National Institute for Public Health
and the Environment
Ministry of Health, Welfare and Sport

Toward a safe and sustainable energy transition

Minimising the use of Substances of Very High Concern in **liquid hydrogen carriers**

Hydrogen (H_2) is an important and renewable energy source that can be transported and stored through liquid hydrogen carriers. These chemical substances may have serious effects on human health and the environment, i.e. they can be Substances of Very High Concern (SVHC, in Dutch 'ZZS'). Additionally, ZZS may be formed during the binding and release of hydrogen. This factsheet explains the concept of liquid hydrogen carriers, providing insights into 10 promising carriers and indicating whether ZZS are used or formed. It also briefly touches upon recent developments in this technology. RIVM recommends avoiding the use of ZZS in new applications, such as liquid hydrogen carriers, wherever feasible.

Context

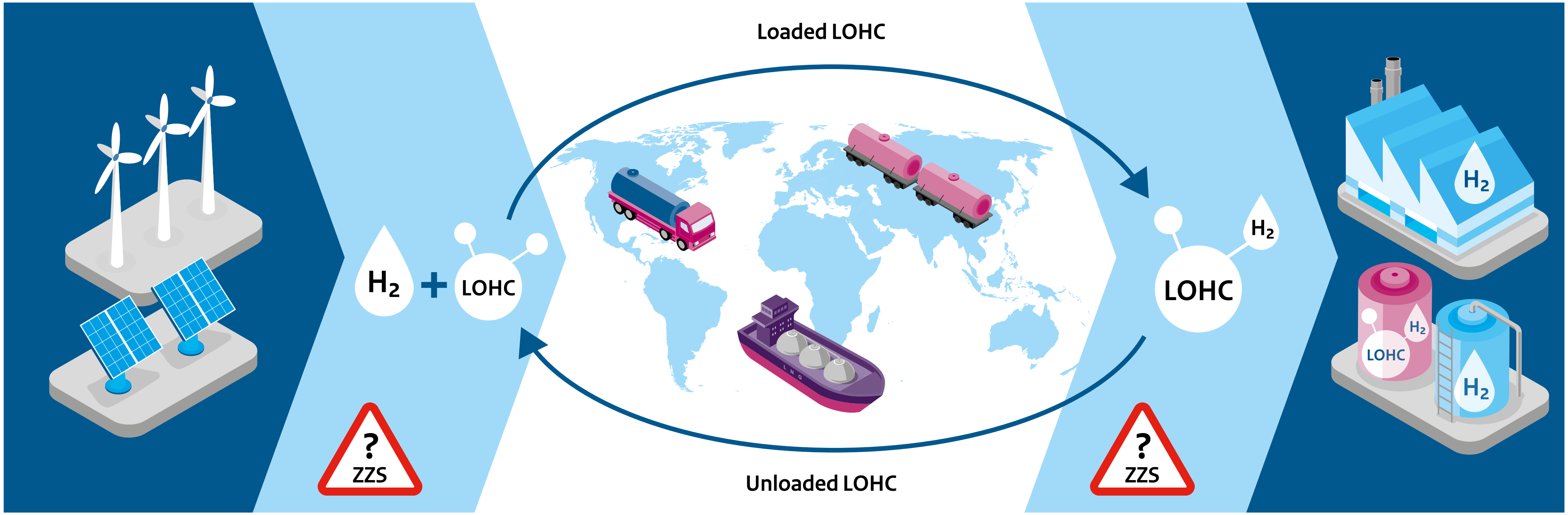
By 2030, the European Union is expected to produce 10 megatons of renewable hydrogen, with an additional 10 megatons to be imported. Dutch ports are expected to play a major role in the import. After 2030, a further increase in volume is anticipated.

Global transportation of hydrogen as (compressed) gas or super-cooled liquid requires dedicated infrastructure, which is currently limited. To import large quantities of hydrogen in the short term, existing fossil fuel infrastructure might be repurposed. A prerequisite is that the hydrogen is liquid under ambient conditions. This can be achieved by binding hydrogen to chemical substances. Such chemical substances are also known as liquid hydrogen carriers.

Liquid hydrogen carriers can include substances with or without carbon in their molecular structure. Those with carbon are called liquid organic hydrogen carriers (LOHC), while those without are referred to as liquid inorganic hydrogen carriers (LIHC). There is a diverse range of substances that can potentially serve as hydrogen carriers.

Concept of liquid hydrogen carriers

The illustration depicts the concept of liquid hydrogen carriers. A carrier without hydrogen is termed a hydrogen-lean carrier. After binding of hydrogen (hydrogenation), it becomes a hydrogen-rich carrier. Since hydrogen becomes part of the molecule, each liquid hydrogen carrier consists of a pair, for example: toluene - methylcyclohexane.



The hydrogen-rich carrier can be transported globally. Upon reaching its destination it can be temporarily stored. Eventually, the hydrogen is to be released (dehydrogenation) for storage, further distribution and/or use. During the process of hydrogen release, the hydrogen-lean carrier is formed again. The hydrogen-lean carrier can then be transported back to repeat the cycle. Such carriers are termed reversible liquid hydrogen carriers.

There are also circular liquid hydrogen carriers where the hydrogen-lean carrier is carbon dioxide or nitrogen. After hydrogen release, these naturally occurring gases can flow back to the atmosphere. There is thus no need for a return transport. Each new cycle begins again with carbon dioxide or nitrogen. When the carbon dioxide is captured from the atmosphere rather than obtained from fossil sources, there is no net increase in carbon dioxide.

RIVM research on selected liquid hydrogen carriers

Before widespread implementation of this technology, it is essential to determine whether liquid hydrogen carriers are hazardous to human health or the environment. The safety assessment so far has focused on external safety, such as explosion risk. RIVM emphasises the importance of addressing Substances of Very High Concern (SVHC, in Dutch 'ZZS'). ZZS are substances that may have serious effects on human health and the environment because they are, for example, carcinogenic, toxic to reproduction or accumulate in the environment and food chains.

Therefore, RIVM selected 8 LOHCs and 2 LIHCs to provide a broad overview of the current field and include candidates considered promising. Of these 10 liquid hydrogen carriers, the technical aspects and ZZS properties of relevant substances have been examined. Relevant substances include the hydrogen-lean and hydrogen-rich carriers, as well as any solvents used and byproducts formed. A complete overview of the derived ZZS statuses can be found in the table. The key findings are summarised on page 4.

ZZS properties of liquid hydrogen carriers

- All LOHCs have one or more substances with ZZS properties. However, the extent to which ZZS are present or formed may vary.
- During the dehydrogenation of the circular LOHCs methanol and formic acid, the ZZS carbon monoxide may be formed. The latter can react in the same process with water to form the hydrogen-lean carrier carbon dioxide (CO_2).
- During repeated hydrogen binding and release of the reversible aromatic LOHC toluene, 3 ZZS by-products are formed with the ZZS benzene being formed in the highest amounts.
- All other investigated reversible (hetero)aromatic LOHCs have at least a hydrogen-lean carrier with ZZS properties. This means that transport and storage of these liquid hydrogen carriers involves handling of substantial ZZS volumes.
- The circular LIHC ammonia does not contain substances with ZZS properties. However, is acutely very toxic, which is concerning from an external safety point of view.
- Unfortunately, it was not possible to investigate the ZZS properties of the reversible LIHC silicon hydride derivatives due to a lack of data. It is crucial that such data become available before any large-scale application takes place.

Current status and recent developments

- Ammonia, toluene and benzyltoluene are closest to large-scale application for the transport and storage of sustainable hydrogen. Interest in methanol is increasing.
- Ammonia, methanol, formic acid and benzyltoluene are in particular being further developed. It is explored if hydrogen can be released into fuel cell containing end devices that directly generate electricity for off-grid energy systems or to power ships and heavy transport. In this scenario, the liquid hydrogen carriers serve as energy carriers, and not just as hydrogen carriers.

What next?

Substances of Very High Concern (SVHC, in Dutch 'ZZS') may have serious effects on human health and the environment. Dutch policy therefore aims to minimise the presence of ZZS in the living environment, ideally replacing them with safer substances whenever possible. If substitution is not feasible, the recommendation is to minimise emissions. For new applications, it is better not to introduce ZZS. That also applies to the production and use of liquid hydrogen carriers.

RIVM recommends that due attention is paid to the potential harmful effects on humans and the environment during the design phase of liquid hydrogen carriers and during their use, following the Safe and Sustainable by Design approach. This is crucial as hydrogen is expected to be widely applied in the future. In that way, the energy transition can be shaped safely and sustainably.

	Type	ZZS-status*					
		ZZS	Consider as ZZS	Potential ZZS	Equivalent to potential ZZS	Probably not ZZS	Cannot be concluded
MCH/TOL	reversible LOHC (aromatic)	3 by-products	-	-	-	MCH TOL	by-product
H18-/H0-DBT	reversible LOHC (aromatic)	by-product	H0-DBT	-	H18-DBT	3 by-products	by-product
H12-/H0-BT	reversible LOHC (aromatic)	by-product	H0-DBT	-	-	-	H12-BT
DHN/NAP**	reversible LOHC (aromatic)	NAP	-	DHN	-	-	solvent
H12-/H0-NEC	reversible LOHC (heteroaromatic)	H0-NEC by-product	-	-	-	H12-NEC	-
EG/EEG	reversible LOHC (coupled)	by-product	-	-	by-product	EG; EEG by-product 2 solvents	-
FA/CO_2	circular LOHC	by-product	-	-	-	FA; CO_2 solvent	-
MET/CO_2	circular LOHC	by-product	-	-	-	MET; CO_2 solvent	-
NH_3/N_2	circular LIHC	-	-	-	-	-	-
SHD/SS	reversible LIHC	-	-	-	-	-	SHD; SS by-products solvents

MCH: methylcyclohexane; TOL: toluene; CHE: cyclohexane; BEN: benzene; H18-DBT: perhydrodibenzyltoluene; H0-DBT: dibenzyltoluene; H12-BT: perhydro-benzyltoluene; H0-BT: benzyltoluene; DHN: decahydronaphthalene; NAP: naphthalene; H12-NEC: dodecahydro-n-ethylcarbazole; H0-NEC: n-ethylcarbazole; EG: ethylene glycol; EEG: esters of ethylene glycol; FA: formic acid; MET: methanol; CO_2: carbon dioxide; NH_3: ammonia; N_2: nitrogen; SHD: silicon hydride derivative; SS: silica and/or silicate compounds.

* *In this factsheet the Dutch methodology for SVHC identification was used, and therefore the abbreviation ZZS is used, which comes from the Dutch translation 'Zeer Zorgwekkende Stoffen'. It is important to realise that SVHC and ZZS are based on exactly the same REACH criteria. The difference between ZZS and SVHC is that ZZS include the formally identified SVHC, but also substances that meet the SVHC criteria and have been identified as hazardous under other regulations, for example a Persistent Organic Pollutants (POP) under the Stockholm Convention.*

** *Recently, LOHC's based on substituted naphthalene have been proposed, e.g. methylbenzyl naphthalene and cis-perhydro-1-(n-phenylethyl)naphthalene. These systems were not extensively reviewed. We do note, however, that the hydrogen-lean carriers are substituted PAHs that belong to the SVHC group of PAHs.*

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