, stability of the hydrogen carrier, availability on the market, production cost, and compatibility with existing logistic structures.

Among the various LOHC systems evaluated for hydrogen storage, compounds such as toluene, benzyltoluene, and dibenzyltoluene are the most prominent, due to their favorable thermophysical properties and liquid phase behavior.

Since material compatibility and chemical safety are critical in maritime environments, the toluene/methylcyclohexane (TOL/MCH) system, though historically the first studied LOHC pair,(9) presents significant drawbacks, such as low flash point, high dehydrogenation temperatures (~320°C at 1 bar), and gaseous operation under process conditions requiring complex hydrogen purification. Moreover, toluene is subject to regulatory restrictions due to its toxicity.

In contrast, the dibenzyltoluene/perhydro-dibenzyltoluene (DBT/DBTH) system, as reported in Figure 1a), offers higher hydrogen capacity (6.2 wt%), operates entirely in the liquid phase, and ensures easier hydrogen purification and improved safety features. Its chemical stability, lower toxicity, and compatibility with shipbuilding materials make it a more viable candidate for marine LOHC applications.

DBT and its hydrogenated form are liquids over a wide temperature range, offering high hydrogen density, stability over multiple cycles, and a low-toxicity profile. Their diesel-like viscosity enables safe handling and use with existing maritime infrastructure, while the absence of hydrogen losses allows for long-term storage. For all these reasons the DBT/DBTH system has been chosen for onboard application of this technology.

2.2. Onboard application of LOHC

A typical LOHC-based energy system comprises four key components: (1) a dehydrogenation unit, (2) onboard storage tanks, (3) a fuel cell system for power conversion, and (4) a hydrogenation facility for LOHC recharging. The primary focus of this study is on the onboard integration of components 1 through 3, particularly the onboard dehydrogenation system installed on the cruise vessel, responsible for supplying hydrogen to the PEM fuel cells for electricity generation. The elements involved in the overall LOHC supply chain are reported in Figure 1b).

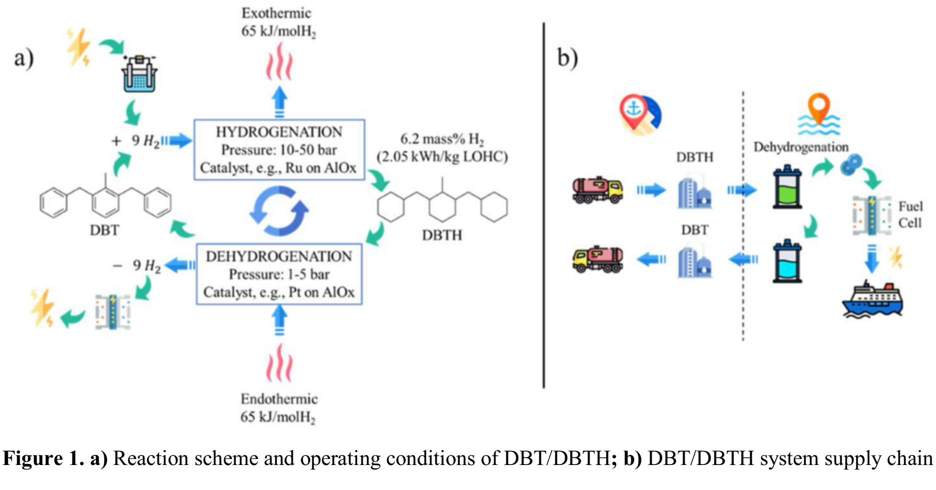

Figure 1. a) Reaction scheme and operating conditions of DBT/DBTH; **b)** DBT/DBTH system supply chain

Hydrogen-lean and hydrogen-rich LOHC are stored in dedicated onboard tanks and are respectively offloaded and filled with fresh products during berthing periods. The transfer of LOHC to and from the shore-based hydrogenation plant is assumed to occur via tanker trucks, or with potential LOHC pipeline to be developed in the future.

Delving into the main focus of this study, Figure 2 shows the Process Flow Diagram (PFD) of a single-stage Dynamic Hydrogen Releaser (DHR) reactor, which forms part of the dehydrogenation system, as developed using Aspen Plus V14 software.

Starting from reservoir V1, DBTH in liquid form at ambient temperature is pumped by P1 into heat exchanger E1. This exchanger preheats the DBTH stream while simultaneously condensing heavier components from the high-temperature gaseous hydrogen stream (stream 7) exiting the reaction system. A second heat exchanger, E3, further recovers reaction heat by exchanging sensible heat from the reacted DBT stream. After passing through these recovery stages, the temperature of the DBTH (stream 4) reaches approximately 270 °C before entering the reaction section in vessel V3.

The reaction system consists of vessel V3, which functions as a liquid accumulator; pump P2, which circulates the reacting fluid; heat exchanger E4, which increase the reagents temperature; and reactor R1, which contains the catalyst. The purpose of recirculating the reacting DBTH is to enhance liquid-solid mass transfer within R1, thereby increasing the dehydrogenation reaction rate.

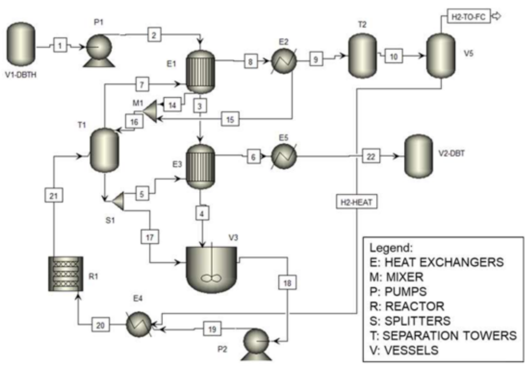

Figure 2. PFD of DBT/DBTH reaction system

Fresh DBTH feed is introduced into V3 and mixed with the recirculated stream (stream 17). The combined stream (stream 18) is then directed through heat exchanger E4 to raise its temperature above the target reaction temperature (310 °C in this case).

Stream 20 then enters the reactor R1, where dehydrogenation takes place and hydrogen is released. The dynamic behavior of the reactor arises from its ability to modulate the hydrogen flowrate in response to the fuel cell's demand, enabled by the adjustable flowrate of DBTH from the accumulation vessel V3. The reactor design and the kinetic parameters used in the present simulation model are reported in the paper published by Delogu et al. (10). The resulting stream (stream 21), a gas-liquid mixture at around 310 °C, contains DBT and partially dehydrogenated intermediates in both phases due to their significant vapor pressures at this temperature. This stream is sent to separation tower T1, along with condensed vapors from E1 and E2. The liquid phase is returned to V3 via stream 17, while the vapor phase (stream 7) proceeds to a series of condensers and then to tower T3 for separation of light impurities generated during the reaction.

Finally, the purified 99.99 %wt. hydrogen stream (stream 11) is split: one part is supplied to external users, such as fuel cells, and the other is directed to the burner feeding heat exchanger E4, providing the thermal energy required for the endothermic reaction.

Since the dehydrogenation reaction is strongly endothermic, the heat required for hydrogen release and for starting the reaction chain can be supplied through two main strategies, i.e., combustion of a portion of the produced hydrogen or thermal integration with the fuel cell system. The former depends on the LOHC type and, assuming ideal thermal efficiency, may consume up to 30% of the generated hydrogen; the latter is particularly suitable with PEM fuel cells, which are favored for maritime applications due to their dynamic response. However, this requires that the dehydrogenation process shall operate at the lower temperature range typical of PEMFC systems. In parallel with thermal management, catalysis plays a fundamental role in enabling both the hydrogenation and dehydrogenation steps of the LOHC cycle. Efficient hydrogen release from rich LOHCs, as well as hydrogen fixation into lean LOHCs, depends on the presence of active and stable catalysts. Transition metals such as nickel, ruthenium, and platinum have proven particularly effective for hydrogenation processes. Although catalyst development is not the central focus of this study, a brief overview of commercially available catalytic systems is included for context.

3. Results and discussion

The reference case study considers the energy demands of a small cruise vessel (60,000 GRT) operating under "zero emissions" conditions during port operations, i.e., arrival, mooring, and departure. In this scenario, all onboard power is supplied by fuel cells fed with hydrogen generated via an onboard dehydrogenation system. During each weekly cruise, which includes two berthing periods, hydrogen-lean and hydrogen-rich LOHC are respectively loaded and offloaded from dedicated storage tanks integrated into the ship's infrastructure, enabling continuous energy supply while at berth.

The energy and hydrogen demands for port operations are reported in the following Table 1.

Table 1. Energy and hydrogen demand for the different operating phases

Phase	Unit	Transit in	Manoeuvre	Mooring at berth	Manoeuvre	Transit out
Duration	h	2	1.5	11	1.5	2
Electrical Power	MWe	6	4.7	3.3	4.7	6
Thermal Power	MWth	13.5	10.6	7.5	10.6	13.5
H_2 required	kg/h	403	316	222	316	403
Consumption	kg	806	474	2440	474	806

A quantified flowsheet was developed to support the sizing of ancillary equipment, such as heat exchangers, vessels, and pumps, and to estimate the overall system footprint. Two configurations were considered: the first, fully quantified, represents a system with a single reactor; the second features three reactors in series and is described and quantified solely in terms of mass and heat balances.

The single-stage DHR system presents several critical issues. In fact, as indicated in Table 2, the percentage of hydrogen effectively released relative to the amount stored in the fresh carrier is relatively low. While this could be improved by increasing the amount of catalyst, the associated investment costs are significant.

Although the unreacted hydrogen is not lost, since it is recycled and subsequently reduces the hydrogen demand for re-hydrogenating DBT to DBTH, the low hydrogen utilization percentage leads to increased storage requirements for the carrier. The total consumption of DBTH is estimated at 153 tons, necessitating approximately 170 m³ for storing the hydrogenated DBTH and 160 m³ for the spent DBT.

Table 2. Outcomes of single-stage DHR system

Quantity	Unit	Mooring	Manoeuvre	Transit
Useful energy produced	MWth	7.5	10.6	13.5
Working times	h	11.0	1.5	2.0
Total power produced	MW	12.2	17.3	22.0
Useful H_2 flowrate	kgH_2/h	225.1	318.1	405.2
Total H_2 flowrate	kgH_2/h	366.5	518.0	659.7
DBTH feed flowrate	tons/h	8.20	13.74	21.29
H_2 used / H_2 stored	%	71.5%	60.4%	49.6%
Feed rates	kmolDBTH/h	28.24	47.29	73.28
H_2 partial pressure	bar	1.25	1.25	1.25
Catalyst mass	kg	7000	7000	7000
Catalyst concentration	kg/m3	500	500	500
Liquid volume	m3	14	14	14

The estimated sizes of the plant components are 14 m³ for the reactor and 4 m³ for the vessel, which occupy the majority of the system volume, while the heat exchangers are relatively compact. Overall, a total volume of 25–30 m³ can be considered as a reasonable estimate for evaluating space requirements.

To increase the percentage of hydrogen utilized while maintaining the same total amount of catalyst, multiple dehydrogenation units must be arranged in series. Figure 3 presents a block diagram of this configuration, which employs a three-stage dehydrogenation system. Each DHR stage includes the set of equipment illustrated in Figure 2.

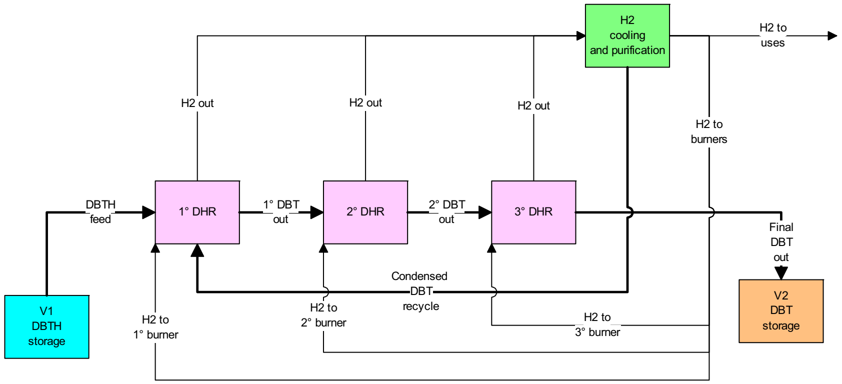

Figure 3. Block diagram of the three-stage dehydrogenation system

The plant configuration is understandably more complex than that of the single-stage DHR system. However, several factors help balance this added complexity. The reactors used in the multi-stage setup are smaller, with each occupying only a third of the volume required in the single-stage system. While the condensers and heat exchangers maintain the same dimensions, only one set of preheating and cooling exchangers is needed, unlike the single-stage design which requires separate units. Additionally, the purification section remains unchanged, and the storage tanks for DBTH and DBT are reduced to about two-thirds of the volume used in the single-stage configuration.

As a result, the overall space required for the multi-stage system remains comparable to that of the simpler, single-reactor layout. To provide a preliminary estimate of the system's spatial footprint, the installation should occupy an area of approximately 15 by 10 meters, with a height requirement of around 3 meters, depending mainly on the size of the reactors.

Table 3 summarizes the input and output values for a complete trip using both system configurations. The data are largely comparable, with the main differences being the amount of DBTH fed and the percentage of hydrogen released relative to the initial amount stored.

Table 3. Comparison between single-stage DHR and 3-stages DHR

Quantity	Unit	Cruise totals with 1 stage reactor	Cruise totals with 3 stages reactor
Total energy produced	GJ	735	675
Useful hydrogen produced	kgH_2	3764	3751
Total hydrogen released	kgH_2	6128	5628
DBTH fed	Ton DBTH	153	109
H_2 used / H_2 stored	%	63.9%	82.8%
DBTH stored	kmoles DBTH	528	375

While the investment cost of the three-stage DHR plant is understandably higher than that of the single-stage system, its operating costs are lower, giving that the primary cost component, i.e., the catalyst, remains unchanged. However, there is potential to reduce the required catalyst quantity through integration with external energy storage systems, such as batteries, offering an opportunity to optimize overall system efficiency and cost-effectiveness.

4. Conclusion

This study has demonstrated the technical feasibility of implementing Liquid Organic Hydrogen Carrier (LOHC) systems based on the dibenzyltoluene/perhydro-dibenzyltoluene (DBT/DBTH) system for dynamic, on-demand hydrogen generation onboard cruise vessels. The proposed system enables zero-emission operations during critical port-related phases such as transit, maneuvering, and mooring, by supplying hydrogen to Proton Exchange Membrane (PEM) fuel cells with a high degree of operational responsiveness and safety.

Two system configurations were analyzed: a single-stage dehydrogenation reactor and a three-stage reactor setup. While the single-stage configuration offers simplicity, it exhibits lower hydrogen utilization efficiency and requires larger LOHC storage volumes. In contrast, the three-stage setup achieves significantly higher hydrogen utilization with a comparable overall system footprint and reduced LOHC consumption, despite a modest increase in system complexity and capital investment.

The integration of the DBT/DBTH-based LOHC system with PEM fuel cells provides a robust solution for low-temperature hydrogen delivery and dynamic response capabilities, making it particularly well-suited for maritime applications. The closed-loop management of hydrogen-rich and hydrogen-lean carriers allows for safe handling, long-term storage, and compatibility with existing fuel logistics, while minimizing hydrogen losses and mitigating safety risks associated with compressed or cryogenic hydrogen.

Acknowledgments

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