LIQUID ORGANIC HYDROGEN CARRIERS – A TECHNOLOGY TO OVERCOME COMMON RISKS OF HYDROGEN STORAGE

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ABSTRACT

In transport and storage of hydrogen the risks are mainly seen in its volatile nature, its ability to form explosive mixtures with air and the harsh conditions (high pressure or low temperature) for efficient storage. The concept of Liquid Organic Hydrogen Carriers (LOHC) offers a technology to overcome the above mentioned threats.

The present submission describes the basics of the LOHC technology. It contains a comparison of a selection of common LOHC materials with a view on physical properties. The advantages of a low viscosity at low temperatures and a high flash point are expressed. LOHCs are also discussed as a concept to import large amounts of energy/hydrogen. A closer look is taken on the environmental and safety aspects of hydrogen storage in LOHCs since here the main differences to pressurized and cryo storage of hydrogen can be found.

The aim of this paper is to provide an overview of the principles of the LOHC technology, the different LOHC materials and their risks and opportunities, and an impression of a large scale scenario on the basis of the LOHC technology.

1.0 INTRODUCTION

Since the European Commission decided to reach carbon neutrality by 2050 many member states but also other political entities have launched their own agendas on the energy turn around and CO2 emissions. One common building block of a carbon neutral industry is the energy vector hydrogen. In 2017 the Hydrogen Council published a forecast that the hydrogen demand will increase tenfold by the year 2050 with transportation being one of the fastest growing sectors.

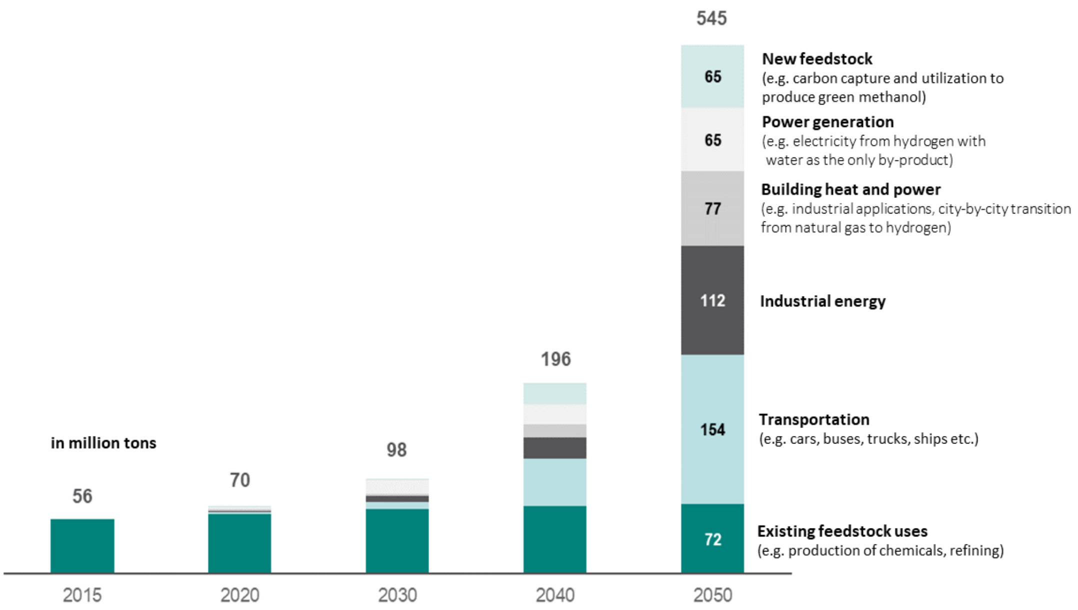


Figure 1. Forecast of the hydrogen demand by sectors [1]

It is obvious that this massive increase in the usage of hydrogen requires a safe and efficient storage and transportation infrastructure to handle these amounts. Compressed gas hydrogen storage has its limitations in storage density and efficiency, besides its limited acceptance in the public (e.g. [2]). Liquified hydrogen excels in storage density but lacks the infrastructure, at least in Europe.

The interest in chemical storage of hydrogen has grown in the last years since the shortfalls of compressed gas and liquified hydrogen storage have become evident for the huge market development ahead of us. Chemical storage of hydrogen requires the transformation of gaseous hydrogen into a suitable carrier molecule, usually forming a liquid. This has the advantage of large storage densities, usually low or no pressure requirements and a lower potential for the formation of explosive atmospheres. This paper will focus on the group of Liquid Organic Hydrogen Carriers (LOHC) since here, also the great advantage of a reusability of oil infrastructures as hydrogen infrastructures comes into place.

2.0 LOHC TECHNOLOGY

2.1 Basics

The basic principle of Liquid Organic Hydrogen Carriers is the application of an organic molecule that has the ability to chemically bind hydrogen to its structure. Thus, unsaturated hydrocarbons that have a high density of double bonds are in the focus of interest.

With these molecules hydrogenation and dehydrogenation reactions can be carried out, following the principal equation, meaning that all hydrogen atoms are covalently bonded to the carrier molecule:

$$\text{LOHC} + nH_2 \leftrightarrow \text{LOHC-2nH}$$

The reactions take place at elevated temperatures and require a catalyst for increased performance. The hydrogenation reaction is usually exothermic, meaning that heat is generated in the course of the reaction. Whereas the dehydrogenation reaction is endothermic, thus, requiring heat to release gaseous hydrogen from the carrier liquid. These reactions can be repeated numerous times leading to the LOHC-cycle depicted in Figure 2 with the example of benzyltoluene as LOHC.

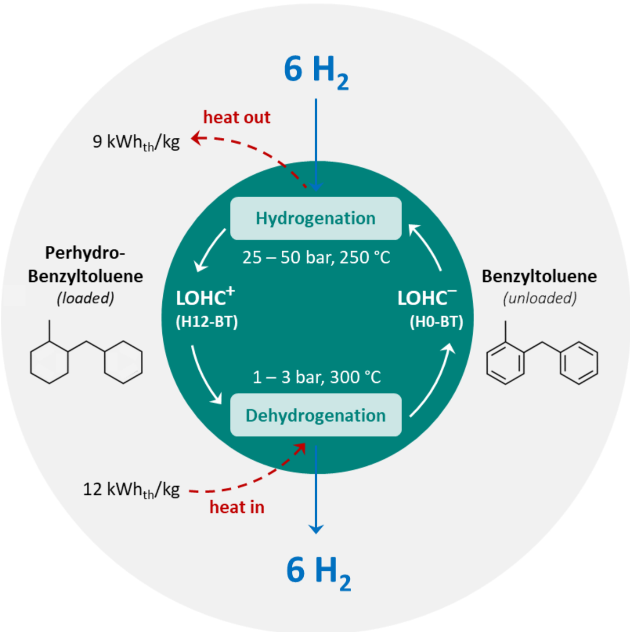


Figure 2. Hydrogen storage and release cycle of the LOHC technology

Balance wise this reaction cycle is energy neutral. In Figure 2 the technical values are given, meaning that the hydrogenation yields 9 kWh/kg_{H2} of usable heat, whereas the dehydrogenation requires 12 kWh/kg_{H2}. The reaction itself has an enthalpy of approx. 10 kWh/kg. It is obvious that in a transport scenario, where hydrogenation and dehydrogenation take place at different sites, heat integration is a key issue of an efficient hydrogen transport cycle.

A key safety issue of this reaction scheme is that the release of hydrogen only takes place when both, heat and a suitable catalyst are present. The lack of one of the two leads to a cease of the hydrogen production. This greatly eases hazard control and diminishes the explosion hazard during transport and in case of fires.

2.2 LOHC materials

As said before, numerous molecules can be considered as hydrogen carriers. On the one hand, there are solid substances like aminoboranes or metal hydrides. On the other hand, one can name mostly organic liquids. The liquids itself divide into liquids that are formed during synthesis with hydrogen, e.g. ammonia and methanol, and liquids that form a carrier which is loaded and unloaded with hydrogen. Examples of the latter ones are shown in Table 1.

Table 1. Comparison of physical properties of different LOHCs

Parameter		Benzyl-toluene	N-Ethyl-Carbazole	Toluene	Diphenylmethane
Storage density	Volumetric / MWh/m^3	1.8	1.9	1.6	2.0
	Gravimetric / wt%	6.2	5.8	6.2	6.9
Melting / Boiling point / °C		-70 / 280	69 / 348	-95 / 111	24 / 264
Flash point / °C		137	- - -	6	127

Table 1 shows a comparison of different liquid organic hydrogen carriers. The volumetric storage density is given in MWh/m^3 calculated from the lower heating value of hydrogen (33 MWh/t) and the volume of LOHC. The gravimetric storage density is given in weight-% calculated from the mass of hydrogen per mass of loaded LOHC molecule. The storage density is the main parameter for the assessment of transport scenarios. The values were calculated from the molecular structure and physical properties taken from the substances' safety data sheets. For all four LOHCs they are in the same range. As a rule of thumb one can state a usable value of 50 kg of hydrogen per cubic meter of LOHC. This value is lower than the maximum volumetric storage densities of the substances since technically the dehydrogenation is for kinetic reasons unusually not driven to a very low loading state. A remaining amount of 10 % of hydrogen in the carrier molecule is common.

Two other parameters become relevant if the LOHC is to be used in large scale applications. For handling purposes, a low melting point is beneficial to overcome efforts for heating during transport and startup especially in cold regions. Here, benzyltoluene and toluene are advantageous over N-ethyl-carbazole and diphenymethane since trace heatings, heated tanks or other means of agitation are not necessary. This is one important aspect for the re-usability of existing oil infrastructures.

3.0 ENVIRONMENTAL AND SAFETY ASPECTS OF LOHCS

One of the main advantages of hydrogen storage and transport via LOHC is its low hazard profile. Of course, having a relatively high flashpoint does not omit all risks (compare [8]). But a high flashpoint combined with a storage and transport at ambient temperature and pressure diminishes the risk for leakage, spray, ignition and fire to a great extent. Whereas gaseous hydrogen bears at leakage a huge potential for the formation of explosive atmospheres with a low ignition energy and the main containment issue are suitable materials that withstand mechanisms of hydrogen embrittlement, leak tight connections and sensitive hydrogen detection systems, the main concern with liquid organic hydrogen carriers is its aquatic toxicity.

Figure 3 shows an ecotoxic comparison of different energy vectors at hand of their GHS symbols and relevant GHS hazard statements. For a simple transition from one energy carrier to a new one, it is important that the hazard potential is at least identical to the carrier to be exchanged. Here, oil like LOHCs like toluene and benzyltoluene are suitable since their physical properties and their hazard profiles are comparable to diesel and gasoline.

The advantage of benzyltoluene in this comparison is that it does not bear the risk of a high flammability which can be seen from the flash point in Table 1 leading to the absence of a corresponding classification. Toluene instead with a flashpoint of 4°C and a vapor density higher than air creates hazard szenarios which are not suitable for densely populated areas [9].

From an occupational health and safety perspective, benzyltoluene shows a lower risk profile due to its low vapor pressure at ambient conditions (<0.1 mbar; 2 mbar at 100°C) and thus a lower tendency of evaporation. Defined maximum concentration levels for work places do not exist according to the safety data sheets. For toluene, TWAs (8h-total weight average) of 100 ppm can be found.

Regarding transport, benzyltoluene is classified as UN3082 falling in class 9 of dangerous goods. This allows for a simple transport infrastructure.

From this comparison a high flashpoint LOHC like benzyltoluene has significant advantages over other chemical hydrogen storage vectors.

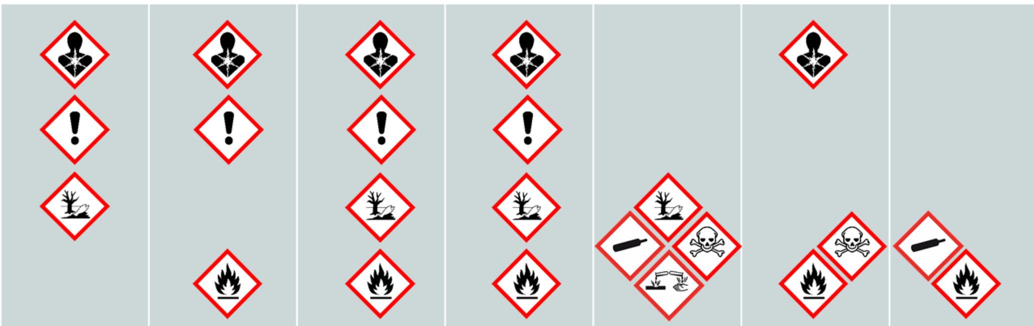
	Benzyl-toluene	Toluene	(Marine) Diesel	Gasoline	NH_3	Methanol	CGH_2 / LH_2
GHS symbol							
Aquatic tox.	H411		H411	H411	H400		
Mutagenicity				H340			
Carcinogenicity			H351	H350			
Reproduct. tox.	H360FD	H361		H361d			
Oral toxicity	H304	H304	H304	H304		H301	
Contact toxicity	H315	H315			H314	H311	
Inhalat. toxicity					H331	H331	
Target organ tox.		H373	H373			H370	

Figure 3. Comparison of safety aspects of different energy carriers

Focussing on benzyltoluene, the main hazard scenario is a large scale leakage into the environment. Thus, proven designs for handling of oil like liquids come into place, e.g. dry couplings, double walled tanks and collection basins. With a density below 1000 kg/m^3 in all loading states, oil barriers and skimmers can be used as hazard control.

Another relevant parameter for an assessment of the environmental consequences of a substance are its degradation kinetics. A recent study following OECD309 standards revealed a dissipation halflife for bezyltoluene in 12°C surface water of 12.4 days. This promising result is a first hint that persistence criteria are not met by benzyltoluene. Further investigation is required and ongoing.

Another advantage of LOHCs in general and bezyltoluene in particular in comparison to nowadays energy carrieres are their high purities. E.g. Sulphur and heavy metals are not present or below detection limit, lowering its ecotoxic potential.

With aquatic toxicity being the only relevant safety issue, for permit engineering no longer the thresholds of hydrogen are relevant. This leads e.g. in Germany to the advantage that up to 10t of hydrogen can be stored in benzyltoluene at one site without reaching the limits of the 12. BImSchV, corresponding to the European directive 2012/18/EU on the control of major-accident hazards involving dangerous substances. This amount is a reasonable storage of hydrogen at an inner city hydrogen refueling station, meaning that efforts in the permitting phase regarding the mentioned directive are reduced.

An important question to answer is the effect of the covalently bonded hydrogen an the (eco)toxic properties of the carrier. The pair toluene/methylcyclohexane is well characterized. Here the comparison of the safety data sheets reveals that their behavior is similar but not identical. The hydrogenated version has a higher aquatic toxicity but no reported effect on reproduction and also TWA is higher (400 ppm).

For benzyltoluene the picture is different. The loaded molecule perhydro-benzyltoluene is not readily available on the market. Therefore only research oriented REACH registrations exist at the European Chemicals Agency (ECHA) with a limited requirement for studies and data. Table 2 gives a direct comparison of relevant physical properties of the loaded and unloaded carrier molecule benzyltoluene.

Table 2. Comparison of physical properties of benzyltoluene and perhydro-benzyltoluene

	Benzyltoluene	Perhydro-benzyltoluene
Molecular weight / g/mol	182	194
Density (20°C) / kg/m^3	996	876
Viscosity (20°C) / mPas	4.3	6.6
Vapor pressure (100°C) / hPa	2.0	0.1
Flash point / °C	137	115

It can be seen that values change but the general characteristic of the substance stays the same, especially regarding hazard prevention and control (flash point and density). For an ecotoxic evaluation, data is currently prepared. The expectation is that the outcomes are comparable to the differences between toluene and methylcyclohexane.

4.0 LARGE SCALE HYDROGEN TRANSPORT

According to a recently published study, Germany will require hydrogen imports of 6 million tons of hydrogen by 2050 to satisfy its energy demand, due to its lack of economic production capacity for green hydrogen [3]. The IEA published a map of potential hydrogen production prices showing that there are regions more prone to low cost hydrogen generation. Thus, large scale transportation of hydrogen will take place just like today large scale transport of oil and gas takes place.

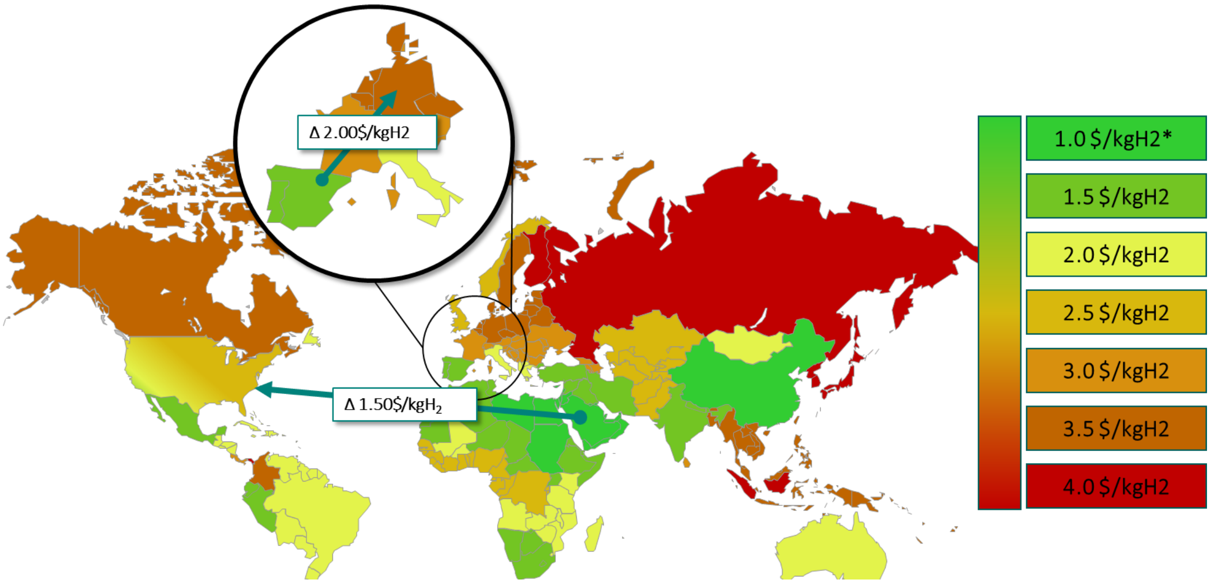


Figure 3. Cost differences for the regenerative generation of hydrogen [4],*[5]

In the course of the Important Projects of Common European Interest (IPCEI) several large scale hydrogen generation and transport scenarios have been engineered and submitted for funding. As an example here, the project „Green Hydrogen on Blue Danube" is taken [6].

In total 80.000 tons of hydrogen per year shall be generated in south eastern Europe and transported up the river Danube to Austria and Germany. Along the way several huge storage locations are envisaged to be prepared for uninterrupted supply of hydrogen to different industrial customers. As transport options, river barges for cryogenic hydrogen, ammonia and LOHC have been evaluated. In an internal study by Roland Berger, LOHC turned out to be the most advantageous transport vector for its economic and safety advantages [7]. Authorities were eager to avoid the hazard scenario of a leaking ammonia barge close to a densely populated city like Passau (GER), Linz (AUT) or Vienna (AUT). Standard river barges for oil transport can be used to carry loaded LOHC up and unloaded LOHC down the Danube iwth the known hazard scenarios from oil transport. This ship type is already available and harbor infrastructure is already installed. For other forms of hydrogen, new infrastructure would be required and more complex hazard scenarios would have to be approved. An extensive description of consequences of ammonia and hydrogen for the maritime sector can be found in [10].

This example shows that the physical and hazard properties described in the chapters above not only become relevant on a molecular level but also pay off on industrial scale giving a realistic opportunity for large scale transport scenarios.

On the logistics side it becomes obvious that the main difference between LOHC and other hydrogen transport solutions is the fact that there is a carrier that can be loaded and unloaded. Therefore, unloaded LOHC has to be carried back to the loading site. Which sounds like a major disadvantage becomes less critical due to the fact that all dedicated transport vessels have to travel back to the source of hydrogen. Speaking in mass, a compressed gas or cryogenic hydrogen tanker will have in both directions almost the same weight. Only for ammonia there will be measureable savings in fuel costs on the route back to the production site. At the sites, the logistics scenario for LOHC requires different compartment tanks or separated tanks for loaded and unloaded LOHC. Having a closer look on nowadays fuel infrastructure one observes that there are already numerous tanks available and handling different types of liquid hydrocarbons at one site is daily business.

5.0 CONCLUSION

In this paper we gave a brief introduction to the LOHC technology with a focus on safety aspects. For opening up the view to new opportunities of hydrogen transport, it is essential to understand the principle cycle of hydrogenation and dehydrogenation of a carrier molecule that is transported back and forth with a heat opportunity and a heat requirement at the different sites.

It was shown that the most important safety aspects of storage and transport of hydrogen in LOHC are the absence of a high pressure and the absence of molecular hydrogen with its risk of forming explosive atmospheres. With only environmental hazards left, known and established procedures can be used in hazard prevention and control.

This leads to the equivalently important aspect of economics to foster the energy turnaround towards a carbon neutral society. Here it was shown that the reusability of existing infrastructure is a key asset when it comes to economic assessments of large scale projects. Physical properties as well as safety aspects strengthen the potential of LOHCs to become a major technology for large scale hydrogen transport and storage.

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