



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

# Liquid hydrogen carriers: an overview of technical aspects and SVHC properties



# **Liquid hydrogen carriers: an overview of technical aspects and SVHC properties**

RIVM letter report 2023-0369

## Colophon

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DOI 10.21945/RIVM-2023-0369

M. Marinković (author), RIVM  
J. Ng-A-Tham (author), RIVM

Contact:  
M. Marinković  
Environment and Safety Division /  
Centre for Safety of Substances and Products  
[Marino.Marinkovic@rivm.nl](mailto:Marino.Marinkovic@rivm.nl)

This investigation was performed within the framework of the project Strengthening the RIVM knowledge base on energy transition and environmental impacts, with finance from the ministry of Economic Affairs and Climate Policy

Published by:  
**National Institute for Public Health  
and the Environment, RIVM**  
P.O. Box 1 | 3720 BA Bilthoven  
The Netherlands  
[www.rivm.nl/en](http://www.rivm.nl/en)

## Synopsis

### **Liquid hydrogen carriers: overview of technical aspects and SVHC properties**

Hydrogen is an important and renewable energy source. It is expected that 10 megatonnes of renewable hydrogen will be produced in the EU in 2030. The same amount will be imported, much of which will take place via Dutch ports. In the years after that, a further increase is expected.

Hydrogen can be transported and stored using substances that can chemically bind and release hydrogen. When the substances are liquid they are called liquid hydrogen carriers. They can be carbon based (LOHC), or without carbon in their structure (LIHC).

So far, the safety aspect of liquid hydrogen carriers has almost exclusively been investigated with regard to external safety, meaning the risk of explosions. RIVM believes that the effects of Substances of Very High Concern (SVHC, in Dutch 'ZZS') on humans and the environment should also be considered. ZZS can be harmful because, for example, they are carcinogenic, hinder reproduction or accumulate in the environment and food chains.

In this report, eight LOHCs and two LIHCs were selected, including the currently most promising candidates. Their technical aspects were elaborated and it was determined if they contain substances with ZZS properties. The LIHC ammonia contains no substances with ZZS properties. In the absence of data, it could not be determined if the LIHC silicone hydride derivatives has substances with ZZS properties. All LOHCs have one or more ZZS. Methanol and formic acid form the ZZS carbon monoxide. The aromatic LOHC toluene forms three ZZS by-products, including benzene. Concerning the other (hetero)aromatic LOHCs, at least the hydrogen-lean carrier has ZZS properties.

Due to the harmful effects of ZZS, policy is to keep ZZS out of the living environment whenever possible, preferably by replacing them with safer substances. If that is not possible, ZZS emissions must be minimised. For new applications, it is better not to use ZZS altogether.

RIVM recommends that due attention be paid to 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 used in the future. This will allow for the energy transition to be shaped safely and sustainably.

**Keywords:** liquid hydrogen carriers, hydrogen, LOHC, LIHC, ammonia, methanol, toluene, benzyltoluene, SVHC, ZZS, SSbD



## Publiekssamenvatting

### **Vloeibare waterstofdragers: een overzicht van technische aspecten en ZZS-eigenschappen**

Waterstof is een belangrijke en duurzame energiebron. Naar verwachting zal in 2030 10 megaton duurzaam opgewekte waterstof in de EU worden geproduceerd. Dezelfde hoeveelheid zal worden geïmporteerd, waarvan een groot deel via de Nederlandse havens. In de jaren erna wordt een verdere stijging verwacht.

Vervoer en opslag van waterstof is mogelijk met behulp van stoffen die waterstof chemisch binden en weer vrijgeven. Wanneer de stoffen vloeibaar zijn, worden ze vloeibare waterstofdragers genoemd. Als ze koolstof bevatten heten ze LOHC, en zonder koolstof heten ze LIHC.

Onderzoek naar de veiligheid van vloeibare waterstofdragers richtte zich tot nu toe vooral op omgevingsveiligheid, zoals explosiegevaar. Het RIVM vindt het belangrijk om ook aandacht te besteden aan de effecten van Zeer Zorgwekkende Stoffen (ZZS) op mens en milieu. ZZS kunnen schadelijk zijn doordat ze bijvoorbeeld kankerverwekkend zijn, de voortplanting belemmeren of in het milieu en voedselketens ophopen.

In dit onderzoek zijn acht LOHC's en twee LIHC's geselecteerd, onder andere omdat ze veelbelovend zijn. Hun technische aspecten zijn uitgewerkt en ook is gekeken of ze stoffen met ZZS-eigenschappen bevatten. De LIHC ammoniak bevat deze stoffen niet. Bij gebrek aan gegevens kon niet onderzocht worden of de LIHC siliconenhydridederivaten dergelijke stoffen bevatten. Alle LOHC's hebben één of meerdere stoffen met ZZS-eigenschappen. Methanol en mierenzuur vormen de ZZS koolmonoxide als bijproduct. De aromatische LOHC toluen vormt drie bijproducten die ZZS zijn, waaronder benzeen. Bij de overige (hetero)aromatische LOHC's heeft ten minste de waterstofarme drager ZZS-eigenschappen.

Vanwege de schadelijke effecten van ZZS is het beleid erop gericht om ze zoveel mogelijk uit de leefomgeving te weren. Het liefst door ze door veiligere stoffen te vervangen, en anders door de uitstoot ervan te minimaliseren. Bij nieuwe toepassingen, is het beter om geen ZZS te gebruiken.

Het RIVM raadt aan om vanaf het ontwerp van vloeibare waterstofdragers tot en met het gebruik aandacht te hebben voor schadelijke effecten voor mens en milieu (*Safe and Sustainable by Design*). Dit is belangrijk vanwege de grote schaal waarop waterstof in de toekomst zal worden gebruikt. Dan kan de energietransitie veilig en duurzaam vorm krijgen.

Kernwoorden: vloeibare waterstofdragers, waterstof, LOHC, LIHC, ammoniak, methanol, toluen, benzyltoluën, ZZS, SVHC, SSbD



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## Summary

Hydrogen electrolytically produced from renewable energy is an important and sustainable energy source that will increasingly be used in the future. The EU ambition for 2030 is to produce domestically 10 megatonnes of renewable hydrogen, and to import the same amount from outside the EU. A large part of these imports is expected to take place via Dutch ports. In the years after that, a steep increase in the use of renewable hydrogen is expected, which will require even more transport and storage of renewable hydrogen.

Many options are currently on the table to facilitate the envisaged large scale transport and storage of renewable hydrogen. These include (compressed) gaseous and liquefied hydrogen both of which need dedicated infrastructure that is not yet in place. Hydrogen can also be bound to substances that can release the hydrogen upon demand, so called hydrogen carriers. When they are liquid under ambient and/or mild conditions they are referred to as liquid hydrogen carriers. Distinction can be made between substances having carbon in their molecular structure (liquid organic hydrogen carriers (LOHC)) and those without carbon (liquid inorganic hydrogen carriers (LIHC)).

Many liquid hydrogen carriers have been proposed over the years. These include circular candidates where the hydrogen-lean carrier is released to the atmosphere during dehydrogenation and a new hydrogen-lean carrier is captured each time the process is repeated. Examples of circular LOHCs are methanol and formic acid, while ammonia is a circular LIHC. There are also candidates that need a return transport of the hydrogen-lean carrier following the release of hydrogen to repeat the process, so called reversible types. Silicone hydrate derivatives is a reversible LIHC. There are many reversible LOHCs including those with an aromatic ring, e.g. toluene, benzyltoluene, dibenzyltoluene, naphthalene, with a heteroaromatic ring, e.g. *n*-ethylcarbazole, or with a certain chemical bond, such as an ester or peptide bond, that is broken during hydrogenation and reformed during dehydrogenation (coupled type), e.g. esters of ethylene glycol.

To facilitate informed decision making regarding the use of liquid hydrogen carriers, this report elaborated on the concept of liquid hydrogen carriers, provided an overview of the field and investigated the ten liquid hydrogen carriers noted above in more detail. These ten liquid hydrogen carriers represent the broadness of the field and include the currently most promising candidates. Their technical aspects were elaborated, and their hazardous properties in terms of Substances of Very High Concern (SVHC) were investigated. SVHC are substances that may be harmful to human health and/or the environment due to their carcinogenic, mutagenic, reprotoxic, persistent and bioaccumulative properties, or properties that lead to an equivalent level of concern. In this report 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 ZSS and SVHC is that ZSS 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.

Substances investigated for the selected liquid hydrogen carriers were the hydrogen-lean and hydrogen-rich carriers, and if applicable the solvents used, and the by-products formed. It was shown that only one of the investigated liquid hydrogen carriers had no substances with ZSS properties, i.e. the circular LIHC ammonia. The circular LOHCs methanol and formic acid formed one ZSS by-product, i.e. carbon monoxide, which can react with water during dehydrogenation to form carbon dioxide. The other investigated LOHCs had two or more ZSS by-products (toluene, esters of ethylene glycol) or used at least a hydrogen-lean carrier with ZSS properties (benzyltoluene, dibenzyltoluene, naphthalene, *n*-ethylcarbazole). Application of the latter category for bulk transport of renewable hydrogen would appear especially troublesome from a ZSS point of view, as it would mean that large quantities of ZSS will be handled and shipped.

Our research further identified a trend where the use of particularly ammonia, methanol, formic acid and benzyltoluene is extended beyond the use as hydrogen carrier to act as an energy carrier that can directly power ships, heavy transport or off-grid energy systems. In those cases the hydrogen-rich carriers are dehydrogenated in end-devices with integrated fuel cells that convert the released hydrogen to electricity. These potentially wide dispersive uses should be considered in the discussions on liquid hydrogen carriers, as they can result in increased and diffused emissions.

Measures can be taken on an EU, national and local level to restrict/ban certain substances and/or applications after their introduction to improve safety, but the dynamics of this process is not in line with a Safe-and-Sustainable by Design (SSbD) approach. The energy transition is an ideal opportunity to get off to a good start, not hampered by legacy uses, aiming at a maximized safety and sustainability. Early on in the design process attention should be given to the identification of ZSS within the liquid hydrogen carrier technology, thereby also considering the impact of these substances on health, climate and the environment during the entire lifecycle. These investigations should include the hydrogen carriers, solvents and by-products investigated in this study, but also the catalysts used, which fell outside the scope of this study. Other hazardous aspects should be considered too. For example, the circular LIHC ammonia, which contains no ZSS, is highly toxic and from an external safety point of view is not an obvious choice especially when used as energy carrier that powers end-devices as that leads to widespread and diffused use. Comparing these different hazardous properties, as well as economic and practical aspects of liquid hydrogen carriers would allow for balanced decisions to be made that can steer towards an energy transition that is green, sustainable and safe.

## 1 Introduction

Hydrogen is enjoying a renewed and rapidly growing attention as feedstock, fuel and energy source. This especially holds true for hydrogen electrolytically produced from renewable energy where carbon dioxide is not emitted during use, and not or limitedly<sup>1</sup> during production (EC, 2023a). Use of renewable or green hydrogen offers other advantages too, allowing global transport of solar and wind generated electricity, as well as the ability to store renewable electricity during peak production for prolonged periods of time. Ambitious goals have been set for renewable hydrogen both on EU and national level regarding in-house production and import from outside the EU (EC, 2022d; NWP, 2022).

The envisaged large-scale use of renewable hydrogen is expected to require considerable transport and storage capacities, which poses the question how this can be done best. Many options are currently on the table relying on different hydrogen forms. These include compressed gaseous and cryogenically liquefied hydrogen, as well as numerous hydrogen derivatives in gaseous, liquid, and solid form, all of which can be transported and stored in different ways. Hydrogen derivatives are substances formed by chemical binding or adsorption of hydrogen, comprising both hydrogen carriers and e-fuels<sup>2</sup>. This report exclusively deals with hydrogen carriers, which are hydrogen derivatives that can release the hydrogen on demand (Ulucan et al., 2023).

Transporting hydrogen in bulk as compressed gas or cryogenic liquid is currently hampered by high costs and lack of dedicated, technically demanding infrastructure. Hydrogen carriers that are liquid at ambient environmental conditions have a better starting position as they can use existing transport and storage infrastructure that is already in place for petroleum and its derivatives (Brückner et al., 2014). Additionally, certain hydrogen carriers benefit from the experiences gained from other large-scale uses, e.g. ammonia for fertilizer production (Valera-Medina et al., 2018) and methanol as raw material in various industrial processes (Olah, 2005). While the race has not been run, some hydrogen carriers appear to be closer to near-future large-scale implementation than others, notably the inorganic hydrogen carrier (LIHC) ammonia and several liquid organic hydrogen carriers (LOHC), such as toluene, benzyltoluene and methanol (Niermann et al., 2021). Other liquid hydrogen carriers both organic and inorganic are in earlier phases of development, but could become relevant with time.

Deploying liquid hydrogen carriers for bulk transport and storage of hydrogen requires several additional steps in comparison to handling pure hydrogen. The hydrogen-lean substances need to be produced in case of most LOHCs, or captured from the atmosphere for circular

<sup>1</sup> The European Commission published a draft delegated act that sets requirements, including greenhouse gas emission thresholds for hydrogen and its derivatives to be considered renewable.

<sup>2</sup> E-fuels, which stands for electro-fuels, are fuels made with captured carbon dioxide and renewable hydrogen that can be used as drop-in in combustion engines. Examples are e-kerosene, e-methane, or e-methanol. In the EU, the term Renewable Liquid and Gaseous Transport Fuels of Non-Biological Origin (RFNBOs) is used (EC, 2023a), which encompasses e-fuels, but also green ammonia that can be used as fuel in combustion engines.

hydrogen carriers, such as ammonia and methanol, whose hydrogen-lean carriers are nitrogen and carbon dioxide, respectively. Next step is to chemically bind the renewable hydrogen to the hydrogen-lean carrier, which requires a dedicated facility. The resulting hydrogen-rich carrier can then be transported using conventional tankers in case of LOHCs or using tankers available for compressed/ liquified ammonia. Upon arrival at the destination site, the hydrogen-rich carrier can be stored for longer periods in existing storage tanks, or can be further transported inland using different transport modalities for on-site storage and dehydrogenation. Hydrogen can also immediately be released at the port of arrival for use or further distribution. Dehydrogenation occurs at a dedicated facility and yields beside the hydrogen also the hydrogen-lean carrier. The latter can be released to the atmosphere when it concerns a circular hydrogen carrier. For other types, known as reversible liquid hydrogen carriers, a return transport is generally needed so the process can be repeated (see Figure 1). There are proposals to extend the use of liquid hydrogen carriers beyond the uses described above. The hydrogen would then be released in fuel cell containing end-devices, such as ships, trains and trucks (Hydrogenious LOHC Maritime, 2023; Marrin & Moss, 2023), where it is directly converted to electrical power. This would make the hydrogen carriers *de facto* energy carriers.

How hydrogen transport chains utilizing different hydrogen forms compare has been the topic of many recent publications. These publications focussed on different aspects, including: feasibility and costs (Johnston et al., 2022; Weichenhain, 2021), energy consumption and costs (JRC, 2021; Niermann et al., 2021), near-future realizability (Zahw et al., 2022), as well as external safety (Arcadis & Berenschot, 2021; Berenschot, Arcadis, & TNO, 2023). These studies showed that certain hydrogen forms can be more suitable than others for specific scenarios, but also that there is no hydrogen form which is optimal for all situations.

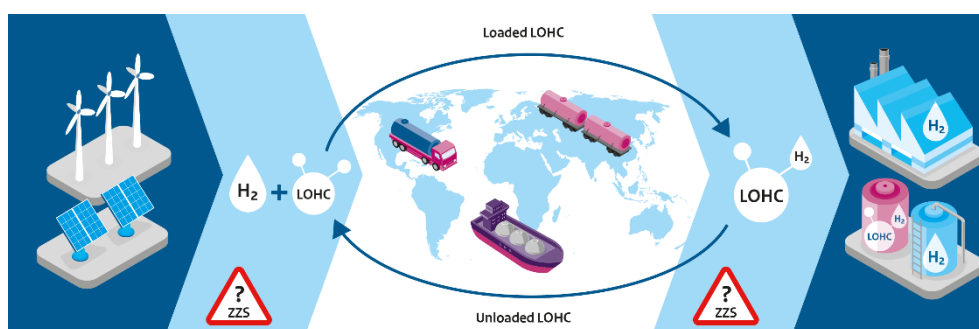


Figure 1 Transport and storage of renewable hydrogen using LOHCs of the reversible type. The hydrogen carriers applied, but also the solvents used and the by-products formed during (de)hydrogenation, can have ZVS (SVHC) properties.

So far, the safety aspect of hydrogen carriers has almost exclusively been assessed from an external safety point of view. This considers the potential for high-risk situations due to the occurrence of accidents and disasters, e.g. risk of explosions or acute toxicity due to ammonia spills (Arcadis & Berenschot, 2021; Berenschot, Arcadis, & TNO, 2023). The risks to workers, general public and the environment caused by emissions during production, the hydrogenation and dehydrogenation processes, the handling during transport and storage, the waste stage and potentially also the use of these substances as energy carriers, have hardly been on the radar, but need to be considered to ensure safe application of liquid hydrogen carriers. For substances that are already used, risk limits may have been derived and their REACH registration dossier may contain relevant exposure and effect data, allowing risk assessments to be conducted. However, for certain substances a hazard-based approach is followed as they may be very harmful to human health and/or the environment due to their carcinogenic, mutagenic, reprotoxic, persistent and bioaccumulative properties, or properties that lead to an equivalent level of concern. These substances can be identified as Substances of Very High Concern (SVHC) with the criteria for identification laid down in Article 57 of the REACH regulation ((EC) 1907/2006) (ECHA, 2023b). Following formal SVHC identification by ECHA, a substance is placed on the Candidate list of SVHCs for Authorisation. This triggers legal obligations under REACH. Downstream users, public and ECHA must be informed when the substance is present in concentrations above 0.1% weight-by-weight in an article, information must be provided to allow safe use of the article, and there is a minimisation of exposure requirement for persistent and bio-accumulative SVHCs (ECHA, 2023c).

In the Netherlands, SVHC are termed ZZS coming from the Dutch translation '*Zeer Zorgwekkende Stoffen*'. ZZS are treated with priority, with national policy aiming to keep them as much as possible out of the living environment by substituting them where possible with less hazardous substances, or, if not possible, by minimizing their releases to the environment (Rijksoverheid, 2023). This approach is in line with a Safe-and-Sustainable by Design (SSbD) approach that is needed to achieve a sustainable energy transition (Caldeira et al., 2022). It is noted that ZZS identification is based on exactly the same criteria as SVHC identification, i.e. Article 57 of the REACH regulation (Rijksoverheid, 2023). Still the Dutch ZZS list is broader than the Candidate List of SVHCs for Authorisation. This is because the Dutch ZZS list includes substances formally identified as SVHC's under the REACH regulation, but also substances that meet the SVHC criteria and have been identified as hazardous under other regulations, for example a substance identified as a Persistent Organic Pollutants (POP) under the Stockholm Convention (de Poorter, Hogendoorn, & Luit, 2011). In this report the Dutch methodology for ZZS identification is used, and therefore the abbreviation ZZS will be used throughout the report.

### ***Aim and scope***

Authorities at different levels of organisation such as the EU, national and local level, are currently thinking along with other stakeholders how to shape the hydrogen economy as part of the energy transition. The decisions taken in the next few years will determine the scale of renewable hydrogen imports and the hydrogen forms in which these imports will occur. The resulting changes will have an impact in decades to come. The options for bulk transport and storage of hydrogen that are on the table will benefit from comprehensive analyses and assessments.

This report aims at contributing to the analyses and assessments made in the decision making processes by providing insight in liquid hydrogen carriers with a specific focus on their ZGS properties. It also aims at raising awareness of this particular aspect of safety. This will enable proactively designing innovations with a view to safety.

This report is not exhaustive. It explores the hazardous properties in terms of ZGS of a limited number of liquid hydrogen carriers, including the solvents used and the by-products formed during the hydrogenation and dehydrogenation processes. Substances involved in the manufacturing of the hydrogen-lean substances as well as the catalysts used during (de)hydrogenation, are not considered. It is noted that especially the LOHC field is very broad and undergoing strong developments. Some LOHCs are being marketed, while at the same time new LOHCs and new uses are being developed, making it unpredictable which liquid hydrogen carrier options will become favourable. The selection in this report is meant to discuss the current main candidates, as well as future options.

We note that this report only considers the hazardous properties of LOHCs in terms of ZGS. Other hazardous properties that could be relevant from an external safety point of view have not been investigated. Also potential exposure to public, workers and the environment was not estimated, as this report did not aim to perform risk-assessments. These aspects could be addressed in a follow-up research.

### ***Reading Guide***

Chapter 2 describes the methodology of this study. Chapter 3 gives background information on the emerging hydrogen economy. Chapter 4 provides information regarding different hydrogen forms, their energy densities and transport options. Chapter 5 details policies and regulation in place to deal with substances of concern, explaining in more detail the Dutch ZGS approach. Chapter 6 details the liquid hydrogen carrier concept and the types of carriers. Chapter 7 elaborates on a number of selected liquid hydrogen carrier: their technical aspects are elaborated, the state of their technology is determined, relevant substances are identified and their ZGS statuses are determined. The insights gained in Chapter 7 allow a discussion in Chapter 8 in which the different liquid hydrogen carriers are compared, followed by conclusions and recommendations.

## 2 Methodology

The current report is an extended and updated English version of an advice to the province of South Holland dated December 2022. The advice was in Dutch and explored liquid organic hydrogen carriers (LOHC) in terms of ZZS properties. The drafting of the advice was supervised by a supervisory committee of varying composition (meetings on 10 February 2022; 4 April 2022; 27 June 2022). Participating organisations were: Province of South Holland; Province of North Holland; Environmental Protection Agency of the Rijnmond area (DCMR); Environmental Service of the Region Noordzee kanaal (OD NZKG); and the Dutch National Institute for Public Health and the Environment (RIVM). The current report also explores liquid inorganic hydrogen carriers, and provides more information on the hydrogen economy and dealing with substances of concern. This report is characterized by two research phases that are detailed below.

### 2.1 Inventory of liquid hydrogen carriers

General information on the hydrogen economy, including hydrogen and hydrogen carriers, was obtained from recently published reports focussing on different aspects of the energy transition. These reports have been published by a wide range of (inter)governmental, non-governmental and industrial organisations.

More detailed and specific information on hydrogen carriers was obtained by searching scientific databases (Scopus and Pubmed) for peer-reviewed publications dealing with the concept of hydrogen carriers as well as individual hydrogen carriers. Attention was paid to the underlying technologies, the stability of the hydrogen carriers and the formation of by-products. Search terms included general hydrogen carrier terms, but also substance-specific characteristics such as chemical and commercial substance names and EU/CAS numbers with or without additional terms focussing on stability, degradation, solvent usage and by-product formation.

Relevant grey literature on hydrogen carriers that has been produced outside of traditional publishing and distribution channels, was searched using Google and Google Scholar similarly as depicted above for the scientific databases.

Aim of this first research phase was to get a better understanding of liquid hydrogen carriers and to identify relevant substances for further investigation as described in the following section.

### 2.2 Determination of ZZS status

For readers less familiar with the dealing of substances of concern and specifically SVHC and ZZS, a short overview of relevant regulations, policies, frameworks and definitions is given in chapter 6.

In the second phase, the ZZS status of the identified substances was determined. To this end, the methodology was applied as detailed in the

Dutch guidance document '*Werkwijze stofadviezen ZZS in de vergunningverlening*', in English: '*Procedure for substance advice SVHC in the permit granting*' (RIVM, 2020). The respective guidance document defines five substance advice categories with regard to the ZZS status of a substance (see Table 1 for the categories and descriptions). The guidance also details which information to take into account and in which order, to ensure consistency in consecutive category assignments (see Annex I for an English summary of the relevant sections of the guidance document). In a few cases there was insufficient information to conclude on the ZZS properties of a substance and none of the described categories could be assigned, concluding them as "*No statement possible about the ZZS status*". Below the table a short description is given of the procedure followed.

Table 1 Overview of substance advice categories (adapted from RIVM (2020))

Substance advice category	Description
'ZZS'	Substances that meet the ZZS criteria in accordance with REACH Art 57 a-f <ul style="list-style-type: none"> <li>▪ Substances and substance groups that have been determined to meet the SVHC criteria.</li> <li>▪ Substances with one or more ZZS components, which are ZZS according to the mixture memorandum<sup>1</sup></li> </ul>
'Consider as ZZS'	<ul style="list-style-type: none"> <li>▪ The substance does not yet have the status of ZZS (see above), but there are sufficient indications that the substance meets the ZZS criteria.</li> <li>▪ Mixtures with one or more ZZS components<sup>1</sup></li> </ul>
'Potential ZZS'	<ul style="list-style-type: none"> <li>▪ Substances published by the RIVM on the '<i>Lijst potentieel Zeer Zorgwekkende Stoffen</i>' (in English: '<i>List of potential Substances of Very High Concern</i>').<sup>2</sup></li> </ul>
'Of equivalent concern as potential ZZS'	<ul style="list-style-type: none"> <li>▪ Substance is not on the potential ZZS list. The available data give a lot of uncertainty. Essential data are missing. Based on expert judgment (including if the substance is a potential PBT/vPvB under REACH), and/or group approach<sup>3</sup>, there is cause for concern.</li> </ul>
'Probably not of equivalent concern to ZZS or potential ZZS'	<ul style="list-style-type: none"> <li>▪ Substance is not on the ZZS list. At the time of the advice, it is concluded that based on the available data and 'expert judgement', that the substance most likely does not meet the ZZS criteria.</li> </ul>

<sup>1</sup> For mixtures, the technical criteria according to the MEMO '*Toelichting over de ZZS-toets voor mengsels met ZZS*' in English: '*Explanation about the SVHC test for mixtures with ZZS*' are followed (van Herwijnen, 2019).

<sup>2</sup> These substances are being examined at EU level for properties that correspond to the ZZS criteria. As a result, these may be identified as ZZS in the future.

<sup>3</sup> This applies to structural similarity with ZZS as well as with substances on the list of potential ZZS.

Substance information was searched on the basis of CAS numbers. If no CAS numbers were reported for hydrogen carriers, solvents and/or by-products, CAS numbers were searched based on the available chemical

names and/or structures. By-products that were not properly described in publications and that could therefore not be matched to a definitive structure or traced back to a CAS number were not further investigated. This also applies to by-products that were found in very small amounts, as well as hydrogenation intermediates that have been described in literature, but that were not detected in experiments. In cases where CAS numbers could not be retrieved for substances, but the structure was available, SMILES codes were used as input for models.

To determine the ZZS status of substances, the stepwise procedure described in Annex I was followed. Main information sources were ECHA webpages and RIVM's Risks of Substances (RvS) website (<https://rvs.rivm.nl>). Substances listed on the Dutch ZZS list or the Dutch potential ZZS list were not further investigated. For other substances, substance properties were researched in more depth by consulting ECHA's dissemination website and the C&L inventory website. Ongoing REACH processes were scrutinized for relevance (harmonised classification proposals, PBT/ vPvB/ PMT/ ED assessments, Regulatory Management Option Analysis (RMOA)). When possible, conclusions were drawn based on experimental data obtained. When no or limited information was found for substances, the similarity tool on the RvS website was used to find structural analogues that could serve as indicators for environmental behaviour or toxicity of the substance (Wassenaar et al., 2019), and models were used to predict substance properties, such as the RIVM PB(t) tool (P(ersistent), B(ioaccumulative) t(oxic)) (Rorije et al., 2011) and the OECD QSAR toolbox (v4.5). As specified in Annex I, when sufficient data were found to allow a conclusion on the ZZS status of a substance, a conclusion was drawn without completing an exhaustive search. Before final conclusions on the ZZS status were drawn, each substance was discussed in an internal RIVM expert group covering a broad field of expertise, including toxicology, toxicokinetics, and environmental toxicology and fate, and consisting of M.E.J. Pronk, E. Rorije, A.G. Schuur, R. van Herwijnen and E.M.J. Verbruggen.



### 3 Setting the scene: onset of a hydrogen economy

The EU ambitions to decarbonize the industry and to transit to climate neutrality by 2050, are increasingly leaning on the deployment of renewable hydrogen. In 2020, the European Commission adopted its Hydrogen Strategy, setting an objective to produce up to 10 million tonnes (Mt) of renewable hydrogen in the EU by 2030 (EC, 2020). In 2021, this objective was anchored in a legislative proposal to reform the EU gas market as part of the 'Fit for 55' package<sup>3</sup> (EC, 2021). In 2022, the European Commission ramped up its ambition level and outlined a 'Hydrogen Accelerator' concept as part of the REPowerEU plan<sup>4</sup> (EC, 2022d). This concept aims to further develop hydrogen infrastructure, storage and terminal facilities and scale up the deployment of renewable hydrogen in the EU to 20 Mt/year by 2030. The additional 10 Mt/year are envisioned to be imported from outside the EU via pipelines and ships (EC, 2022c).

In parallel to the developments at the EU level, many Member States adopted national hydrogen strategies. Collectively, these plans add up to an electrolyser capacity of 40 gigawatt (GW) by 2030, equalling 5.6 Mt of renewable hydrogen (EC, 2023b). Measures have also been defined to stimulate trade of renewable hydrogen on an industrial scale, but these are generally less tangible, including infrastructure plans and memoranda of understanding between importing and exporting countries and individual companies. A concrete example is the German establishment of the H2Global instrument and its associated Hydrogen Intermediary Company (Hint.co) with the latter acting as an intermediate between supply and demand side, offering long-term certainty to suppliers of renewable hydrogen and a transparent and liquid market to buyers, thereby matching when needed price differences with public funds (Bauer, 2023).

Zooming in on the Netherlands, in 2022 a Hydrogen Roadmap has been published by a broad group of public and private stakeholders that participate in the National Hydrogen Programme (in Dutch: '*Nationaal Waterstof Programma*') (NWP, 2022). In this report commissioned by the Ministry of Economic Affairs and Climate Policy, it was pointed out that the national target for electrolyser capacity should be 6 to 8 GW by 2030 in order to meet the EU target. The report states that the Netherlands aims to retain and strengthen its function as energy hub for North-western Europe. To achieve that goal, the NWP considers it vital that on the short run preconditions are met that will enable large-scale import and transit of renewable and low-carbon hydrogen. These preconditions consist of the realisation of infrastructure, storage capacity, safety policy, regulation and certification of renewable hydrogen. Dutch ports and individual companies are already seen working on necessary terminals and facilities. NWP estimates that the

<sup>3</sup> The 'Fit for 55' package is a set of proposals to revise and update EU legislation and to put in place new initiatives with the aim of ensuring that EU policies are into line with the climate goals agreed by the Council and the European Parliament, which target a reduction of net greenhouse gas emissions by at least 55% by 2030 compared to 1990 levels and to achieve climate neutrality in 2050.

<sup>4</sup> REPowerEU is a plan to rapidly reduce dependence on Russian fossil fuels and fast forward the green transition

first Dutch imports of renewable and low-carbon hydrogen will take place in 2025 amounting to 0.3 Mt and that the volume will increase to 3 to 5 Mt by 2030. In the period after 2030, import of renewable hydrogen is expected to reach 20 Mt/year. In analogy to fossil energy sources, a large fraction of the imported renewable hydrogen is expected to be transited to the hinterlands, mainly Germany.

The ambitions, however, are still a far cry from the current situation. In 2022, less than 0.3 Mt of the 8 Mt of hydrogen consumption in the EU was produced electrolytically (EC, 2023b). The vast majority of hydrogen was produced from fossil fuels either by dedicated production, i.e. steam reforming of methane (~75%) or as by-product in refineries and other industrial processes (~25%). The produced hydrogen was almost exclusively used on-site or in the near vicinity as feedstock in industrial processes. Only a minor fraction (~5%) of the dedicated production was traded (IEA, 2022). These figures illustrate the share magnitude of the tasks that lie ahead to scale up the production and import of renewable hydrogen in order to reach the EU targets for 2030 of 10 Mt/year of domestic production and 10 Mt/year import into EU.

## 4 Transport and storage of renewable hydrogen

Importing large quantities of renewable hydrogen into the EU is likely to entail intercontinental trade in hydrogen and numerous hydrogen carriers. The form in which the hydrogen will be traded will have a profound impact on the hydrogen transport chain determining its overall efficiency and the transport modalities that can be used, but also the infrastructure requirements in producing and importing countries. Further inland distribution of the imported, but also the domestically produced renewable hydrogen will also be shaped by the hydrogen form used. Below these aspects are discussed in further detail.

### 4.1 Trading hydrogen in its pure form

Trading hydrogen in its pure form requires no conversions. However, hydrogen is characterized by a low volumetric energy density at standard temperature and pressure, meaning that the energy content per litre is very low (as detailed in section 4.3). Under ambient environmental conditions gaseous hydrogen can be transported by pipelines, but to be efficiently transported by ship, train, or truck, it must be compressed or cryogenically liquified to reach a higher volumetric energy density.

In the long term, pipelines are expected to play a major role in the import of renewable hydrogen in gaseous form from EU neighbouring regions, such as Norway and North-Africa. Between these countries and the EU, pipelines already exist that are currently used for the import of natural gas. Repurposing of these pipelines to transport gaseous hydrogen and extension of the network with new pipelines is foreseen. The resulting pan-European hydrogen pipeline network, also known as the European Hydrogen Backbone (EHB), will also simplify the distribution of gaseous hydrogen to regional demand centres across Europe (van Rossum et al., 2022). However, such capital processes take time, and international hydrogen trade through pipelines is expected to occur nearer to the end of this decade (EC, 2023b).

Import of hydrogen in its pure form in the near future is more likely to be conducted as compressed gas or liquified hydrogen by means of tankers with the former being cost-effective for short distances and the latter for longer distances (JRC, 2021). This resembles the practice that is currently in place for natural gas. However, the pressure required to compress hydrogen and the low temperature needed to liquefy hydrogen are much extremer for hydrogen compared to natural gas (350-700 vs. 250 bar; -253 vs. -162° C) (US DoE, 2023). This corresponds to higher energy uses and costs. Furthermore, the repurposing of natural gas infrastructure, other than pipelines, appears to be rather complex (Riemer, Schreiner, & Wachsmuth, 2022). Especially when considering that dealing with hydrogen poses additional challenges such as potential embrittlement of equipment, higher boil-off losses, increased risk of leakages, leakages that are generally difficult to detect, and increased danger of fires and explosions (Al Ghafri et al., 2022). Development of dedicated infrastructure is needed. In 2022, a

demonstration project showed that intercontinental bulk transport of liquid hydrogen is feasible with hydrogen produced and liquified in Australia and transported to Japan in a ship specifically build for that purpose (Pekic, 2022). The liquified hydrogen can be stored as is, or regasified for use, further distribution or storage. From a technical and economic point of view, storing large amounts of hydrogen is most efficiently conducted in gaseous form in salt caverns under ambient environmental conditions, both for the long and short term. Such caverns are being developed, with the first cavern in the Netherlands expected to be operational in 2028 (Gasunie, 2023). Smaller quantities of renewable hydrogen can be efficiently stored in tanks in compressed form with limited losses provided the tanks are appropriately sealed and no energy requirements besides the energy needed for the initial compression process (Serpell et al., 2023).

#### 4.2 Trading hydrogen bound to hydrogen carriers

To kick start the hydrogen economy, options other than hydrogen in its pure form, are being explored for international trade in renewable hydrogen. Shipping of substances that can chemically bind or adsorb hydrogen and release the hydrogen on demand, i.e. hydrogen carriers, seem particularly suitable. Not only to enable import from nearby regions until a hydrogen infrastructure is in place (NZTC, 2022). Hydrogen carriers might be particularly suitable for bulk shipping of renewable hydrogen from far away regions, such as Australia and South-America, for which hydrogen pipelines are not a favourable option and the distance is too long for efficient shipping of compressed or cryogenically liquified hydrogen (Johnston et al., 2022; JRC, 2021).

Over the years, many different types of hydrogen carriers have been proposed, including: solid inorganic hydrogen carriers, such as: metal & complex hydrides (Rusman & Dahari, 2016), metal oxides (Brinkman, Bulfin, & Steinfeld, 2021) and silicon (Brack et al., 2017); liquid inorganic hydrogen carriers (LIHCs), such as: ammonia<sup>5</sup> (Klerke et al., 2008) and silicon hydride derivatives (Burcher et al., 2021); and liquid organic hydrogen carriers (LOHCs), such as: toluene, benzyltoluene and methanol (Niermann et al., 2019).

Liquid hydrogen carriers seem particularly suitable for near future bulk transport of renewable hydrogen. LOHCs are liquid at ambient environmental conditions and as such can benefit from the vast fossil fuel transport and storage infrastructure that is expected to gradually become available. Ammonia is liquified under relatively mild conditions (-33° C at standard pressure) and being the second most traded substance worldwide, there is ample experience and dedicated infrastructure already in place to ship, handle, store and distribute compressed or liquified ammonia in large volumes (Marrin & Moss, 2023).

Several studies compared the effectiveness of hydrogen transport chains utilizing different liquid hydrogen carriers. Johnston et al. (2022) concluded that for bulk transport of renewable hydrogen from Australia

<sup>5</sup> Ammonia is gaseous under ambient environmental conditions, but can be liquified under relatively mild conditions (-33° C at standard pressure) and as such is considered a LIHC in this report.

to Rotterdam ammonia is the cheapest option, closely followed by methanol, while toluene and liquified hydrogen were substantially more expensive. The difference between carriers became less pronounced when the travel distance was reduced (e.g. Australia to Tokyo). In a study by the JRC (2021) travel distance was also shown to be a major determinant, with liquid hydrogen carriers becoming more favourable than gaseous or liquified hydrogen at distances of 16000 km and above. The latter study also pointed out that key in increasing the competitiveness of liquid hydrogen carriers is the optimization of the energy intensive dehydrogenation process. Besides these factors, other aspects that also play a role in determining the overall efficiency of hydrogen transport using liquid hydrogen carriers, include: the costs to purchase, produce or capture the hydrogen-lean carriers; the costs of installations to bind and release hydrogen; the amount of hydrogen that can transported per shipment (see next section); the need for hydrogen purification following release, and the need for return transport/ repeated capturing of the hydrogen-lean carrier (Johnston et al., 2022; Niermann et al., 2019).

### 4.3 Comparing energy densities of hydrogen and hydrogen carriers

The energy content of a substance can be expressed based on mass or volume, referred to as the gravimetric, respectively, volumetric energy density. With respect to bulk transport of hydrogen, the volume aspect plays an especially critical role as it determines (in contrast to mass) how much energy a tanker can carry and how much energy a storage facility can hold.

Hydrogen has one of the highest gravimetric energy densities (sometimes referred to as specific energy) with the usable energy per kg amounting to 33.3 kWh (= 120 MJ), which is around three times that of petrol (12 kWh/kg<sub>carrier</sub>). Looking at the volumetric energy density at ambient temperature and pressure the situation is completely reversed with petrol carrying around 8.8 kWh/L<sub>carrier</sub> and hydrogen just 0.003 kWh/L<sub>carrier</sub> (IDEALHY, 2013). The volumetric energy density of hydrogen can be increased to 0.78 and 1.31 kWh/L by compressing it at 350 and 700 bar, respectively. Liquifying hydrogen at -253° C yields a volumetric energy density of 2.36 kWh/L (Al Ghafri et al., 2022). Obtaining these higher volumetric densities comes at a cost, as compression costs 2-7 kWh/kg and liquification 12-15 kWh/kg, corresponding to 5-20%, respectively, 33-45 % of the energy contained in a kilogram of hydrogen. The liquification energy demand might eventually be reduced to around 6 kWh/kg (Al Ghafri et al., 2022), but it will still remain an energy-intensive process. Transporting and storage of liquified hydrogen is further hampered by boil-off losses that are around 0.5% of volume per day, but which can increase a factor 10 under suboptimal conditions (Serpell et al., 2023).

To facilitate the comparison in energy densities of hydrogen carriers between themselves and between hydrogen, the gravimetric and volumetric energy densities can be expressed in hydrogen equivalents. Hydrogen has a gravimetric energy density of 1000 kg H<sub>2</sub>/ton<sub>carrier</sub>, also referred to as a hydrogen capacity of 100 weight percent (wt%). The volumetric energy density of hydrogen amounts to 0.090 kg H<sub>2</sub>/m<sup>3</sup><sub>carrier</sub>

at ambient environmental conditions, and increases to 23 kg H<sub>2</sub>/m<sup>3</sup><sub>carrier</sub> at 350 bar, 39 kg H<sub>2</sub>/m<sup>3</sup><sub>carrier</sub> at 700 bar and 71 kg H<sub>2</sub>/m<sup>3</sup><sub>carrier</sub> at -253° C, respectively (Al Ghafri et al., 2022).

Ammonia is a gas at ambient environmental conditions, which translates in a relatively low volumetric energy density of only 0.13 kg H<sub>2</sub>/m<sup>3</sup><sub>carrier</sub> at ambient environmental conditions, while the gravimetric energy density is 178 kg H<sub>2</sub>/ton<sub>carrier</sub>. By liquefying ammonia under relatively mild conditions (>8.6 bar at ambient temperature; or -33°C at ambient pressure), a volumetric energy density of 121 kg H<sub>2</sub>/m<sup>3</sup><sub>carrier</sub> can be obtained. Boil off losses are limited for liquified ammonia amounting to around 0.025% of volume per day (Lucentini et al., 2021; Serpell et al., 2023). For more details on ammonia, see section 7.10.

Liquid hydrogen carriers, both LOHCs and LIHCs, are liquid at ambient environmental conditions. The gravimetric energy densities of the selected liquid hydrogen carriers range from 44 to 126 kg H<sub>2</sub>/ m<sup>3</sup><sub>carrier</sub>, and the volumetric energy densities range from 48 to 100 kg H<sub>2</sub>/ m<sup>3</sup><sub>carrier</sub> (for details see chapter 7). It should be noted that these are theoretical energy densities, which may be lower in practice. Examples include the use of solvents that have a diluting effect, or incomplete (de)hydrogenation due to processes such as: suboptimal reaction conditions, formation of hydrogenated intermediates or due to functional limitations of LOHCs. Where relevant with a view to substances of concern, these processes are detailed for the selected LOHCs.

## 5 Liquid hydrogen carriers

### 5.1 The underlying principle

Liquid hydrogen carriers can be carbon based substances (Liquid Organic Hydrogen Carriers; LOHC) or substances without carbon in their molecular structure (Liquid Inorganic Hydrogen Carriers; LIHC). The hydrogen-lean carrier can chemically bind hydrogen, thereby forming a different substance, i.e. the hydrogen-rich carrier. Upon request the hydrogen can be released from the hydrogen-rich carrier yielding the hydrogen-lean carrier again. Hydrogen pressure, temperature and type of catalyst play an important role in these processes. A solvent may also be required.

The uptake of hydrogen is an exothermic reaction that produces energy in the form of heat. This process is termed hydrogenation. The release of hydrogen, i.e. dehydrogenation, is an endothermic reaction that cost energy. As discussed in section 7.11, there is one exemption to this general principle, with the LIHC silicone hydride derivatives requiring energy during hydrogenation and releasing heat during dehydrogenation.

The amount of hydrogen that can be bound depends on the substance and varies for the most common liquid hydrogen carriers from one to nine hydrogen molecules per molecule of carrier. Hydrogen capacity can be expressed by weight or volume of the carrier as discussed in section 4.3. For a selected number of liquid hydrogen carriers, chapter 7 will provide an overview of their most important technical characteristics as illustrated in the figure shown below.

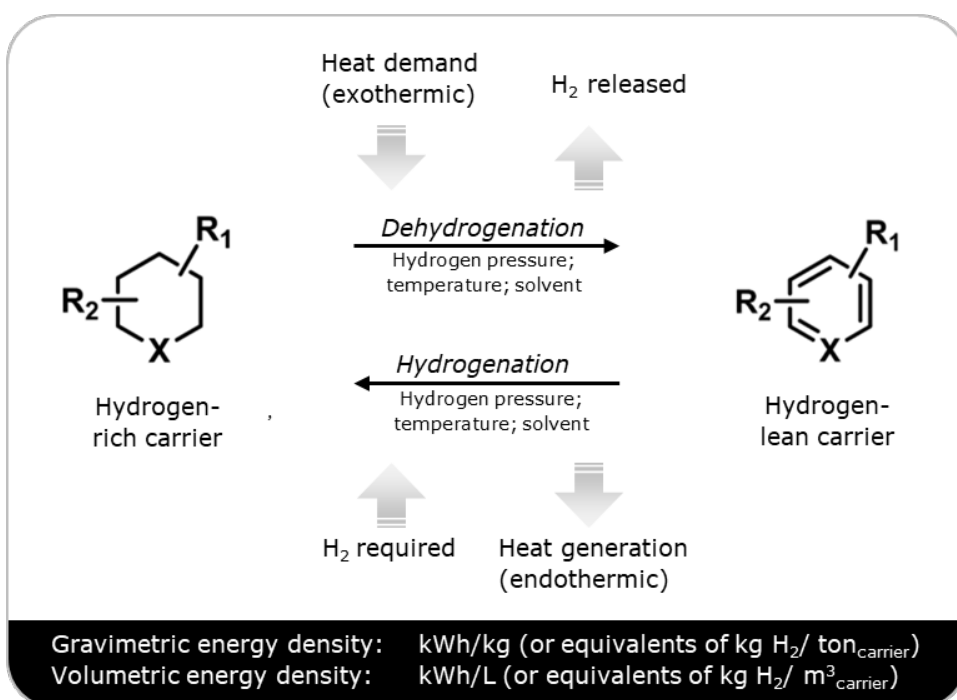


Figure 2 Schematic representation of a liquid hydrogen carrier.

## 5.2 Properties of liquid hydrogen carriers

For a substance to be used as a liquid hydrogen carrier, several requirements need to be met. The requirements can relate to functional and practical substance properties, with the most important ones being discussed below. For a comprehensive review of relevant substance properties see Niermann et al. (2019), Rao and Yoon (2020) and Cho et al. (2021). Except for Cho et al. (2021) who included ammonia in their review, the other studies only considered LOHCs. For LIHCs in principle the same considerations apply as for LOHCs.

From a functional point of view, it is crucial that a liquid hydrogen carrier can sufficiently and efficiently bind hydrogen, that a high degree of hydrogenation can be achieved and that practically all hydrogen can be released during dehydrogenation. Rapid hydrogenation and dehydrogenation of the hydrogen carriers is preferred, preferably under relatively mild conditions (e.g. not too high energy demand), with the necessary catalysts being stable, reusable, and active under relatively mild conditions. When the liquid hydrogen carrier is of the reversible type, with the hydrogen-lean carrier being repeatedly hydrogenated and dehydrogenated, it is important that (thermal) stable substances are used to minimize degradation and by-product formation.

Other more practical considerations are that the hydrogen-lean and hydrogen-rich carriers are both liquid under ambient environmental conditions (e.g. low melting point) and not too viscous. In some cases this requires the use of a solvent (e.g. toluene is used to keep naphthalene liquid (see section 7.5)), or the lowering of the temperature (e.g. ammonia is liquefied at -33 °C (see section 7.10)). Another practical advantage is when the released hydrogen can easily be separated or purified from the reaction mixture after dehydrogenation (e.g. a high boiling point and low vapor pressure of the carriers). Finally, the availability and price of the hydrogen-lean carriers and the necessary catalysts are important aspects too.

In addition to these functional and practical requirements, the hazardous properties of the substances should be taken into account, preferably as early in the process as possible. Thereby also considering their impact on health, climate and the environment during the entire lifecycle of the substances. This complies with a SSbD approach (Caldeira et al., 2022) and can help preventing the introduction of substances that can cause serious problems in the future.

## 5.3 Overview of the field and selection of liquid hydrogen carriers

There is a clear distinction between LIHCs and LOHCs with respect to the number of potential candidates. For LIHCs, two candidates have been found, one of the verge of commercial application, the other in an earlier development phase. Both types were selected for further investigation in chapter 7. With respect to LOHCs, many organic substances are being proposed as candidates, with some of them already extensively researched and on the verge of commercial application. At the same time, the search for new LOHC candidates is still ongoing and various chemical structures that are able to bind and release hydrogen are considered (see Figure 3). Based on the overview provided in Figure 3,

several LOHCs that represent the broadness of the field, including the currently most promising candidates, were selected for further investigation in Chapter 7. The selected substances are shown in Table 2.


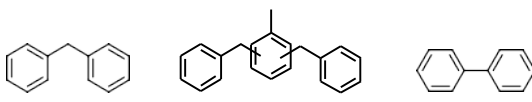
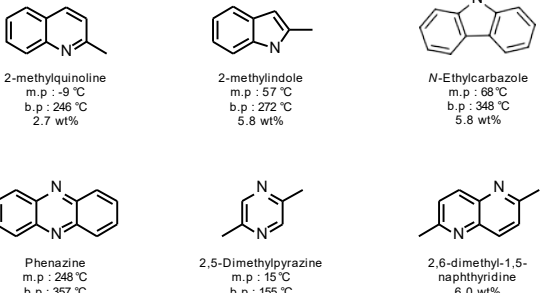


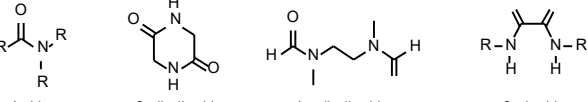
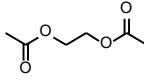





<b>Formic Acid, Formaldehyde</b>  Formic acid m.p.: 8.4 °C b.p.: 100.8 °C 4.4 wt% Formaldehyde m.p.: -92 °C b.p.: -19 °C 8.4 wt%		<b>Homocyclic Compound</b>  Diphenylmethane m.p.: 22 °C b.p.: 264 °C 6.9 wt% Dibenzyltoluene m.p.: -39 °C b.p.: 390 °C 6.2 wt% Biphenyl m.p.: 69 °C b.p.: 255 °C 6.9 wt%		
<b>N-Heterocyclic compound</b>  2-methylquinoline m.p.: -9 °C b.p.: 246 °C 2.7 wt% 2-methylindole m.p.: 57 °C b.p.: 272 °C 5.8 wt% N-Ethylcarbazole m.p.: 68 °C b.p.: 348 °C 5.8 wt% Phenazine m.p.: 248 °C b.p.: 357 °C 7.2 wt% 2,5-Dimethylpyrazine m.p.: 15 °C b.p.: 155 °C 5.3 wt% 2,6-dimethyl-1,5-naphthyridine 6.0 wt%			<b>Urea</b>  Urea m.p.: 133 °C b.p.: 165 °C	
			<b>Carbamate</b>  Carbamate m.p.: 60 °C b.p.: 25 °C 5.3 wt%	
<b>Amide</b>  Amide Cyclic diamide m.p.: 311 °C b.p.: 574 °C 6.6 wt% Acyclic diamide Oxalamide				<b>Ester/Alcohol</b>  Ester m.p.: -31 °C b.p.: 190 °C 6.5 wt%
<b>Imide</b>  Cyclic imide 6.7 wt%	<b>Nitrile</b>  Benzonitrile m.p.: -13 °C b.p.: 191 °C 13.3 wt%	<b>Amine Borane</b>  B,N-Heterocycle 4.7 wt%	<b>Silane/Alcohol pair</b>  1,4Disilabutane b.p.: 235 °C 4.3 wt%	<b>Ketone</b>  Acetophenone m.p.: 16 °C b.p.: 202 °C

Figure 3 Overview of chemical structures characteristic of substances that can be used as LOHC. Relevant parameters such as melting point (mp), boiling point (bp) and hydrogen capacity are also given (adapted from Cho et al. (2021)).

## LOHC

LOHCs can be broadly divided into three groups:

### Group 1: Reversible (n-hetero)aromatic LOHCs

The hydrogen-lean carriers of this group have conjugated double bonds within an aromatic ring. Cycloalkanes are obtained after hydrogenation. While dehydrogenation of alkanes (without double bonds) to alkenes (having isolated or conjugated double bonds) is thermodynamically hardly feasible, the dehydrogenation of cycloalkanes back to the corresponding aromatic structures is possible due to the very stable aromatic system that is formed (Müller, Völkl, & Arlt, 2013). This has been recognized early on in the LOHC development process, and

aromatic LOHCs are the best researched group and closest to application. They are termed reversible LOHCs, as the hydrogen-lean carrier is transported back to repeat the process (Cho et al., 2021). Examples include substances with one aromatic ring (e.g. benzene and toluene), substances with two or more aromatic rings (e.g. benzyltoluene and dibenzyltoluene), as well as substances with conjugated aromatic structures (e.g. naphthalene) (Niermann et al., 2019). The conjugated aromatic structures can also be substituted (e.g. methylbenzyl naphthalene) (Rao et al., 2023).

Characteristic of aromatic LOHCs is the relatively high temperature required to dehydrogenate the hydrogen-rich LOHCs. Presence of one or more nitrogen atoms in the aromatic ring makes dehydrogenation generally thermodynamically more favourable (Müller, Völkl, & Arlt, 2013). The substance *n*-ethylcarbazole has been investigated for LOHC use. Other nitrogen substituted compounds are also proposed, but have been less researched (e.g. various indole, quinoline, phenazine, pyrazine and pyridine compounds (Cho et al., 2021; Hu et al., 2015; Rao & Yoon, 2020)). *n*-Heteroaromatic compounds with boron, i.e. azaborines (e.g. 1,2-dihydro-1,2-azaborine) have also been proposed (Niermann et al., 2019). As their dehydrogenation should be thermodynamically even more favourable. They do suffer from complex synthesis and lower stability in the long term (Müller, Völkl, & Arlt, 2013). Besides nitrogen, heteroatoms can also be substituted with oxygen or sulphur. These LOHCs are considered less attractive as the substitutions have a negative effect on dehydrogenation (Müller, Völkl, & Arlt, 2013) and hydrogenation (Eblagon & Tsang, 2015).

In addition to the above noted (hetero)aromatic LOHCs, new candidates are being researched either on a case-by-case assessment (Jeong et al., 2023; Rao et al., 2023), or using high-throughput methods. Verevkin et al. (2021) used an *in silico* method to find new pyrazine derivatives, while Paragian et al. (2020) designed a workflow searching a database with 1 million substances for promising LOHC pairs based on LOHC relevant properties such as melting point, boiling point, dehydrogenation enthalpy, hydrogen capacity and synthetic accessibility of the substances.

#### *Group 2: Reversibly coupled LOHCs*

The hydrogen-lean carriers of this group are esters, peptides or amides that are catalytically cleaved during hydrogenation. The resulting hydrogen-rich carriers are substances, such as alcohols, amines and ethylene glycol. Dehydrogenation occurs during catalytic coupling of the hydrogen-rich carriers yielding the initial structures and thereby releasing the hydrogen (Kumar, Daw, & Milstein, 2022). Hence, the name reversible coupled LOHCs. Examples are: esters formed from ethylene glycol (Zou et al., 2019); ester formed from ethylene glycol and ethanol (Zhou et al., 2020); glycine anhydride (piperazine-2,5-dione) formed from 2-aminoethanol (Hu et al., 2015); and amides formed from various amines and alcohols (Kar et al., 2020).

Research on reversibly coupled LOHCs is still in an early phase and relies heavily on a specific type of organometallic catalysts called ruthenium pincer complexes. A recent review article showed that

(de)hydrogenation and dehydrogenation using these catalysts can take place with and without solvent at a range of hydrogen pressures and temperatures (Kumar, Daw, & Milstein, 2022).

### *Group 3: Circular LOHCs*

The hydrogen-lean carrier of circular LOHCs is carbon dioxide. Following hydrogenation small organic molecules such as formic acid and methanol are formed. These hydrogen-rich carriers have widely been used as raw material and/or fuel, which delayed investigations into their use as LOHCs. This is changing and especially methanol is in the focus as LOHC (Araya et al., 2020; Niermann et al., 2021). After dehydrogenation, the gaseous hydrogen-lean carrier carbon dioxide is released to the atmosphere, hence the name circular LOHCs (Cho et al., 2021). There is no return transport for the hydrogen-lean carrier, instead during each cycle carbon dioxide is captured. Provided that the carbon dioxide is captured from the atmosphere in the first place, there is no net increase in carbon dioxide with the use of circular LOHCs. The challenge for this type of LOHCs is to efficiently capture carbon dioxide from the atmosphere and to efficiently convert it into organic molecules.

### **LIHC**

For the circular LIHC ammonia, the same principle applies as described above for circular LOHCs, with the difference that nitrogen is the hydrogen-lean carrier and not carbon dioxide.

Information on the recently proposed LIHC silica hydrate derivatives (Burcher, Lome, & Benoit, 2019; Burcher et al., 2021) is very limited. The hydrogen-lean carriers are indicated as silica and/or silicate compounds and a return transport of the hydrogen-lean carriers is foreseen after dehydrogenation (i.e. hydrolytic oxidation), corresponding to a reversible LIHC. However, other sources of silica and/or silicate containing minerals are also indicated as usable starting material (e.g. sand, quartz, zircon). In either case the silica and/or silicate is first reduced to elemental silicon that is then stepwise hydrohalogenation to halosilanes that are hydrolysed to the hydrogen-rich carriers, i.e. halogen terminated carbon-free linear siloxanes (see section 7.11 for details). There might be no need for a return transport of the hydrogen-lean carriers, as silica and/or silicate containing minerals are generally abundantly present, and in practice it might resemble a circular LIHC. For now, silica hydrate derivatives is considered a reversible LIHC.

*Table 2 Liquid hydrogen carriers selected for further investigation in chapter 7*

<b>Liquid hydrogen carrier</b> (H <sup>+</sup> and H <sup>-</sup> -carrier)	<b>Type</b>
Methylcyclohexane and toluene	Reversible aromatic LOHC
Perhydrodibenzyltoluene and dibenzyltoluene	Reversible aromatic LOHC
Decahydronaphthalene and naphthalene	Reversible aromatic LOHC
Dodecahydro- <i>n</i> -ethylcarbazole and <i>n</i> -ethylcarbazole	Reversible heteroaromatic LOHC
Ethylene glycol and esters of ethylene glycol	Reversible coupled LOHC

<b>Liquid hydrogen carrier</b> (H <sup>+</sup> and H <sup>-</sup> -carrier)	<b>Type</b>
Formic acid and carbon dioxide	Circular LOHC
Methanol and carbon dioxide	Circular LOHC
Ammonia and nitrogen	Circular LIHC
Silica hydrate derivatives and silica/silicate	Reversible LIHC

## 6 Dealing with substances of concern

Substances, i.e. chemicals, possess various properties. Certain properties are needed for a substance to fulfil the function intended, in this case the ability to bind and release hydrogen. Other properties might be less desirable and can make a substance hazardous, for example explosive or carcinogenic, leading to concerns.

From a Safe-and-Sustainable by Design (SSbD) point of view, substances of concern should early on in the process be identified and should wherever possible be substituted with less hazardous alternatives. If that is not possible, their production and use should be minimized in line with, and beyond existing and upcoming regulatory obligations. At the same time, the impact on health, climate and the environment during the entire lifecycle of substances of concern should be minimized. These considerations are meant to steer the innovation process towards a green and sustainable industrial transition (Caldeira et al., 2022). Such an integral approach is advocated by the European Commission who recently recommended the establishment of a SSbD framework (EC, 2022b) with support from the Netherlands (Rijksoverheid, 2022).

When substances of concern are used it is necessary to adequately deal with them. To do so, different laws, policies, regulations, and transport agreements have been put in place on national, EU and international level aiming to protect public, workers and/or the environment. These can be hazard- or risk-based, with the latter assessing risks arising from exposure to hazardous substances.

### 6.1 Current state for liquid hydrogen carriers

In the ongoing liquid hydrogen carrier discussions, focus has so far primarily been on substances of concern in terms of external safety (Arcadis & Berenschot, 2021; Berenschot, Arcadis, & TNO, 2023). This risk-based approach assess the potential for high-risk situations to occur during transport, production, storage and use of hydrogen carriers with the aim to protect the public and the environment. The hazards considered are mainly flammability, explosiveness and acute toxicity to man and the environment (Timmers, Uijt de Haag, & Verklei, 2022). In the light of hydrogen transport and storage, one can think of hydrogen leakages leading to fires and explosions, as well as ammonia accidents resulting in toxic clouds, both of which can potentially lead to high number of casualties.

Niermann et al. (2019) reported for several LOHCs Toxic Potential Indicator (TPI) values in order to compare their toxicity. The methodology to derive these environmental screening indicators was developed by Fraunhofer IZM and is based on German legal classifications, i.e. risk values derived from chemical legislations (R-values), maximum workplace concentrations (MAK), water hazard classes (WGK) and carcinogenic classifications as input. The use of these

TPI values for other means than the broad comparison between substances seems limited.

Focus on hazard properties that are generally less evident in the short run, but may have serious effects on human health and the environment, have generally not received a lot of attention in the liquid hydrogen carrier discussions. To our knowledge, only Markiewicz et al. (2015) stressed the importance to investigate early on in the LOHC development process the harmful effects of substances on human health and/or the environment, thereby specifically referring to the hazardous properties that are under the REACH regulation ((EC) 1907/2006) considered as criteria to identify a substance as a Substance of Very High Concern (SVHC) (see section below).

## 6.2 SVHCs under the REACH regulation

For a substance to be identified as a SVHC under the REACH regulation, it must meet one or more of the criteria laid down in Article 57 of the REACH regulation, being:

- a) Carcinogenic (C)\*;
- b) Mutagenic (M)\*;
- c) Toxic to reproduction (R)\*;
- d) Persistent, bioaccumulative and toxic (PBT)\*\*;
- e) Very persistent and very bioaccumulative (vPvB)\*\*;
- f) Equivalent level of concern for human health or the environment (for example due to endocrine disrupting (ED), but also persistent, mobile and toxic (PMT); and very persistent and very mobile (vPvM) properties).

\* *Category 1A or 1B according to the CLP regulation (EC) 1272/2008.*

\*\* *In accordance with the criteria set out in REACH Annex XIII.*

A substance becomes formally a SVCH under the REACH regulation after it has been identified as such by the European Chemicals Agency (ECHA) Member State Committee (MSC) and has been added to the Candidate list of SVHC for Authorisation. As of June 2023, the Candidate list contains 235 entries, with some entries being for groups of substances, making the overall number of listed substances 476 (ECHA, 2023a).

Listing of a SVCH on the Candidate List triggers legal obligations under REACH. Suppliers of articles containing the SVHC in a concentration above 0.1% weight of the article, must inform their customers (and upon request consumers too) about the presence of the substance, and must provide them with sufficient information to allow safe use of the article. Furthermore, the suppliers must notify ECHA under the REACH regulation and the waste framework directive. For substances identified as SVHC based on their PBT and/or vPvB properties, suppliers and downstream users must also implement necessary measures for minimising the releases and exposures in the whole supply chain and lifecycle. SVHCs can eventually also be prioritised for Authorisation (Annex XIV) which would prevent their placement on the market and their use, unless an authorisation for specific use(s) is granted by the European Commission. Alternatively, the Restriction route (Annex XVII) can be chosen, limiting or banning their manufacture, placing on the market (including imports) or use. Both processes aim to reduce SVHC

emissions where possible, but add up to the already long timelines as is detailed below.

SVHC identification under the REACH regulation can be a lengthy process. It requires an EU Member State or ECHA (upon request by the European Commission) to file a proposal for inclusion, i.e. an Annex XV SVHC report. This is also the case for carcinogenic, mutagenic or reprotoxic (CMR) substances that are listed in Table 3 to Annex VI of the CLP regulation as C, M or R category 1A or 1B substances, and that thus already meet the SVHC criteria. For CMR substances that are not listed in Annex VI to the CLP regulation, while strictly no required, a harmonised classification as C, M or R category 1A or 1B is generally first pursued. Addition of a substance to Annex VI of the CLP regulation is also a process that can take several years, as it requires an EU Member State or ECHA to fill a proposal for harmonised classification, assessment by ECHA's Committee for Risk Assessment (RAC) and adoption by the European Commission. It is expected that in the near future the same approach will be followed for SVHC identification of substances with PBT, vPvB or equivalent level of concern properties, as is now the case for substances with CMR properties. The underlying reason is that per 20 April 2023 the CLP regulation has been amended, including new hazard classes and classification criteria, namely: PBT, vPvB, PMT, vPvM, ED human health and ED environment. The new hazard classes can already be used, but will become mandatory for new substances per 1 May 2025, and for existing substances per 1 November 2025 (EC, 2022a).

### 6.3 Dutch policy on ZZS

On a national level, the Dutch government made it a priority to address Substances of Very High Concern, which are in Dutch termed '*Zeer Zorgwekkende Stoffen*' (ZZS). Aim is to keep ZZS as much as possible out of the living environment (Heijnen, 2022). This can be achieved by preventing emissions to air and water through substitution with safer alternatives as well as by organisational and technological changes. When emissions cannot be prevented, emissions are to be minimized as much as possible. This has been laid down in the Environmental Management Activity Decree (Rijksoverheid, 2023). This decree also states that the criteria for ZZS are derived from Article 57 of the REACH Regulation (see above).

The criteria to derive ZZS are identical to the criteria used for SVHC identification under the REACH regulation. Still the Dutch ZZS list covers a broader range of substances (2172 substances as of 25 August 2023) compared to ECHA's Candidate list. This is because the ZZS list contains the formally identified SVHC on the Candidate list, but also substances that comply with the SVHC criteria regardless of a formal SVHC status under the REACH regulation. This specifically concerns substances that have been listed in one of the following international regulations:

- Substances that are classified as C, M, or R category 1A or 1B according to the CLP regulation (EC) 1272/2008.
- Substances that are identified as Persistent Organic Pollutant (POP) in the Stockholm Convention regulation (EC) 850/2004.

- Priority Hazardous substances according to the Water Framework Directive 2000/60/EC.
- Substances on the OSPAR list for priority action.

Thus, while the term ZZS does not exclusively refer to formally identified SVHC's under the REACH regulation, the criteria used to reach a SVHC conclusion are identical. It is stressed that the difference between substances listed in ECHA's Candidate list and the Dutch ZZS list is in principle only procedural in nature.

In addition to the non-exhaustive ZZS list, there is also an exhaustive list of potential ZZS available (<https://rvszoekstysteem.rivm.nl/ZZSlijst/PotentieleZZSlijst>). Potential ZZS are substances that may meet the ZZS criteria, but have not yet been identified as ZZS. This could be because certain data are missing, or because the evaluation of the available data has yet to take place. The potential ZZS list is meant as a tool for competent authorities. Substances that have a CLP self-classification as CMR cat. 1A/1B are not added to the potential ZZS list, but should be treated as falling in the category "consider as ZZS".

Both the ZZS list as the potential ZZS list are updated by the Dutch National Institute for Public Health and the Environment (RIVM) twice yearly.

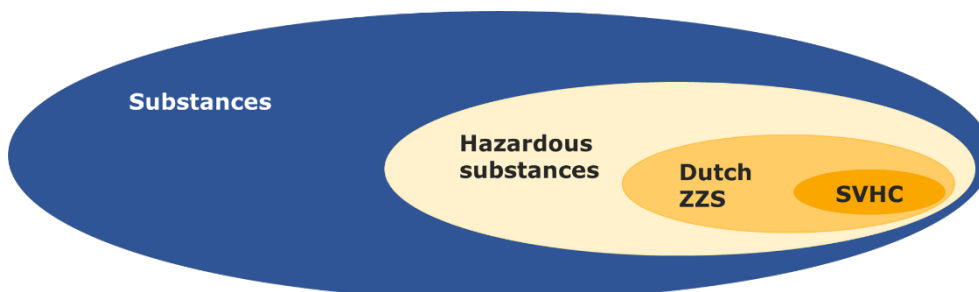


Figure 4 Dutch ZZS put in perspective.

## 7 Selected liquid hydrogen carriers and their ZZS properties

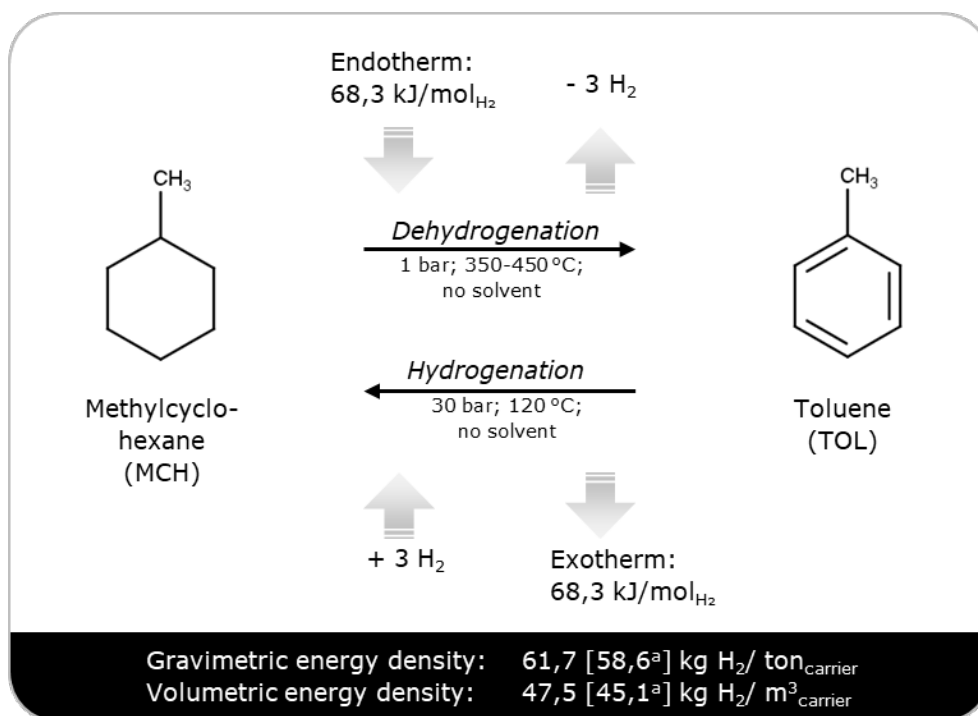
The liquid hydrogen carriers elaborated in this chapter have been selected to cover the width of the field, including the different LOHC types available, and the identified LIHCs. Inherent to this choice is that the information density of the discussed liquid hydrogen carriers can vary. After all, while for some candidates large-scale demonstration projects are ongoing, for others it remains to be determined whether laboratory-scale tests can be scaled up.

Each of the selected liquid hydrogen carriers is discussed in a separate section consisting of four paragraphs. The first paragraph gives the main ZZS conclusions and present the key technical characteristics of the liquid hydrogen carrier in a graphical overview. The following three paragraphs elaborate on the technical aspects of the liquid hydrogen carrier, the by-product forming and the derivation of the ZZS status of relevant substances, respectively. Relevant substances include the hydrogen-rich and hydrogen-lean carriers, but also the identified solvents and by-products.

### 7.1 **Methylcyclohexane and toluene (MCH/TOL)**

#### 7.1.1 *ZZS conclusions and system overview*

The hydrogen-lean carrier methylcyclohexane and the hydrogen-rich carrier toluene are not likely to have ZZS properties. However, the ZZS benzene was detected as substantial by-product in all the studies that investigated the stability of the MCH/TOL system. The polycyclic aromatic hydrocarbons (PAHs) phenanthrene and naphthalene were also found, albeit in very low concentrations. Both PAHs are ZZS. It is noted that by-product formation can play a far greater role under operational conditions where numerous hydrogenation-dehydrogenation cycles will be conducted under potentially less optimal conditions.



<sup>a</sup> In practice, maximum dehydrogenation is not achieved (Niermann et al., 2019)

Figure 5 Schematic representation of the MCH/TOL system.

### 7.1.2 Characteristics of the MCH/TOL system

#### **Type:**

Reversible aromatic LOHC. Return transport of the hydrogen-lean carrier is required to repeat the cycle.

#### **Availability:**

Toluene is widely available as raw material and solvent (REACH registration: 1 to 10 million tons per year). Methylcyclohexane is available in somewhat smaller quantities and is primarily used as solvent (REACH registration: 1 to 10 thousand tons per year). The price toluene is low, 0.3 €/kg (Niermann et al., 2019).

#### **Dehydrogenation:**

High temperature (350-450 °C) required, making it an energy demanding process (Niermann et al., 2019; Rao & Yoon, 2020). Both the hydrogen-rich and the hydrogen-lean carriers are gases during dehydrogenation, which complicates the purification of hydrogen (Niermann et al., 2019). As dehydrogenation progresses, hydrogen release becomes inhibited as the formed hydrogen-lean carrier blocks the catalyst (Pt, Ni) (Geißelbrecht et al., 2020). This limits dehydrogenation in practice to 95% (Niermann et al., 2019).

#### **Transport and storage:**

Under ambient environmentally conditions, both substances are volatile, flammable and non-viscous liquids. Transport and storage is comparable to current fuels (Arcadis & Berenschot, 2021).

#### **State of technology:**

The MCH/TOL system has been extensively tested by a Japanese consortium under the name SPERA Hydrogen<sup>®</sup>, including a demonstration shipment from Brunei to Japan in 2020 (Chiyoda Corporation, 2022). In 2022, a project using the MCH/TOL system was announced from Scotland to the Port of Rotterdam in cooperation with

Chiyoda. No timelines, nor target volumes have been announced (Net Zero Technology Centre, 2022). In 2023, Honeywell announced that they are offering a MET/TOL system for long-distance transport of clean hydrogen (Honeywell, 2023).

### 7.1.3 *Stability of the MCH/TOL system*

By-product formation during methylcyclohexane dehydrogenation has been studied extensively (Alhumaidan et al., 2013; Hamayun et al., 2020; Okada et al., 2006; Usman, Cresswell, & Garforth, 2011). In all studies benzene was formed, regardless of the test duration, reactor type, and test conditions (e.g. temperature, hydrogen pressure and type of catalyst). Usman, Cresswell and Garforth (2011) also identified cyclohexane, dimethylcyclopentanes and ethylcyclopentane. Alhumaidan et al. (2013) reported many more by-products, including: paraffins (methylhexane and heptane), substituted-cyclopentanes (dimethyl- and ethyl-cyclopentanes), methylcyclohexene, xylene isomers, substituted biphenyls (biphenyl, methylbiphenyl and dimethylphenyl isomers) and very low concentrations of the polycyclic aromatic hydrocarbons naphthalene and phenanthrene.

Alhumaidan et al. (2013) showed that the forming of the two primary by-products benzene and xylene depended on the type of platinum catalysts used (all test were performed under operational conditions: pressure of 1 bar and temperature of 350-380 °C). The amount of by-products generally increased with increasing degree of dehydrogenation. For example, benzene concentrations were ~120-1500 ppm (1 ppm = 1 mg/L) at 93% dehydrogenation and increased to ~200-6700 ppm at 99% dehydrogenation. For xylene this was ~240-670 ppm and ~280-1600 ppm, respectively.

It is noted that under operational conditions, where numerous cycles of hydrogenation and dehydrogenation will take place at high temperature and potentially less optimal conditions, more (and possibly other) by-products can be formed.

### 7.1.4 *ZZS status derivations for the MCH/TOL system*

The table below summarizes the derived ZZS statuses for the hydrogen carriers of the MCH/TOL system and the by-products identified. The ZZS derivations are elaborated after the table.

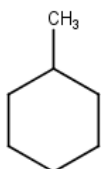
*Table 3. ZZS statuses of substances relevant for the MCH/TOL system*

<b>CAS number</b>	<b>Substance name</b>	<b>ZZS status</b>	<b>Type of substance/ Remarks</b>
108-87-2	Methylcyclohexane	Probably not of equivalent concern as ZZS or potential ZZS	Hydrogen-rich carrier
108-88-3	Toluene	Probably not of equivalent concern as ZZS or potential ZZS	Hydrogen-lean carrier
71-43-2	Benzene	ZZS	By-product

CAS number	Substance name	ZZS status	Type of substance/ Remarks
108-38-3; 95-47-6; 108-38-3; 106-42-3	Xylene	No statement possible about the ZZS status	By-product; racemic mixture; isomers
85-01-8	Phenanthrene	ZZS	By-product
91-20-3	Naphthalene	ZZS	By-product

#### Elaborations on ZZS status derivation

#### **Methylcyclohexane: hydrogen-rich carrier**



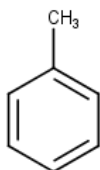
CAS number: 108-87-2

Type: mono-constituent substance (structure shown)

Conclusion: Probably not of equivalent concern as ZZS or potential ZZS.

Substantiation: Following a substance evaluation, the substance was assessed in 2017 as not being bioaccumulative, and therefore not a PBT nor a vPvB substance (Finnish CA, 2017). There are no harmonized CLP classifications or CLP-self classifications as CMR category 1A or 1B. There are also no category 2 CLP (self) classifications or other indications for CMR or ED properties. Altogether, the data available for methylcyclohexane do not indicate a ZZS-related concern.

#### **Toluene: hydrogen-lean carrier**



CAS number: 108-88-3

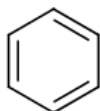
Type: mono-constituent substance (structure shown)

Conclusion: Probably not of equivalent concern as ZZS or potential ZZS.

Substantiation: The harmonized CLP classification is Repr. 2 (index no. 601-021-00-3). There are some CLP self-classifications (18 of >8000) that classify the substance as Repr. 1A or Muta. 1B + Carc. 1A. The data in the registration dossier do not support the heavier self-classifications. The similarity tool gives no hits with reproduction toxic substances. The hits with carcinogenic substances are irrelevant. The latter considers, chlorotoluene (CAS 100-44-7), o-toluidine (CAS 95-53-4) and dichlorotoluene (CAS 98-07-7) with agreements of 97, 52 and 50%, respectively. These substances have different functional groups (chloro and amine) than toluene (methyl), which makes them more reactive than toluene and therefore not good predictors for the toxicity of

toluene. Altogether, the data available for toluene do not support the CMR 1A/B self-classifications and do not indicate a ZS-related concern

**Benzene: by-product**



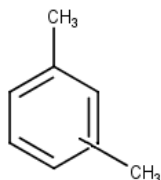
*CAS number:* 71-43-2

*Type:* mono-constituent substance (structure shown)

*Conclusion:* ZS

*Substantiation:* Benzene is on the ZS list due to harmonized CLP classifications as Carc. 1A and Muta. 1B (index no. 601-020-00-8).

**Xylene: by-product**



*CAS numbers:* 108-38-3 (racemic mixture of isomers); 95-47-6 (ortho-isomer); 108-38-3 (meta-isomer); 106-42-3 (para-isomer)

*Type:* Multi-constituent (isomer structures shown)

*Conclusion:* No statement possible about the ZS status.

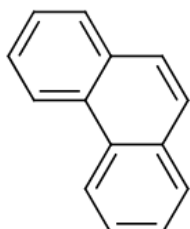
*Substantiation:* The meta and ortho isomers were listed on the potential ZS list (due to CoRAP<sup>6</sup> listing), but were removed in 2022 following the finalization of the Substance Evaluation (SEv). The SEv noted that in absence of an immediate concern for developmental toxicity a developmental toxicity in a second species (rabbit) (PDNT; OECD TG 414) study was requested via ECHA's dossier evaluation procedure. The study showed no developmental toxicity, but as it became only very late in the SEv process available, it could not be assessed in depth. The SEv concluded that the reproductive toxicity concern remained unresolved (BAuA, 2021). There are some CLP self-classifications for Repro. 1B (1 of 1282 for p-xylene; and 18 of 7342 for the racemic mixture).

However, there is no data to support these CLP self-classifications. The models applied also do not give a clear picture. While the OECD toolbox gives CMR alerts for DNA binding (Michael addition) and reprotoxic and developmental toxicity potential (DART), the similarity tool gives no hits with reproduction toxic substances. The hits with carcinogenic substances are irrelevant. Chlorotoluene (CAS 100-44-7) and o-toluidine (CAS 95-53-4) with an agreement of 84 and 51%, respectively, have different functional groups (chloro and amine) than xylene (methyl), which makes them more reactive than xylene and therefore not good predictors for the toxicity of xylene. An extended one-generation reproductive toxicity study (EOGRT; OECD TG 443) with the para isomer is in the planning stage and may provide a definitive answer on reproductive toxicity in due course. The conclusion is that, pending the

<sup>6</sup> CoRAP stands for Community Rolling Action Plan under the REACH regulation. Listing a substance under CoRAP precedes a Substance Evaluation (SEv) of the substance.

outcome of the EOGRT study, at this stage no statement can be made regarding the ZZS status of xylene.

**Phenanthrene: by-product**



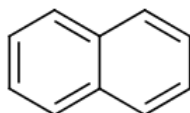
*CAS number:* 85-01-8

*Type:* mono-constituent substance (structure shown)

*Conclusion:* ZZS

*Substantiation:* Phenanthrene is on the ZZS list because of its placement on the candidate list for REACH Annex XIV on the basis of vPvB properties. Phenanthrene is also part of the group of polycyclic aromatic hydrocarbons (PAHs) that are on the ZZS list because they are on the Water Framework Directive list of priority hazardous substances; on the OSPAR list of substances for priority action; and based on the POP regulation.

**Naphthalene: by-product**



*CAS number:* 91-20-3

*Type:* mono-constituent substance (structure shown)

*Conclusion:* ZZS

*Substantiation:* Naphthalene is not identified as an individual substance as ZZS but falls under the ZZS substance group for PAHs. Based on the POP regulation, all PAHs are identified as ZZS.

**7.2 Perhydrodibenzyltoluene and dibenzyltoluene (H18-/H0-DBT)**

**7.2.1 ZZS conclusions and system overview**

The hydrogen-lean carrier dibenzyltoluene is considered as ZZS, as there are sufficient indications that the substance meets ZZS criteria. The hydrogen-rich carrier perhydrodibenzyltoluene is of equivalent concern as ZZS or potentially ZZS. In addition, benzene is formed as a by-product. Benzene is a ZZS.



**Transport and storage:**

Under ambient environmentally conditions, both substances are viscous and flammable liquids. At lower temperatures, the substances tend to clump. Transport via pipelines is not considered plausible (Arcadis & Berenschot, 2021). The viscosity of dibenzyltoluene can be reduced by mixing with benzyltoluene (Jorschick et al., 2020). Transport and storage comparable to current fuels although complicated by the higher viscosity. Pipelines not possible.

**State of the technology:**

The H18-/H0-DBT system has been extensively tested and appeared to be marketed by a German company focusing on LOHCs. However, the company seems to have opted for the comparable LOHC system perhydrobenzyltoluene/ benzyltoluene (Hydrogenious LOHC Technologies, 2023).

7.2.3 *Stability of the H18-/H0-DBT system*

Dehydrogenation of perhydrodibenzyltoluene produces by-products, especially at a higher degree of dehydrogenation (Fikrt et al., 2017; Modisha & Bessarabov, 2020).

Fikrt et al. (2017) detected after one dehydrogenation under standard conditions (platinum catalyst; ~305 °C; 1.2 to 1.5 bar) up to 0.044 wt% of volatile by-products: cyclohexane (30-40%); methylcyclohexane (17-35%); benzene (17-34%); toluene (5.6-10.2%) and methane (8.5-9.5%). The authors indicated that detection of methane indicates the formation of substances such as dibenzylbenzene and benzyltoluene, which remain in the liquid phase. Liquid phase was not investigated. Modisha and Bessarabov (2020) performed 15 hydrogenation/dehydrogenation cycles (nickel catalyst; 8 bar overpressure; temperature was increased every 5 cycles 300, 320 and 340 °C). By-product formation increased with time and higher temperatures and amounted to 4.7, 5.8 and 6.5 mol%, respectively. In a stress test conducted at 355 °C for 2.2 hours, the following by-products were found: benzyltoluene (4.3 mol%), xylene (0.33%), toluene (1.3 mol%), benzene (0.22 mol%) and methane (1.9 mol%). But also benzylmethylfluorene and other unspecified by-products C<sub>13-15</sub> (0.32 mol%) and C<sub>21</sub> (0.32 mol%). The authors point out that hydrogenation of by-products can yield other by-products, but can also lead to complete degradation (hydrocracking).

7.2.4 *ZZS status derivations for the H18-/H0-DBT system*

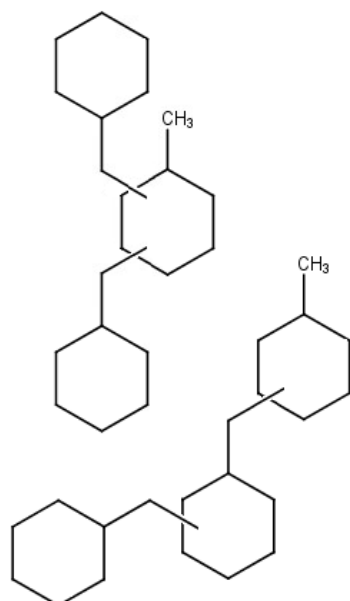
The table below summarizes the derived ZZS statuses for the hydrogen carriers of the H18-/H0-DBT system and the by-products identified. The ZZS derivations are elaborated after the table.

Table 4 ZZS statuses of substances relevant for the H18 /H0-DBT system

CAS number	Substance name	ZZS status	Type of substance/ Remarks
CAS no.: -; EC no.: 943-342-4	Perhydro-dibenzyltoluene	Of equivalent concern as potential ZZS	hydrogen-rich carrier; UVCB; Assessment based on perhydro - dibenzyltoluene.
53585-53-8	Dibenzyltoluene	Consider as ZZS	hydrogen-lean carrier; UVCB;
110-82-7	Cyclohexane	Probably not of equivalent concern as ZZS or potential ZZS	By-product
108-87-2	Methyl cyclohexane	Probably not of equivalent concern as ZZS or potential ZZS	By-product
71-43-2	Benzene	ZZS	By-product
108-88-3	Toluene	Probably not of equivalent concern as ZZS or potential ZZS	By-product
108-38-3; 95-47-6; 108-38-3; 106-42-3	Xylene	No statement possible about the ZZS status	By-product; racemic mixture; isomers

#### Elaborations on ZZS status derivation

##### **Perhydrodibenzyltoluene: hydrogen-rich carrier**



EC name: Dibenzylbenzene, ar-methyl derivative, hydrogenated  
Commercial name: MarloHC18/90

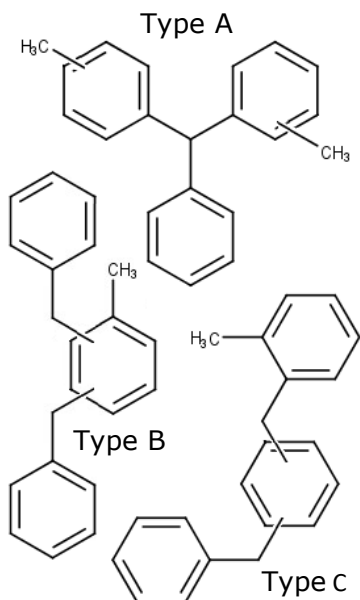
CAS number: - ; EC no: 943-342-4

Type:UVCB substance

Conclusion:Of equivalent concern as potential ZZS.

Substantiation:The amount of experimental data for this UVCB is very limited due to an intermediate registration under REACH. Using the SMILES codes of the isomers, QSAR and model screenings were performed. The PBT model estimates vP properties, which is supported by a biodegradation screening study conducted with the UVCB showing no degradation (0% after 28 days). Given the estimated log  $K_{ow}$  values of 9.95 (KOWWIN v1.68) and 10.21 (ClogP v1.5), bioaccumulation is possible. No experimental bioaccumulation data are available. There are no experimental data on CMR, except for an *in vitro* screening test. There are no CLP self-classifications as CMR cat. 1A/B or 2. Screening with the OECD toolbox does not generate CMR alerts, and the similarity tool returns no hits. There are no chronic ecotoxicity data, and limited acute toxicity data (algae, invertebrates). The acute test with aquatic invertebrates showed sublethal effects which precede immobility. Considering the hydrophobicity of the substance and the short test duration of 48 hours, equilibrium was likely not achieved. These observations are sufficient reason not to rule out chronic toxicity. Considering all of the above, the conclusion is that the substance is of equivalent concern as potential ZZS.

### **Dibenzyltoluene: hydrogen-lean carrier**



EC name: Dibenzylbenzene, ar-methyl derivative

Commercial name: Marlotherm SH

CAS number: 53585-53-8

Type: UVCB substance; containing dibenzyltoluene isomers (structures shown) and benzyltoluene isomers (see section 7.4.4 for structures)

Conclusion: Consider as ZZS

Substantiation: There are two registrants under REACH with one of them concluding PBT and vPvB. The other concluded not PBT referring to a PBT assessment from 2008 conducted for the multi-constituent substance dibenzyltoluene (CAS 26898-17-9), which consists of isomers

with the structure indicated as 'type B' in the figure to the right. The former PBT assessment concluded not persistent based on equivocal screening level data and QSAR estimates with most weight given to a closed bottle test showing primary degradation (58% after 62 days). Experimentally derived BCF values in the range 301-8180 L/kg (OECD TG 305) were noted as showing a very high bioaccumulation potential, but were not used for conclusions as they could not be matched to individual isomers. Substance was concluded bioaccumulative based on an estimated log  $K_{ow}$  of 6.59, while the first metabolite was concluded not meeting the B screening criterion. The former PBT assessment did not conclude on toxicity (PBT working group, 2008). In 2018, ECHA requested via the dossier evaluation procedure additional studies for Marlotherm SH (ECHA, 2018), including a 60-day water simulation degradation study (OECD TG 309). The study was conducted at two concentrations using two radiolabelled isomers and one radiolabelled impurity. Full names of the tested isomers are not reported on ECHA's dissemination, but based on the abbreviations and QSAR estimates provided it can be concluded that o,m-DBT is a 'type B' isomer, and o,o-DTPM a 'type A' isomer. The following degradation half-lives were reported: 56.9 days for o,m-DBT, >10,000 days for o,o-DTPM, and 32.8 days for the impurity. o,m-DBT can be concluded persistent and o,o-DTPM very persistent. The new persistence data supersede the former PBT assessment. The registrant estimated BCF values of 10,280 L/kg for o,m-DBT, 8,513 L/kg for o,o-DTPM and 2,619 L/kg for the impurity using EPIsuite. Both isomers can be concluded as very bioaccumulative. Regarding toxicity, there is an EC10 for aquatic invertebrates of 1.4 µg/L for the UVCB and the registrant self-classified the UVCB as Repr. 1B. The UVCB meets the toxicity criteria. The registrant concluded o,m-DBT as PBT, and o,o-DTPM as PBT and vPvB. In 2020, a Risk Management Option Analysis (RMOA) concluded that the PBT/vPvB properties of two heat transfer oils, including Marlotherm SH, should be further investigated, possibly through a substance evaluation (Finnish CA, 2020). The substance has not (yet) been placed on ECHA's CoRAP. The UVCB is self-classified as Repr. 1B by practically all notifiers (129 of 130). Considering all above, and especially that the two tested isomers are considered PBT and/or vPvB and that the majority of the self-classifications are Repr. 1B, the substance should be considered as ZZS.

*Toluene, methylcyclohexane, benzene and xylene: by-products.*

See section 7.1.4

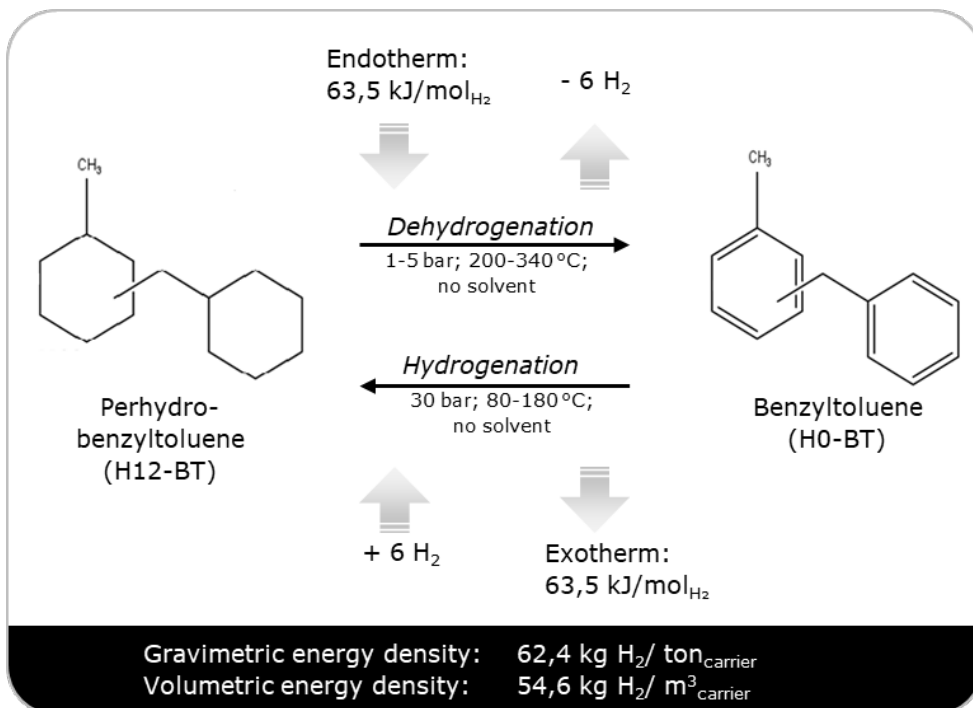
*Cyclohexane: by-product*

See section 7.2.4

## **7.3 Perhydrobenzyltoluene and benzyltoluene (H12-/H0-BT)**

### **7.3.1 ZZS conclusions and system overview**

The hydrogen-lean carrier benzyltoluene is considered a ZZS, as there are sufficient indications that the substance meets ZZS criteria. The ZZS status of the hydrogen-rich carrier perhydrobenzyltoluene cannot be assessed due to a lack of data. The by-product methylfluorene belongs to ZZS group of PAHs.



<sup>a</sup> In practice, maximum dehydrogenation is not achieved (Niermann et al., 2019).

Figure 7 Schematic representation of the H12-/H0-BT system.

### 7.3.2

#### Characteristics of the H12-/H0-BT system

##### **Type:**

Reversible aromatic LOHC. Return transport of the hydrogen-lean carrier is required to repeat the cycle.

##### **Availability:**

Benzyltoluene is commercially available as a heat transfer oil under the name Marlotherm LH (REACH registration: 1 to 10 thousand tons per year). Perhydrobenzyltoluene is not registered under REACH. The price of the Marlotherm LH is reported to be lower than Marlotherm SH (see section 7.3.2) due to lower production costs (Rüde et al., 2022).

##### **Dehydrogenation:**

The H12-/H0-BT system is comparable to the H18-/H0-DBT system (section 7.3), but dehydrogenation of H12-BT is slower and technically more complex than that of H18-DBT. H12-BT has a lower boiling point and a higher vapor pressure. As a result, even at a lower dehydrogenation temperature, more LOHC enters the gas phase, requiring additional purification steps (Geißelbrecht et al., 2020; Jorschick et al., 2020). There are developments to use other types of reactors (reactive distillation) where this is less of an issue. Dehydrogenation could then already take place at 200 °C (Geißelbrecht et al., 2020). As for all aromatic LOHCs, desorption of the hydrogen-lean LOHC from the catalyst slows down as dehydrogenation progresses, inhibiting hydrogen release (Geißelbrecht et al., 2020).

##### **Transport and storage:**

H12-/H0-BT system is easier to transport and store than H18-/H0-DBT system due to its lower viscosity (H0-BT vs. H18-DBT is 3.94 vs. 49 mPa/s at 20 °C) and the hydrogen-rich carriers (H12-BT vs H18-DBT is 6.97 vs. 389 mPa/s at 20 °C). It should be taken into account that

transport becomes more difficult at a viscosity of >10 m.Pa/s (Jorschick et al., 2020). Transport and storage comparable to current fuels.

**State of technology:**

The H12-/H0-BT system is commercialized by a German company for bulk transport and storage of hydrogen as well as use as energy carrier (Hydrogenious LOHC Technologies, 2023). Pilot projects have been conducted, and demonstration projects are on the way, including: a joint-venture formed in January 2023 to transport the hydrogen-rich carrier from Chempark Dormagen (Germany) to the Port of Rotterdam where the hydrogen will be released (1.5 ton per day) (LOHC logistix, 2023), and a joint venture established in July 2021 that is developing an integrated LOHC - Solid Oxide Fuel Cell (SOFC) system to power an offshore ship (Hydrogenious LOHC Maritime, 2023). The port of Amsterdam also aims to import this LOHC and to reach a daily release of renewable hydrogen of 100-150 tonnes by 2028 (Hydrogenious LOHC Technologies, 2022). A demonstration project that is already running is the supply of a hydrogen refuelling station in Erlangen (Germany) using the H12-/H0-BT system. Usability of this technology to power trains is also investigated, but appears to be in an earlier research phase (HI ERN, 2023).

7.3.3 *Stability of the H12-/H0-BT system*

Dehydrogenation of H12-BT appears to yield fewer by-products than dehydrogenation of H18-BT. This may be because the dehydrogenation takes place at a lower temperature (200-340 °C).

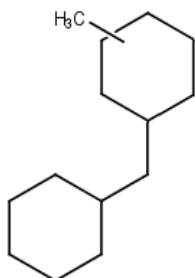
A recent study does report the formation of low amounts of by-products such as methylfluorene during seven successive hydrogenation-dehydrogenation cycles (platinum catalyst; 1 bar; 290 °C) (Rüde et al., 2022).

7.3.4 *ZZS status derivations for the H12-/H0-BT system*

The table below summarizes the derived ZZS statuses for the substance relevant for the H12-/H0-BT system, which include the hydrogen carriers and the identified by-product. The ZZS derivations are elaborated after the table.

*Table 5 ZZS statuses of substances relevant for the H12 /H0-BT system*

<b>CAS number</b>	<b>Substance name</b>	<b>ZZS status</b>	<b>Type of substance/ Remarks</b>
54824-04-3; 4823-96-0; 54823-97-1	Perhydro benzyltoluene	No statement possible about the ZZS status	hydrogen-rich carrier; isomers
27776-01-8; 713-36-0; 620-47-3; 620-83-7	Benzyltoluene	Consider as ZZS	hydrogen-lean carrier; multi- constituent; isomers
2523-39-9; 1730-37-6; 1430-97-3	Methylfluorene	ZZS	By-product; isomers

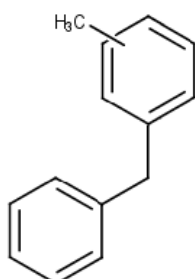
*Elaborations on ZZS status derivation***Perhydrobenzyltoluene: hydrogen-rich carrier**

*CAS numbers:* 54824-04-3 (ortho-isomer); 4823-96-0 (meta-isomer); 54823-97-1 (para-isomer)

*Type:* not registered (structure shown)

*Conclusion:* No statement possible about the ZZS status

*Substantiation:* The substances are not registered under REACH, they are not listed on the ZZS or potential ZZS list. There are no CLP (self-)classifications. Experimental data were not found. Using the SMILES codes of the isomers, QSAR and model screenings were performed. Screening with the OECD toolbox did not generate CMR alerts. Similarity tool returns no hits. The PBT tool estimated the isomers as not persistent and very bioaccumulative. The persistence estimate is inconsistent with the knowledge of cyclic aliphatic compounds that generally do not degrade quickly. It is possible that the methyl group forms an attack point for oxidation, which could speed up the degradation. Altogether, there are insufficient data to make any statement about the ZZS status of perhydrobenzyltoluene.

**Benzyltoluene: hydrogen-lean carrier**

*Commercial name:* Marlotherm LH

*CAS numbers:* 27776-01-8 (multi-constituent); CAS 713-36-0 (ortho-isomer); CAS 620-47-3 (meta-isomer); CAS 620-83-7 (para-isomer)

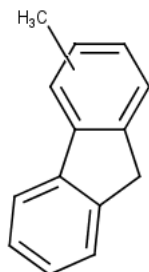
*Type:* multi-constituent substance (structure shown)

*Conclusion:* Consider as ZZS.

*Substantiation:* The multi-constituent substance is included in ECHA's PBT assessment list. This process is ongoing. Individual isomers are not registered under REACH. There are three REACH registrants of the multi-constituent substance with one of them concluding that the substance is PBT/vPvB as it contains the PBT and vPvB substance dibenzyltoluene (see section 7.3.4) at a concentration above 0.1% w/w. The other two registrant concluded that the multi-constituent substance is not PBT, with one of them proposing read-across to SAS-296 (2-(1-phenylethyl)-p-xylene; CAS 6165-51-1) for which experimental BCF

values of 620 and 760 L/kg were reported. There are no bioaccumulation data for benzyltoluene. Estimated log  $K_{ow}$  values are around the B screening criterion of  $BCF > 4.5$  (HPLC: 4.31 and 4.44 for two isomers; KOWWIN: 4.55 for all isomers; ClogP 4.66 for o-isomer, and 4.71 for m- and p-isomers). Benzyltoluene screens as potentially bioaccumulative. The multi-constituent substance was not readily biodegradable in a  $CO_2$  evolution test with degradation amounting to 46% after 29 days. There are no simulation degradation data. Benzyltoluene screens as potentially persistent. The multi-constituent substance is self-classified as Repr. 1B by 4 of the 82 notifiers. In the registration dossier, a reproduction/ developmental toxicity screening test (OECD TG 421) in rats is available. This recent study (2022) reports effects on both reproductive performance and fetal development. The former include a lower number of implantation sites, associated with higher post-implantation loss, leading to a lower number of pups at birth. The latter include lower live birth and viability indices, correlating with a higher number of pups found dead between days 1-4 post partum, and lower pup body weights. Based on these data, one of the three registrants of the multi-constituent substance proposed classification of the substance as Repr. 1B for fertility and development (H360FD). Considering all of the above, and especially the data substantiating a concern for reproductive toxicity (leading to the Repr. 1B selfclassification) and the presence of PBT and vPvB constituents, the substance should be considered as ZZS.

#### **Methylfluorene: by-product**



*CAS numbers:* 2523-39-9; 1730-37-6; 1430-97-3

*Type:* not registered (structure shown).

*Conclusion:* ZZS

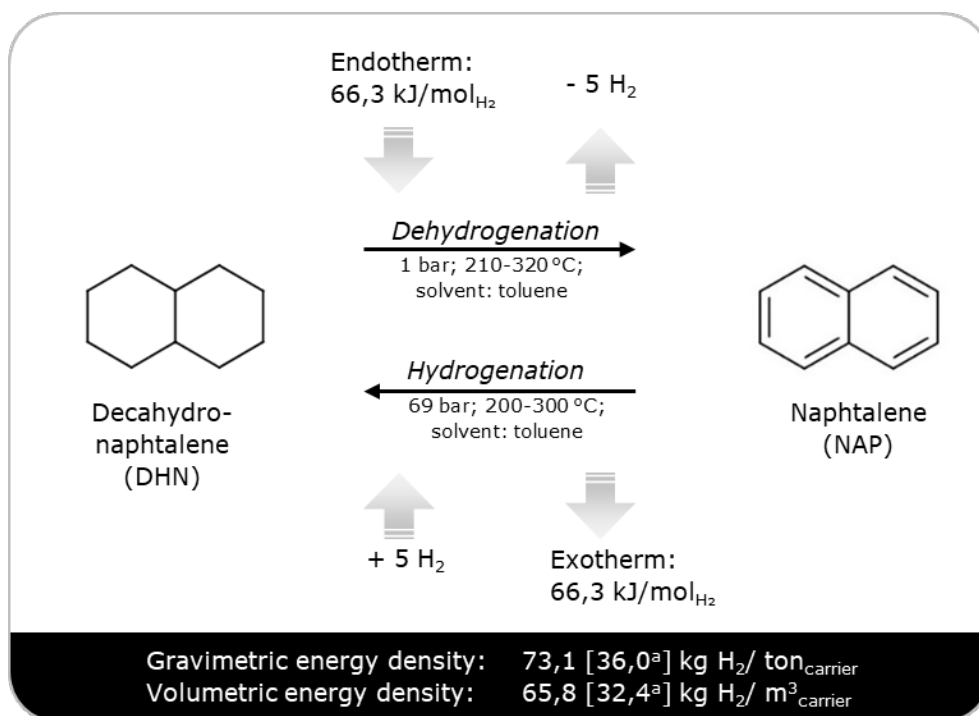
*Substantiation:* Methylfluorene is a substituted polycyclic aromatic hydrocarbon (PAH). Based on the POP regulation, all PAHs, including substituted PAHs, are identified as ZZS.

## **7.4 Decahydronaphthalene and naphthalene (DHN/NAP)**

### **7.4.1 ZZS conclusions and system overview**

The hydrogen-lean carrier naphthalene belongs to the ZZS group of PAHs. The hydrogen-rich carrier decahydronaphthalene is a potential ZZS.

We note that recently LOHCs have been proposed using substituted naphthalene as hydrogen-lean carrier (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 ZZS group of PAHs.



<sup>a</sup> Considering toluene as a solvent (Niermann et al., 2019).

Figure 8 Schematic representation of the H12-/H0-BT system.

#### 7.4.2 Characteristics of the DHN/NAP system

##### **Type:**

Reversible aromatic LOHC. Return transport of the hydrogen-lean carrier is required to repeat the cycle.

##### **Availability:**

Naphthalene is used as a raw material to produce phthalic anhydride, which in turn is a raw material for plasticizers and dyes (REACH registrations: (i) intermediate use only; (ii) 100,000 to 1 million tonnes per year). Decahydronaphthalene is an industrial solvent (REACH registration: 100 to 1000 tons per year). The price of naphthalene is 0.6 €/kg (Niermann et al., 2019).

##### **Dehydrogenation:**

Dehydrogenation takes place at a temperature of 210-320 °C (Niermann et al., 2019). As Naphthalene is solid at room temperature, a solvent such as toluene is added to keep the DHN/NAF system fluid. Addition of the solvent lowers the hydrogen capacity and makes the purification of hydrogen after dehydrogenation more complex. The dehydrogenation, but also hydrogenation of this LOHC goes through the intermediate product 1,2,3,4-tetrahydronaphthalene (also called tetralin).

##### **Transport and storage:**

When solvent is added the system remains fluid, making transport and storage comparable to current fuels.

##### **State of technology:**

Research on this LOHC has only been done on a laboratory scale. Naphthalene has a high storage density, but its development is hampered due to its solid form at ambient temperatures. Recently, focus has been shifting from naphthalene to naphthalene derivatives with improved LOHC properties being liquid at ambient temperatures, having lower dehydrogenation enthalpies, and having higher gravimetric energy

densities. Examples are methylbenzyl naphthalene (Rao et al., 2023) and cis-perhydro-1-(*n*-phenylethyl)naphthalene (Jeong et al., 2023). These LOHCs have not been elaborated in this study.

#### 7.4.3 *Stability of the DHN/NAP system*

Dehydrogenation of naphthalene can yield the intermediate product tetralin which can result in the formation of alkylbenzenes if ring-opening occurs (McVicker et al., 2002). The respective study did not examine if this process also occurs under LOHC-relevant conditions. As it remains unknown if the substances are formed, they were not further investigated.

#### 7.4.4 *ZZS status derivations for the DHN/NAP system*

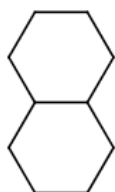
The table below summarizes the derived ZZS statuses for the hydrogen carriers of the DHN/NAF system and the by-products identified. The ZZS derivations are elaborated after the table

*Table 6 ZZS statuses of substances relevant for the DHN/NAP system*

<b>CAS number</b>	<b>Substance name</b>	<b>ZZS status</b>	<b>Type of substance/ Remarks</b>
91-17-8	Decahydro-naphthalene	Potential ZZS	Hydrogen-rich carrier
91-20-3	Naphthalene	ZZS	Hydrogen-lean carrier
108-88-3	Toluene	Probably not of equivalent concern as ZZS or potential ZZS	Solvent

*Elaborations on ZZS status derivation*

#### ***Decahydronaphthalene: hydrogen-rich carrier***



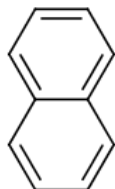
*CAS number:* 91-17-8

*Type:* mono-constituent substance (structure shown)

*Conclusion:* Potential ZZS.

*Substantiation:* Decahydronaphthalene is on the potential ZZS list due to its inclusion on ECHA's CoRAP and PBT assessment list. The substance evaluation was started in 2012. The substance is considered bioaccumulative. Aquatic toxicity tests and a water simulation degradation test were requested. The SEv is still ongoing. Altogether, decahydronaphthalene is a potential ZZS.

**Naphthalene: hydrogen-lean carrier**



CAS number: 91-20-3

Type: mono-constituent substance (structure shown)

Conclusion: ZZS

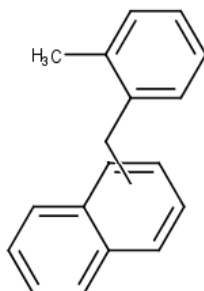
Substantiation: Naphthalene is a polycyclic aromatic hydrocarbon (PAH). Based on the POP regulation, all PAHs are identified as ZZS.

**Toluene: solvent**

See section 7.1.4.

*Exploration of naphthalene derivatives LOHCs, thereby only considering the hydrogen-lean carrier*

**Methylbenzyl naphthalene: hydrogen-lean carrier**



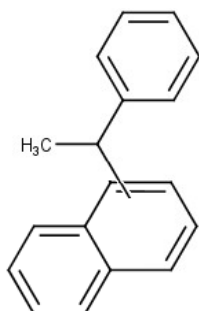
CAS number: -Type:

multi-constituent substance (structure shown)

Conclusion: ZZS

Substantiation: Methylbenzyl naphthalene is a substituted polycyclic aromatic hydrocarbon (PAH). Based on the POP regulation, all PAHs, including substituted PAHs, are identified as ZZS.

**cis-perhydro-1-(n-phenylethyl)naphthalene: hydrogen-lean carrier**



CAS number: 60466-61-7

Type: multi-constituent substance (structure shown)

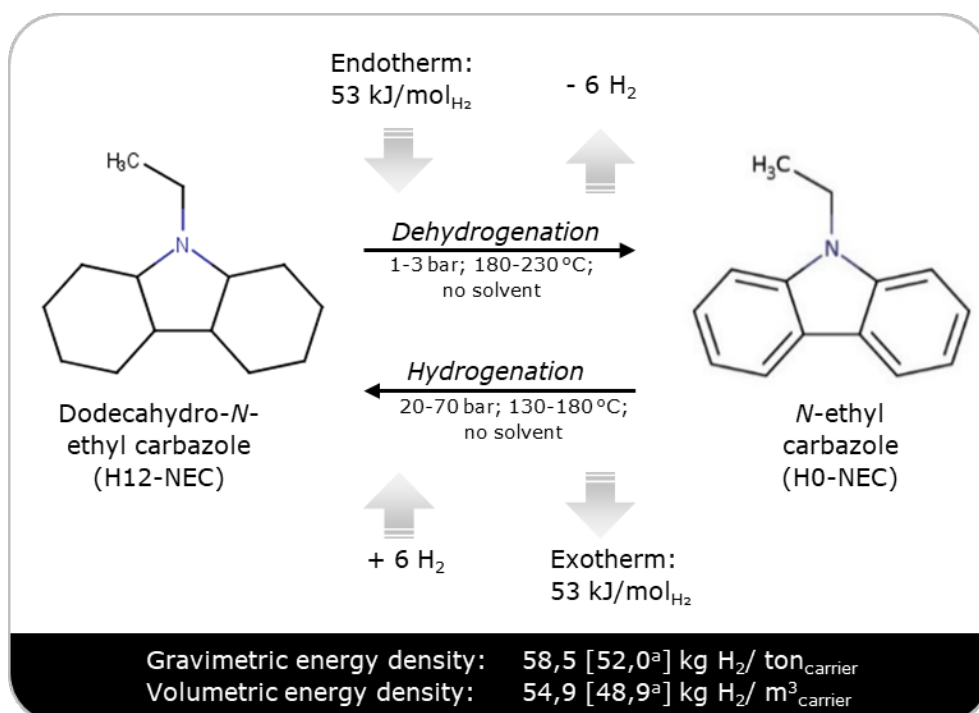
Conclusion: ZZS

*Substantiation:* cis-perhydro-1-(n-phenylethyl)-naphthalene is a substituted polycyclic aromatic hydrocarbon (PAH). Based on the POP regulation, all PAHs, including substituted PAHs, are identified as ZZS.

## 7.5 Dodecahydro-*n*-ethylcarbazole and *n*-ethylcarbazole (H12-/H0-NEC)

### 7.5.1 ZZS conclusions and system overview

The hydrogen-lean carrier *n*-ethylcarbazole and the by-product carbazole belong to the ZZS group for PAHs.



<sup>a</sup> Not completely dehydrogenated in order to keep the LOHC system liquid (Niermann et al., 2019).

Figure 9 Schematic representation of the H12-/H0-NEC system.

### 7.5.2 Characteristics of the H12-/H0-NEC system

#### **Type:**

Reversible aromatic LOHC. Return transport of the hydrogen-lean carrier is required to repeat the cycle.

#### **Availability:**

Dodecahydro-*n*-ethylcarbazole is not registered under REACH. *N*-ethylcarbazole is registered as intermediate (no information on volumes) and is used as raw material for other chemicals. Brückner et al. (2014) reports annual production of <10,000 tonnes per year. *N*-ethylcarbazole is a raw material for other chemicals. The price is 40 €/kg which is high compared to other LOHCs (Niermann et al., 2019).

#### **Dehydrogenation:**

Dehydrogenation occurs at 180-270 °C (Niermann et al., 2019). The higher the temperature, the faster the dehydrogenation.

Dehydrogenation as well as hydrogenation are stepwise. The charge state is indicated as the number of hydrogen atoms bonded to *n*-ethylcarbazole (NEC): H0-NEC, H4-NEC, H8-NEC and H12-NEC

(Markiewicz et al., 2015; Yang et al., 2014). Considering that at room temperature *N*-ethylcarbazole is a solid and H4-NEC remains a liquid, dehydrogenation is limited to 90% to prevent the use of a solvent (Yang et al., 2014).

**Transport and storage:**

Under ambient conditions, *n*-ethylcarbazole is a viscous liquid. Substances have low vapour pressure at ambient conditions. Transport and storage comparable to current fuels, although complicated by higher viscosity.

**State of technology:**

State of the technology: *n*-ethylcarbazole was proposed as LOHC in 2003 by a hydrogen producing company (Pez, 2006). While the LOHC has been considered promising in many publications, it appears that research has so far only taken place on a laboratory scale (Niermann et al., 2019).

7.5.3 *Stability of the H12-/H0-NEC system*

The by-product carbazole is formed at a dehydrogenation temperature of 270 °C and higher (~2%) (Brückner et al., 2014). (De)hydrogenation occurs via intermediates, but it remains unclear if they are formed in detectable concentrations under LOHC relevant conditions. Consequently, they have not been further investigated.

7.5.4 *ZZS status derivations for the H12-/H0-NEC system*

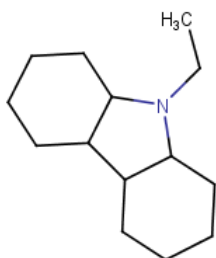
The table below summarizes the derived ZZS statuses for the hydrogen carriers of the H12-/H0-NEC system and the by-product identified. The ZZS derivations are elaborated after the table.

*Table 7 ZZS statuses of substances relevant for the H12-/H0-NEC system*

CAS number	Substance name	ZZS status	Type of substance/ Remarks
146900-30-3	Dodecahydro- <i>N</i> -ethyl carbazole	Probably not of equivalent concern as ZZS or potential ZZS	Hydrogen-rich carrier
86-28-2	<i>N</i> -ethyl - carbazole	ZZS	Hydrogen-lean carrier
86-74-8	Carbazole	ZZS	By-product

*Elaborations on ZZS status derivation*

**Dodecahydro-*n*-ethylcarbazole: hydrogen-rich carrier**

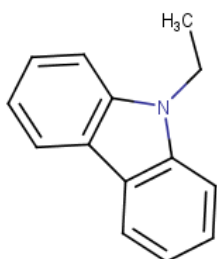


CAS number: 146900-30-3

Type: not registered (structure shown)

**Conclusion:** Probably not of equivalent concern as ZS or potential ZS  
**Substantiation:** There are no experimental data for this substance. Conclusion is based on models. The PBt tool estimates not persistent and not bioaccumulative. Screening with OECD toolbox yields one CMR alerts for DNA binding on (SN1). The similarity tool yields hits with two reprotoxic substances, 61% agreement with 'Representing ethanol, 2,2'-iminobis-, N-(C13-15-branched and linear alkyl) derivs.' (CAS 97925-95-6) and 55% agreement with tridemorph (CAS 24602-86-6). These hits are irrelevant due to the structural differences, i.e. two substances are linear substances with OH groups and dodecahydro-*n*-ethyl carbazole has cyclic rings and no OH groups. Altogether, the data available for this substance does not indicate ZS-related concern.

### ***N*-ethylcarbazole: hydrogen-lean carrier**



**EC name:** 9-ethylcarbazole

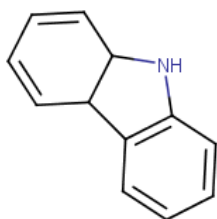
**CAS number:** 86-28-2

**Type:** mono-constituent substance (structure shown)

**Conclusion:** ZS

**Substantiation:** *N*-ethylcarbazole is a heterocyclic, substituted polycyclic aromatic hydrocarbon (PAH). Based on the POP regulation, all PAHs, including heterocyclic and substituted PAHs, are identified as ZS.

### ***Carbazole: by-product***



**CAS number:** 86-74-8

**Type:** mono-constituent substance (structure shown)

**Conclusion:** ZS

**Substantiation:** Carbazole is a heterocyclic PAH. Based on the POP regulation, all PAHs, including heterocyclic PAHs, are identified as ZS.

## **7.6 Ethylene glycol and esters of ethylene glycol (EG/EEG)**

### **7.6.1 ZS conclusions and system overview**

There are no ZS-related concerns for the hydrogen carriers and the solvents used. The ZS carbon monoxide can be formed as by-product as well as the by-product (1,3-dioxolan-2-yl)methanol for which there is an equivalent concern as for potential ZS.



catalysators required. At this stage, it cannot be foreseen how this technology will further develop.

### 7.6.3 *Stability of the EG/EEG system*

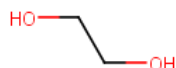
By-products can be formed, such as the cyclic by-product (1,3-dioxolan-2-yl)methanol. In addition, dehydrogenation of 2-hydroxyethyl glycolate (ester of 2 EG molecules) can yield an  $\alpha$ -keto ester that can decompose into an aldehyde, i.e. 2-hydroxyethyl formate, and carbon monoxide. Formation of carbon monoxide inactivates the catalyst (Zou et al., 2019).

### 7.6.4 *ZZS status derivations for the EG/EEG system*

The table below summarizes the derived ZZS statuses for the hydrogen carriers of the EG/EEG system, solvent used and by-products identified. The ZZS derivations are elaborated after the table

*Table 8 ZZS statuses of substances relevant for the EG/EEG system.*

<b>CAS number</b>	<b>Substance name</b>	<b>ZZS status</b>	<b>Type of substance/ Remarks</b>
107-21-1	Ethylene glycol	Probably not of equivalent concern as ZZS or potential ZZS	Hydrogen-rich carrier
14396-72-6	2-hydroxyethyl glycolate (ester of 2 EG)	Probably not of equivalent concern as ZZS or potential ZZS	Hydrogen-lean carrier
CAS unknown	Ester of 3 EG	Probably not of equivalent concern as ZZS or potential ZZS	Hydrogen-lean carrier
CAS unknown	Ester of 4 EG	Probably not of equivalent concern as ZZS or potential ZZS	Hydrogen-lean carrier
CAS unknown	Ester of 5 EG	Probably not of equivalent concern as ZZS or potential ZZS	Hydrogen-lean carrier
CAS unknown	Ester of 6 EG	Probably not of equivalent concern as ZZS or potential ZZS	Hydrogen-lean carrier
115-10-6	Dimethyl ether	Probably not of equivalent concern as ZZS or potential ZZS	Solvent
108-88-3	Toluene	Probably not of equivalent concern as ZZS or potential ZZS	Solvent
5694-68-8	(1,3-dioxolan-2-yl)methanol	Of equivalent concern as potential ZZS	By-product
628-35-3	2-Hydroxyethyl formate	Probably not of equivalent concern as ZZS or potential ZZS	By-product
630-08-0	Carbon monoxide	ZZS	By-product

*Elaborations on ZZS status derivation***Ethylene glycol: hydrogen-rich carrier**

*EC name:* Ethane-1,2-diol

*CAS number:* 107-21-1

Type: mono-constituent substance (structure shown)

*Conclusion:* Probably not of equivalent concern as ZZS or potential ZZS

*Substantiation:* The substance is readily biodegradable (83 to 96% degradation in 14 days) in a MITI I (OECD TG 301C) test. The log  $K_{ow}$  is estimated to be -1.36 by KOWWIN. The substance does not screen as persistent or bioaccumulative. There are some CLP self-classifications that classify the substance as Repr. 1B (2 of 8083) or Muta. 1B + Repr. 1B (2 of 8083), with no Repr. 2 classifications. This is a relatively small number compared to the total number of CLP self-classifications. Several reproduction and developmental toxicity studies are available for the substance. The fertility is not affected in these studies. Developmental toxicity is observed in rats and mice, but not in rabbits. Based on these data, the registrant proposes no classification for developmental toxicity. Screening with OECD toolbox provides CMR alerts for in vivo mutagenicity (micronucleus) and reprotoxic and developmental toxicity potential (DART). The similarity tool yields three hits with reproductive toxicants. Ethylene glycol monomethyl ether (CAS 109-86-4), 2-ethoxyethanol (CAS 110-80-5) and 2-methoxypropanol (CAS 1589-47-5) with agreements of 51, 27 and 27%, respectively. The common denominator of these three substances is an ether bond, that is not present in 2-hydroxyethyl glycolate. There are no indications that the ether containing substances can be formed from 2-hydroxyethyl glycolate. Therefore, the hits are not considered good predictors. In 2021, the Netherlands indicated it will submit a proposal for harmonized classification for the substance as Repr. 2 (expected date of submission December 2024). Repr. 2 is not a criterion for ZZS identification. Altogether, the data available for this substance do not support the Muta and Repr 1B self-classifications and do not indicate a ZZS-related concern

**Esters of ethylene glycol: hydrogen-lean carriers**

*Substances:* see table below

*Conclusion:* Probably not of equivalent concern as ZZS or potential ZZS

*Substantiation:* The esters investigated in this report are formed from two to six ethylene glycol molecules, indicated as 2EEG to 6EEG. A CAS number could only be retrieved for the ester made of 2 ethylene glycol molecules (=2 EEG), i.e. 2-hydroxyethyl glycolate (CAS 14396-72-6). This substance is not registered under REACH. There are no CLP (self-)classifications for any of the esters of ethylene glycol investigated in this report. Experimental data were not found. Using the SMILES codes of the substances (see below), QSAR and model screenings were performed. The PBT tool estimated all substances as not persistent and not bioaccumulative. Screening with the OECD toolbox generated for all substances a CMR alert for in vivo mutagenicity (micronucleus). For 2EEG, additionally an alert for reprotoxic and developmental toxicity potential (DART) was yielded. The similarity tool yielded hits to

reproduction toxic substances (see table below for the results). The common denominator of all these substances is an ether bond, that is not present in the investigated esters (2EEG – 6EEG). There are no indications that the ether containing substances can be formed from the investigated esters. Therefore, the hits are not considered good predictors. Altogether, the data available for the investigated esters (2EEG – 6EEG) do not indicate a ZZS related concern.

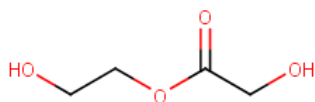
Table 9 Names and structures of investigated EEG.

### 2EEG

EC name: 2-hydroxyethyl glycolate

CAS no.: 14396-72-6

SMILES: OCCOC(=O)CO

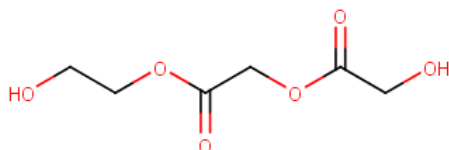


### 3EEG

IUPAC name: 2-(2-hydroxyethoxy)-2-oxoethyl 2-hydroxyacetate

CAS no.: -

SMILES: OCCOC(=O)COC(=O)CO

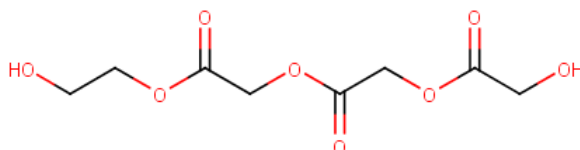


### 4EEG

IUPAC name: 2-[2-(2-hydroxyethoxy)-2-oxoethoxy]-2-oxoethyl 2-hydroxyacetate

CAS no.: -

SMILES: OCCOC(=O)COC(=O)COC(=O)CO

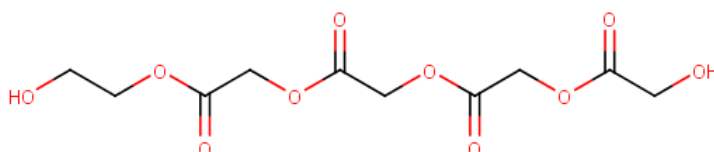


### 5EEG

IUPAC name: 2-(2-[2-(2-hydroxyethoxy)-2-oxoethoxy]-2-oxoethoxy)2-oxoethyl 2-hydroxyacetate

CAS no.: -

SMILES: OCCOC(=O)COC(=O)COC(=O)COC(=O)CO



**6EEG**

IUPAC name: 2-[2-(2-[2-(2-hydroxyethoxy)-2-oxoethoxy]-2-oxoethoxy)-2-oxoethoxy]-2-oxoethyl 2-hydroxyacetate

CAS no.: -

SMILES: OCCOC(=O)COC(=O)COC(=O)COC(=O)COC(=O)CO

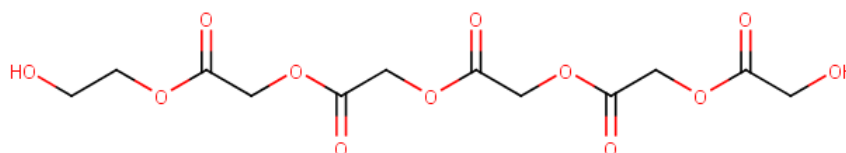
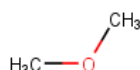


Table 10 Results of the similarity tool for the investigated EEG

Similarity tool hits	Similarity (%) indicated per ester of ethylene glycol (2EEG-6EEG)				
	EE2	EE3	EE4	EE5	EE6
2-ethoxyethanol (CAS 110-80-5)	93%	-	-	-	-
2-methoxyethyl acetate (CAS 110-49-6)	56%	56%	52%	52%	52%
2-methoxyethanol (CAS 109-86-4)	52%	-	-	-	-
2-ethoxyethyl acetate (CAS 111-15-9)	51%	75%	63%	63%	63%
methoxyacetic acid (CAS 625-45-6)	51%	-	-	-	-
2-methoxypropyl acetate (CAS 70657-70-4)	-	50%	-	-	-
1,2-bis(2-methoxyethoxy)ethane (CAS 112-49-2)	-	50%	49%	49%	49%
Tetraglyme (CAS 143-24-8)	-	50%	-	-	-

**Dimethyl ether: solvent**

CAS number: 115-10-6

Type: Mono-constituent substance (structure shown)

Conclusion: Probably not of equivalent care as ZZS or potential ZZS

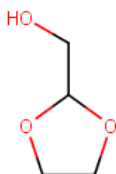
Substantiation: The substance is not readily biodegradable. The estimated log K<sub>ow</sub> is 0.07 (KOWWIN v1.67). There are no simulation degradation or bioaccumulation data available. The PBT tool estimates the substance as not persistent and not bioaccumulative. There is no PBT concern. The substance does not have a harmonized CLP classification as CMR. There are some CLP self-classifications that classify the substance as Muta. 1B + Carc. 1A (40 of 1444), and no CMR cat. 2 classifications. The available in vitro and in vivo toxicity data in the REACH dossier do not warrant a classification as Muta. 1B and Carc.

1A. Altogether, there are currently insufficient indications for a ZZS related concern.

**Toluene: solvent**

See section 7.1.4.

**(1,3-dioxolan-2-yl)methanol: by-product**



CAS number: 5694-68-8

Type: mono-constituent substance (structure shown)

Conclusion: Of equivalent concern as potential ZZS

Substantiation: The substance is not registered under REACH. There are no CLP (self-)classifications. Experimental data were not found. The PBt tool estimates the substance as not persistent and not bioaccumulative. The persistence estimate is inconsistent with the knowledge of heterocyclic ethers not degrading quickly. For the similar substance 1,4-dioxane (CAS 123-91-1) that has two ether bonds in a six-atom ring (without a hydroxyl group), the PBt tool also estimates 'not persistent', while the substance has been shown to be very persistent in the aquatic environment. 1,4-dioxane has a harmonized classification as Carc. 1B and has been identified in 2021 as an SVHC under REACH based on an equivalent level of concern, being a very persistent, mobile and toxic (PMT) substance. Screening with the OECD toolbox generated a CMR alert for in vivo mutagenicity (micronucleus). The similarity tool yields a hit with the carcinogenic substance 2,3-epoxypropan-1-ol (CAS 556-52-5; CAS 57044-25-4) with an agreement of 50%. There is no hit for 1,4-dioxane. There are three hits with reproduction toxic substances: (1) 95% agreement with 2-ethoxyethanol (CAS 110-80-5); (2) 54% agreement with 2-methoxyethanol (CAS 109-86-4); (3) 51% agreement with 2,3-epoxypropan-1-ol (CAS 556-52-5; CAS 57044-25-4). (1,3-dioxolan-2-yl)methanol shares an ether functionality with all hits indicating reactivity. Still there are differences with 2-ethoxyethanol and 2-methoxyethanol being linear substances and 2,3-epoxypropan-1-ol being a highly reactive epoxide consisting of a three-atom ring. Nevertheless, as (1,3-dioxolan-2-yl)methanol has two ether bonds in a five-atom ring it cannot be excluded that it will also exert reactivity. Taken all above into consideration, an equivalent concern as potential ZZS is concluded.

**2-Hydroxyethyl formate: by-product**



CAS number: 628-35-3

Type: mono-constituent substance (structure shown)

Conclusion: Probably not of equivalent concern as ZZS or potential ZZS

Substantiation: The substance is not registered under REACH. There are no CLP (self-)classifications. Experimental data were not found. The PBt

tool estimated the substance as not persistent and not bioaccumulative. Screening with the OECD toolbox generated a CMR alert for in vivo mutagenicity (micronucleus) and oncology primary classification. The similarity tool yields one hit with the carcinogenic substance 2,3-epoxypropan-1-ol (CAS 556-52-5; CAS 57044-25-4) with an agreement of 52%. There are five hits with reprotoxic substances: (i) 96% agreement with 2-methoxyethanol (CAS 109-86-4); (ii) 61% agreement with 2-ethoxyethanol (CAS 110-80-5); (iii) 61% agreement with 2-methoxypropanol (CAS 1589-47-5); (iv) 54% agreement with methoxyacetic acid (CAS 625-45-6); (v) 52% agreement with 2,3-epoxypropan-1-ol (CAS 556-52-5; CAS 57044-25-4). The substance 2,3-epoxypropan-1-ol has structurally little in common with 2-hydroxyethyl formate being a highly reactive three-atom cyclic ether. The other substances are linear substances with an ether functionality; however, they are not conjugated bases as is 2-hydroxyethyl formate. Furthermore, 2-hydroxyethyl formate is structurally very similar to ethyl formate (CAS 109-94-4). The latter substance has harmonized CLP classifications (index no. 607-015-00-7) for several hazards, but not CMR cat. 1 or 2. It has also no CMR self-classifications. Developmental and reproduction toxicity data are available for 2-hydroxyethyl formate, indicating no concern. Considering all above, there are currently insufficient indications for a ZZS concern for 2-hydroxyethyl formate.

### **Carbon monoxide: by-product**



*CAS number:* 630-08-0

*Type:* mono-constituent substance (structure shown)

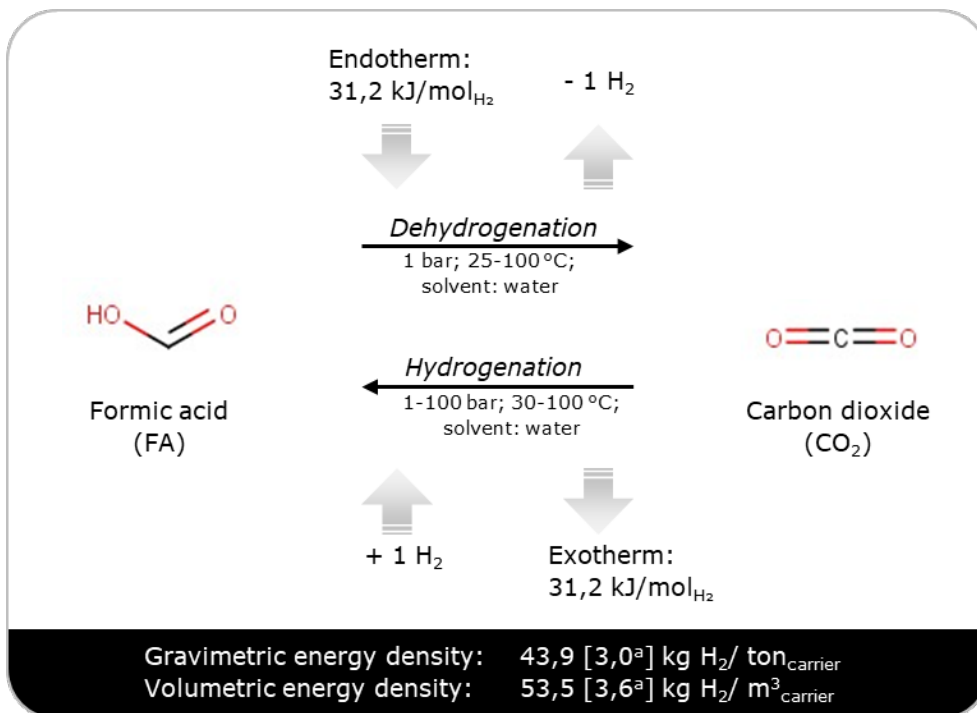
*Conclusion:* ZZS

*Substantiation:* Carbon monoxide is on the ZZS list due to harmonized CLP classification (index no. 006-001-00-2) as Repro. 1A.

## **7.7 Formic acid and carbon dioxide (FA/CO<sub>2</sub>)**

### **7.7.1 ZZS conclusions and system overview**

There are no ZZS-related concerns for the hydrogen carriers formic acid and carbon dioxide, or the solvent water. During dehydrogenation the by-product carbon monoxide can be formed. Carbon monoxide is a ZZS. However, carbon monoxide can react during dehydrogenation with water to form carbon dioxide.



<sup>a</sup> Strongly water diluted formic acid (1.5 M = 0.07 wt%) (Niermann et al., 2019).

Figure 11 Schematic representation of the FA/CO<sub>2</sub> system.

### 7.7.2 Characteristics of the FA/CO<sub>2</sub> system

#### **Type:**

Circular LOHC; The hydrogen-lean carrier can be released to the atmosphere. Return transport is not required. No net carbon dioxide increase provided the carbon dioxide was captured from the atmosphere.

#### **Availability:**

Current formic acid volumes (REACH registration: 100 thousand to 1 million tons per year) are not relevant for LOHC use, because the substance is produced from fossil sources or biomass fermentation (Kumar, Daw, & Milstein, 2022). Production of renewable formic acid is often seen as a bottleneck for the FA/CO<sub>2</sub> system. Various techniques are being developed (see 'State of technology' subsection below).

#### **Dehydrogenation:**

Dehydrogenation occurs at temperatures below 100 °C in a process called reforming. If the hydrogen is meant for further distribution, it must be purified, as the gas also contains carbon dioxide (Niermann et al., 2019). If the gas mixture is used directly in a fuel cell, purification is not necessary provided that the amount of carbon monoxide is low (<10 ppm) in order to prevent fuel cell poisoning (van Putten et al., 2019). Catalytic dehydrogenation has been reported, but is still in research phase (Kumar, Daw, & Milstein, 2022).

**Transport and storage:** Flammable and corrosive liquid. All transport options are possible, taking into account the corrosive nature of formic acid, which is detrimental to installations

#### **State of technology:**

Dehydrogenation is operational, although new technology is researched (see above). Other aspects need further development, notably capturing

of the hydrogen lean carrier, the hydrogenation process and the envisaged uses, as elaborated below:

*Capturing of carbon dioxide:* Carbon dioxide can be captured from emission sources, for example flue gasses generated by industrial plants that run on fossil fuels or biomass. Carbon dioxide can also be captured from the atmosphere, a process referred to as direct air capture (DAC). The latter process is more sustainable, but has a high energy demand and is costly. DAC technology is at demonstration scale since 2021 (Climeworks, 2021).

*Hydrogenation:* Different technologies are available to produce formic acid from carbon dioxide: (i) Currently methanol is oxidized to formic acid via intermediate steps (Bulushev & Ross, 2018). This technique is energy intensive and cumbersome, but connects to existing installations; (ii) Direct hydrogenation of carbon dioxide to formic acid can be performed under high pressure and basic (Klankermayer et al., 2016) or buffered conditions (Weilhard, Argent, & Sans, 2021). This technique has so far only been demonstrated on a laboratory scale; (iii) Formic acid can be produced by electrochemical reduction of carbon dioxide by directly transferring two electrons to carbon dioxide in an electrochemical cell under high electrical power. This process allows hydrogenation without the need to produce renewable hydrogen first. However, the process is very energy intensive, and catalysator technology needs to be further optimization (Ai, Ng, & Ong, 2022). Electrochemical reduction is at laboratory scale. A pilot plant is being developed by a Dutch company named COVAL energy under a Horizon2020 project (ConsenCUS, 2023).

*Applications:* Formic acid use as LOHC is mainly investigated from an energy carrier perspective. For example, a Dutch company commercialized a generator that works on pure formic acid to deliver off-grid electricity (DENS, 2022).

#### 7.7.3 *Stability of the FA/CO<sub>2</sub> system*

During dehydrogenation carbon monoxide and water can be produced instead of hydrogen and carbon dioxide (Niermann et al., 2019). The by-product carbon monoxide can react again with water to carbon dioxide and hydrogen.

#### 7.7.4 *ZZS status derivations for the FA/CO<sub>2</sub> system*

The table below summarizes the derived ZZS statuses for the different relevant substance of the FA/CO<sub>2</sub> system, which include the hydrogen carriers and the identified by-product. The ZZS derivations are elaborated after the table.

Table 11 ZZS statuses of substances relevant for the FA/CO<sub>2</sub> system.

CAS number	Substance name	ZZS status	Type of substance/ Remarks
64-18-6	Formic acid	Probably not of equivalent care as ZZS or potential ZZS	Hydrogen-rich carrier
124-38-9	Carbon dioxide	Probably not of equivalent care as ZZS or potential ZZS	Hydrogen-lean carrier
7732-18-5	Water	Probably not of equivalent care as ZZS or potential ZZS	Solvent
630-08-0	Carbon monoxide	ZZS	By-product

#### Elaborations on ZZS status derivation

##### **Formic acid: hydrogen-rich carrier**



EC name: Ethane-1,2-diol

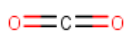
CAS number: 64-18-6

Type: mono-constituent substance (structure shown)

Conclusion: Probably not of equivalent concern as ZZS or potential ZZS

Substantiation: Formic acid is not considered persistent or bioaccumulative, as it is readily biodegradable and has very low log *D*<sub>ow</sub> values. The substance does not have CLP harmonised or self-classifications as CMR cat. 1, with only one self-classification as Repr. 2 (1 of 3367). There are no data indicating a CMR concern. The endocrine disrupting (ED) properties of the substance are investigated under the Biocidal Products Regulation, which is a standard procedure since July 2018 for new applications for use as active substance. There are no specific ED concerns for formic acid. Altogether, the available data do not indicate a ZZS-related concern.

##### **Carbon dioxide: low hydrogen carrier**

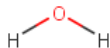


CAS number: 124-38-9

Type: mono-constituent substance (structure shown)

Conclusion: Probably not of equivalent concern as ZZS or potential ZZS

Substantiation: The substance is not listed on the ZZS or potential ZZS list. Altogether, there are no data for this substance that indicate a ZZS related concern.

**Water: solvent**

CAS number: 7732-18-5

Type: mono-constituent substance (structure shown)

Conclusion: Probably not of equivalent concern as ZZS or potential ZZS

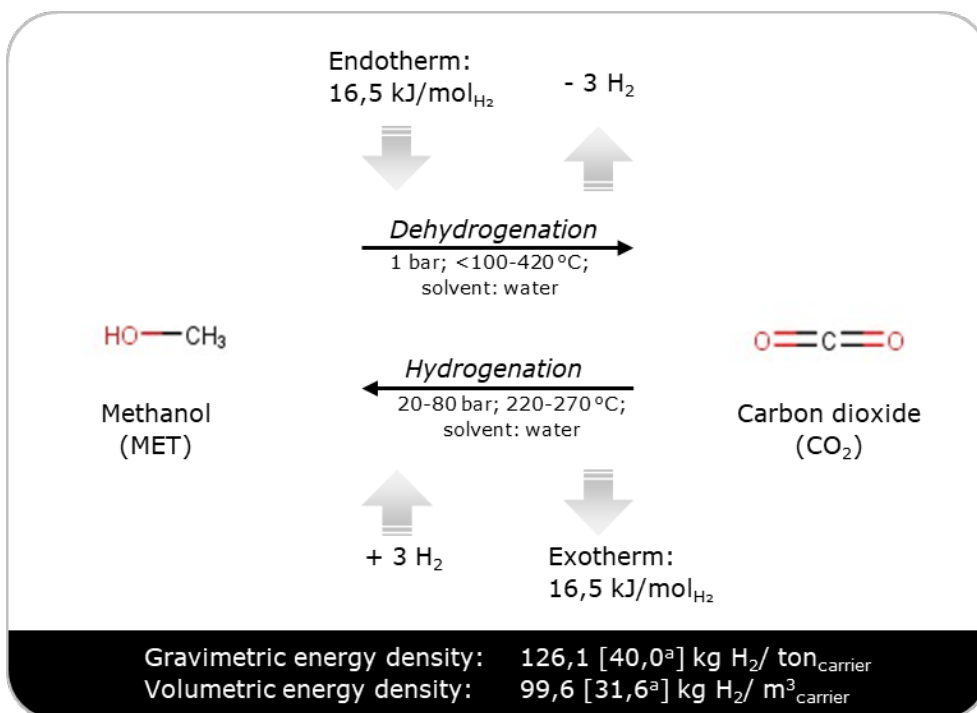
Substantiation: The substance is not listed on the ZZS or potential ZZS list. Altogether, there are no data for this substance that indicate a ZZS related concern.

**Carbon monoxide: by-product**

See section 7.7.4

**7.8 Methanol and carbon dioxide (MET/CO<sub>2</sub>)****7.8.1 ZZS conclusions and system overview**

There are no ZZS-related concerns for the hydrogen-rich carrier methanol and the hydrogen-lean carrier carbon dioxide, or the solvent water. During dehydrogenation the by-product carbon monoxide can be formed. Carbon monoxide is a ZZS. However, carbon monoxide can react during dehydrogenation with water to form carbon dioxide.



<sup>a</sup> In practice, maximum dehydrogenation is not achieved (Niermann et al., 2019)

Figure 12 Schematic representation of the MET/CO<sub>2</sub> system.

**7.8.2 Characteristics of the MET/CO<sub>2</sub> system****Type:**

Circular LOHC; The hydrogen-lean carrier can be released to the atmosphere. Return transport is not required. No net carbon dioxide increase provided the carbon dioxide was captured from the atmosphere.

**Availability:**

Current methanol volumes (REACH registration: 10 to 100 million tonnes per year) are not relevant for LOHC use, as they are mainly produced from fossil sources, and in lower amounts from biomass. Production of renewable methanol is often seen as a bottleneck for the MET/CO<sub>2</sub> system. Various techniques are being developed (see 'State of technology' subsection below).

**Dehydrogenation:**

Steam reforming at temperature of 200-300 °C with high hydrogen yield and low levels of carbon monoxide (Sá et al., 2010). Research is conducted to dehydrogenise methanol at lower temperatures (<200 °C) using various catalysators in a process termed aqueous-phase reforming of methanol (Kumar, Daw, & Milstein, 2022; Lin et al., 2017).

**Transport and storage:**

Flammable liquid that can be transported and stored using existing petroleum and its derivatives infrastructure.

**State of technology:**

Dehydrogenation is operational, although new technology is researched to lower the temperature and reduce amount of carbon monoxide formed (see above). Other aspects need further development, notably capturing of the hydrogen-lean carrier, the hydrogenation process and the envisaged uses, as elaborated below:

*Capturing of carbon dioxide:* see formic acid on DAC developments (section 7.8.2).

*Hydrogenation:* Hydrogenation of carbon dioxide is operational at production scale. In 2022, a plant has opened in China producing 110.000 tons methanol per year from 160.000 tons carbon dioxide captured from coke oven gas (Carbon Recycling International, 2022). The same Icelandic company is developing a plant in Norway with a capacity of 100.000 tons methanol per year from carbon dioxide captured from a ferrosilicon plant. Besides hydrogenation of carbon dioxide, research is conducted to electrochemically reduce carbon dioxide to methanol. This is same approach as previously described for formic acid, but requires six electrons to be transferred instead of two, and as such is more complex. Research is still in an early phase (Sheppard et al., 2023). Electrochemical reduction using enzymes has been proposed (Schlager et al., 2016), but fundamental issues such as enzyme stability, availability and costs of cofactors and the low conversion efficiencies must be tackled before research can be scaled up.

*Applications:* Methanol is being proposed as hydrogen carrier (Niermann et al., 2021) (Schorn et al., 2021), but no large scale project have been identified. Focus is primarily on the use as energy carrier in applications where a reformer is combined with a High-Temperature Proton Exchange Membrane (HT PEM) fuel cell. These applications include automotive, heavy transport, marine shipping and various off-grid electricity applications and are commercialized by an American company (Advent, 2023) and a Danish company (Blue World Technologies, 2023).

### 7.8.3 *Stability of the MET/CO<sub>2</sub> system*

During steam reforming, carbon monoxide can be formed as a by-product. Carbon monoxide can further react with water to form carbon dioxide and hydrogen, but the hydrogen gas can contain trace amount of carbon monoxide.

#### 7.8.4 ZSS status derivations for the MET/CO<sub>2</sub> system

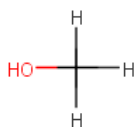
The table below summarizes the derived ZSS statuses for the different relevant substance of the MET/CO<sub>2</sub> system, which include the hydrogen carriers and the identified by-product. The ZSS derivations are elaborated after the table.

Table 12 Determination of ZSS status of relevant substances for the MET/CO<sub>2</sub> system.

CAS number	Substance name	ZSS status	Type of substance/ Remarks
67-56-1	Methanol	Probably not of equivalent care as ZSS or potential ZSS	Hydrogen-rich carrier
124-38-9	Carbon dioxide	Probably not of equivalent care as ZSS or potential ZSS	Hydrogen-lean carrier
7732-18-5	Water	Probably not of equivalent care as ZSS or potential ZSS	Solvent
630-08-0	Carbon monoxide	ZSS	By-product

Elaborations on ZSS status derivation

##### **Methanol: hydrogen-rich carrier**



CAS number: 67-56-1

Type: mono-constituent substance (structure shown)

Conclusion: Probably not of equivalent concern as ZSS or potential ZSS

*Substantiation:* The harmonized CLP classification for this substance is Acute Tox.3, Flam. Liq.2 and STOT SE 1. The RAC has been considering a proposal to use the substance as Repro. 1B to classify. This proposal was rejected by consensus because there is insufficient evidence of harmful effects on reproduction. The harmonized CLP classification currently in force is regarded as leading. Altogether, there are insufficient indications for a ZSS-related concern.

##### **Carbon dioxide: hydrogen-lean carrier**

See section 7.8.4

##### **Water: solvent**

See section 7.8.4

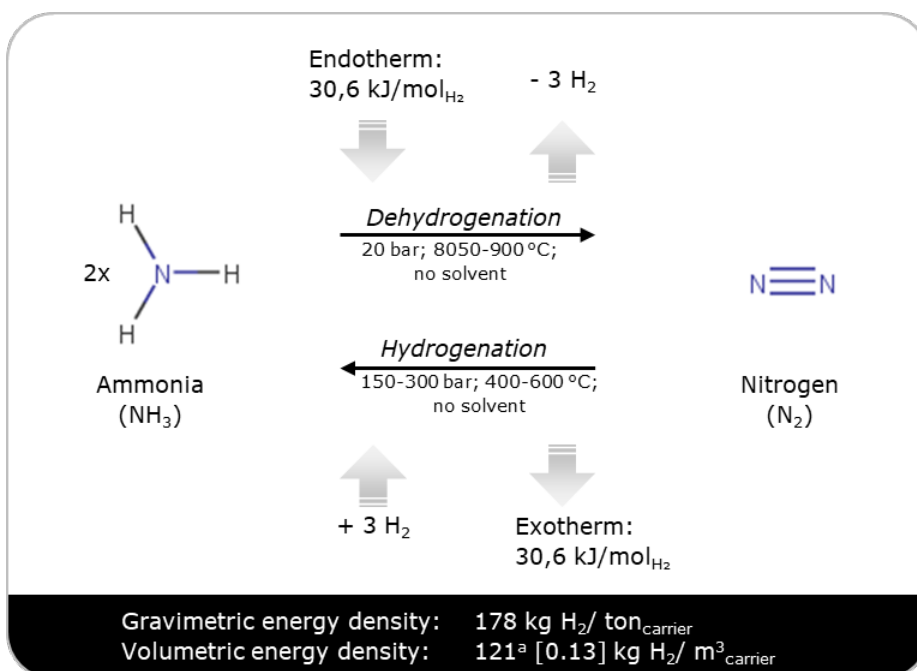
##### **Carbon monoxide: by-product**

See section 7.7.4

## 7.9 Ammonia and nitrogen (NH<sub>3</sub>/N<sub>2</sub>)

### 7.9.1 ZSS conclusions and system overview

There are no ZSS-related concerns for the hydrogen carrier-rich carrier ammonia and the hydrogen-lean carrier nitrogen.



<sup>a</sup> Property of liquid ammonia at 10 bar and 20 °C. At ambient pressure and temperature, ammonia is a gas with a very low volumetric density as given between brackets.

Figure 13. Schematic representation of the NH<sub>3</sub>/N<sub>2</sub> system.

### 7.9.2 Characteristics of the NH<sub>3</sub>/N<sub>2</sub> system

#### **Type:**

Circular LIHC; The hydrogen-lean carrier nitrogen can be released to the atmosphere. Return transport is not required.

#### **Availability:**

Current ammonia volumes (REACH registration: 10 to 100 million tons per year) are not relevant for LIHC use, as the hydrogen used for the ammonia production is derived from fossil energy sources. Ammonia is 2<sup>nd</sup> most produced substance worldwide and is primarily used in fertilizer manufacturing, but also for the production of other chemicals, as cleaning agent or refrigerant. Current ammonia production capacity can be adapted to produce ammonia relevant for LIHC use (see below). Nitrogen is not registered under REACH. Nitrogen is captured from the atmosphere and is commercially available.

#### **Dehydrogenation:**

Thermal cracking of ammonia into nitrogen and hydrogen is currently applied for certain industrial processes (e.g. galvanizing) at temperatures of 800-950 °C and a pressure up to 20 bar using nickel supported on aluminium oxide as catalyst (Lucentini et al., 2021; Papadias, Peng, & Ahluwalia, 2021). The method is energy intensive, and the hydrogen needs to be purified after cracking as the gas mixture contains nitrogen and trace amounts of ammonia. Currently, there are no industrial scale ammonia crackers for LIHC use.

#### **Transport and storage:**

Infrastructure for storing, transporting and handling of gaseous and liquified anhydrous (without water) ammonia are in place and already mature. Due to the high acute toxicity of ammonia and its corrosive properties, transport is heavily regulated. In the EU, ammonia is generally produced and used on-site. In the USA, ammonia is nationally transported by pipelines (Papadias, Peng, & Ahluwalia, 2021).

**State of technology:**

Production of ammonia is operational at large scale. Other aspects need further development, notably the dehydrogenation process, as detailed below.

*Hydrogenation:* Ammonia is currently produced with the Haber-Bosch process using hydrogen derived from natural gas. The hydrogen-nitrogen mixture reacts over an iron catalyst at a temperature of 400-600 °C and a pressure around 150-300 bar. Newer plants use a ruthenium-based catalyst at lower pressure. The Haber-Bosch process is characterised by recycling of the unconverted part of the synthesis gas and separation of the ammonia product under high pressure (Lucentini et al., 2021). This energy intensive method can be adapted to use renewable hydrogen as starting material. Various projects are announced globally, including an ammonia demonstration plant in Northern Chile that is expected to be operational by 2025 and that will produce 18000 tons renewable ammonia annually using hydrogen produced by solar power (Mitsui & Co., 2023), and a larger project that is expected to be constructed in 2025 and that will produce 1 million tons of ammonia annually from renewable wind energy generated in Chile (HNH Energy, 2022). Besides the Haber-Bosch process, research is conducted toward electrochemical reduction of nitrogen to ammonia which requires the transfer of 6 electrons. This process is considered challenging and is still in an early research phase (Ulucan et al., 2023; Yang et al., 2021).

*Dehydrogenation:* Thermal cracking of ammonia (as described above) is being further developed to reduce the energy demand, for example by optimizing catalysts and reactor design and application of selective membranes (Lucentini et al., 2021). Other techniques that are still in research phase are electrochemical decomposition of ammonia under ambient temperature and pressure, and photocatalytic ammonia decomposition (Yousefi Rizi & Shin, 2022). Currently, there are no industrial scale ammonia crackers for LIHC use. A pre-feasibility study has been conducted for a centralized ammonium cracker in the Port of Rotterdam with a capacity of 7.3 million tons of ammonia yielding 1 million tons of hydrogen annually (Port of Rotterdam, 2023). A pilot scale ammonium cracker is being constructed in the Port of Antwerp (Belgium) that should be operational in 2024 (Air Liquide, 2023).

*Applications:* Use of ammonia for large scale hydrogen transport is extensively investigated with projects ongoing in exporting and importing countries (see above). Use of ammonia as energy carrier also caught momentum. The proposals to use ammonia as fuel in combustion engines in the maritime and heavy duty transport sectors are outside the scope of this report, but it is important to realise that while no carbon dioxide is released, other pollutants are released including nitrous oxide. Nitrous oxide is a potent ozone-depleting greenhouse gas (Tian et al., 2020). The application of ammonia to power devices using fuel cells is within the scope. Different demonstration scale projects are running. A system with an onboard cracker and an integrated hydrogen fuel cell is being developed by a company named Amogy. The system was demonstrated in a truck (300 kW) with plans to up scale the modular system to power a tugboat (1 MW) (Marrin & Moss, 2023). The Norwegian company Alma Clean Power is developing a solid oxide fuel cell system that directly feeds in the ammonia without need for cracking (direct ammonia fuel cell). They successfully tested a 6 kW unit that will

become part of a 100 kW module aimed to power maritime ships (Alma Clean Power, 2023). Use of ammonia for powering of trains is also being investigated (Zhang et al., 2023).

### 7.9.3 Stability of the NH<sub>3</sub>/N<sub>2</sub> system

By-products during (de)hydrogenation have not been identified.

### 7.9.4 ZZS status derivations for the NH<sub>3</sub>/N<sub>2</sub> system

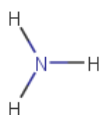
The table below summarizes the derived ZZS statuses for the hydrogen carriers of the of the HN<sub>3</sub>/N<sub>2</sub> system. The ZZS derivations are elaborated after the table.

Table 13 ZZS statuses of substances relevant for the NH<sub>3</sub>/N<sub>2</sub> system.

CAS number	Substance name	ZZS status	Type of substance/ Remarks
7664-41-7	Ammonia	Probably not of equivalent care as ZZS or potential ZZS	Hydrogen-rich carrier
7727-37-9	Nitrogen	Probably not of equivalent care as ZZS or potential ZZS	Hydrogen-lean carrier

#### Elaborations on ZZS status derivation

##### **Ammonia: hydrogen-rich carrier**



EC name: Ammonia, anhydrous

CAS number: 7664-41-7

Type: mono-constituent substance (structure shown)

Conclusion: Probably not of equivalent concern as ZZS or potential ZZS

Substantiation: The substance is not listed on the ZZS or potential ZZS list. The substance does not have CLP harmonised or self-classifications as CMR cat. 1 or 2. The aqueous solution of ammonia (in water) (CAS 1336-21-6) has one Muta. 1B + Carc. 1A self-classification (1 of 5872). The available toxicity data in the REACH dossier do not warrant a classification as Muta. 1B and Carc. 1A. Altogether, there are currently insufficient indications for a ZZS-related concern

##### **Nitrogen: low hydrogen carrier**



CAS number: 7727-37-9

Type: mono-constituent substance (structure shown)

Conclusion: Probably not of equivalent concern as ZZS or potential ZZS

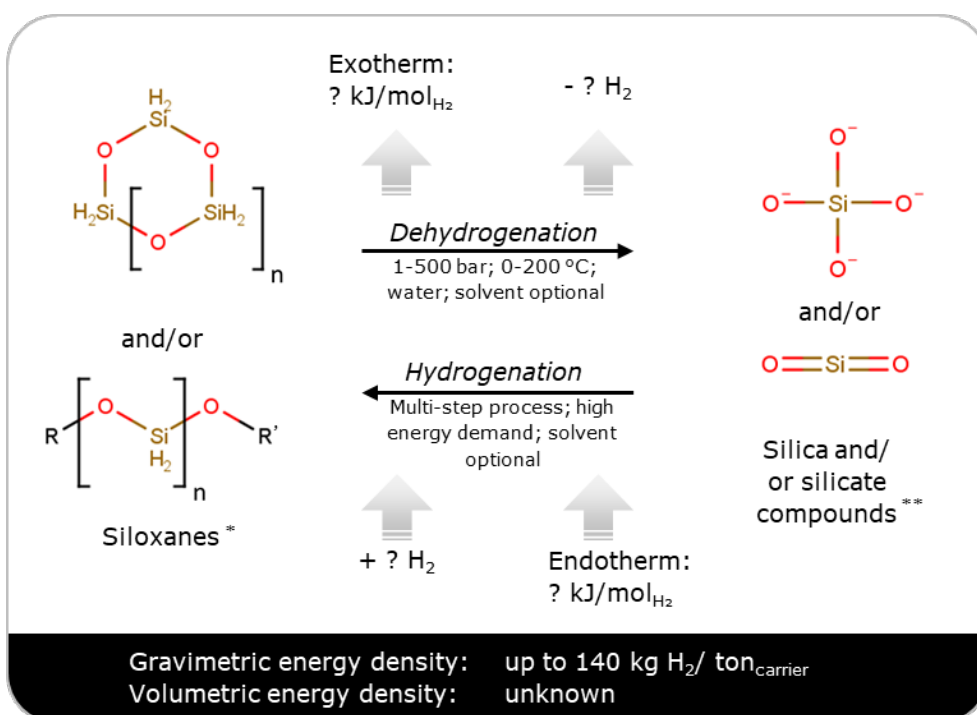
Substantiation: The substance is not listed on the ZZS or potential ZZS list. The substance has one Muta. 1B + Carc. 1A self-classification (1 of 982). One ECHA's CLP site it is indicated that this classification is

affected by impurities/additives. Altogether, there are no data for this substance that indicate a ZZS related concern.

## 7.10 Silicon hydride derivatives and silica/silicate (SHD/SS)

### 7.10.1 ZZS conclusions and system overview

No ZZS conclusions can be drawn for this system as it remains unclear which substances are used as hydrogen carriers, with only broad descriptions being available (see overview below). It is not clear if solvents are used. Silanes as well as silicate-type by-products are reported, but substance details are not available.



\* The hydrogen-rich carriers are described as poly(dihydro)siloxanes without carbon in their structure, having a linear or cyclic structure. The number of repeating units (n) is broadly specified as being between 1 and 500. The linear structures are at least on one side terminated by an end group (R/R') containing one or more halogens: -SiH<sub>3</sub>, -SiH<sub>2</sub>X, -SiHX<sub>2</sub>, -SiX<sub>3</sub>, -SiH<sub>2</sub>OH, -SiH(OH)<sub>2</sub>, or -Si(OH)<sub>3</sub> with X being preferably Cl (but could also be F, Br, or I). The molecular weight of the cyclic siloxanes is indicated as being between 130 and 800 g/mol, corresponding to substances with 3 to 17 repeating units. The number average molecular weight (M<sub>n</sub>) of the linear siloxanes is indicated to range between 64 and 30 000 g/mol, with the corresponding molecular weight distribution (Đ) being 1.1 and 50. The lower range corresponds to a linear siloxane without halogens, i.e. SiH<sub>2</sub>(OH)<sub>2</sub>, which is not in agreement with the description given in the patent (Burcher et al., 2021). The linear siloxanes are polymers. The hydrogen-rich blend consists of the halogen terminated carbon-free liquid linear siloxane hydrogen carriers together with cyclic siloxanes and/or cyclic silanes. The latter being substances consisting of only of silicon and hydrogen.

\*\* The hydrogen-lean carriers are described as being silica or silicate compounds (graph depicts the structure of orthosilicate as an example).

Figure 14 Schematic representation of the SHD/SS system.

### 7.10.2 Characteristics of the SHD/SS system

The information provided in this section is almost exclusively obtained from a patent granted to the company commercializing this technology (HSL technologies, formerly HySiLabs) (Burcher, Lome, & Benoit, 2019;

Burcher et al., 2021). The amount of information available in the public domain is very limited, with no peer-reviewed sources that can substantiate the claims.

**Type:**

Reversible LIHC. Return transport of the hydrogen-lean carrier is in principle required to repeat the cycle.

**Availability:**

Silica and silicate compounds can be easily obtained, but not clear if that is also the case for the compounds used in this technology.

**Hydrogenation:**

The binding of hydrogen is a multi-step process that requires energy (in contrast to LOHCs). The process can be roughly described as the reduction of silica/silicate compounds to elemental silicon (Si) using plasma at temperatures between 2000 and 20000 °K. The elemental silicon is hydrohalogenated to halosilanes using a hydrogen halide source (e.g. HF or HCl, the latter yielding  $\text{H}_2\text{SiCl}_2$ ,  $\text{HSiCl}_3$  or  $\text{SiCl}_4$ ). The halosilanes are then hydrolysed to yield the hydrogen-rich siloxanes. Different operating conditions are reported, including temperatures ranging from -50 to 6000 °C and pressure from 0.00001 to 100 bar. Various by-products are reported, some of them indicated to be reused during different steps of the production process.

**Dehydrogenation:**

Hydrogen is released by hydrolytic oxidation of the siloxanes in the presence of a hydrogen release initiator and water, with the latter acting as a proton source. Various substances are indicated as potential hydrogen release initiators, including the preferred substance sodium hydroxide. This exothermic reaction is reported to occur quickly releasing hydrogen in large amounts and with high yields, without the need for energy input (in contrast to LOHCs). The operating temperature is indicated as preferably between 15 and 30 °C, but can be within a wider range of 0 to 200 °C. The pressure is indicated as 1 to 500 bar. The patent indicates that catalysators and solvents (e.g. alcohols, aqueous solvents or organic solvents) are optional. The resulting silica/silicate compound(s) are preferentially used to repeat the process.

**Transport and storage:**

The hydrogen-rich carriers are liquids at ambient environmental conditions that can be transported and stored using existing infrastructure. It is not clear if the hydrogen-lean carriers are solids or liquids (with the silicate compounds being dissolved).

**State of technology:**

The technology is on the verge of demonstration phase. The synthesis of the hydrogen-rich carriers consists of several steps and is considered the most challenging aspect. In a Horizon2020 project a synthesis demonstration plant producing 20 kg/year was developed (HySiLabs, 2022). Different pilot projects are announced, including cooperation with the Port of Amsterdam for storing hydrogen on an industrial scale (H2Gate) and the coupling with fuel cells (QualifHY). The status of the latter projects is not known.

7.10.3 *Stability of the SHD/SS system*

Stability of the hydrogen-rich blend containing halogen terminated carbon-free liquid linear siloxane hydrogen carriers is apparently increased by addition of cyclic siloxanes and/or cyclic silanes. It is

reported that the hydrogen-rich blend was stored for several months at room temperature without loss of hydrogen content or noticeable degradation. No details were provided to underpin these statements. Following release of hydrogen, silica/silicate compound(s) are formed that are used as starting material to repeat the process. It is unclear if other by-products are formed.

#### 7.10.4 *ZZS status derivations for the SHD/SS system*

Several substances could be identified as hydrogen-rich and hydrogen-lean carriers from the broad descriptions provided. However, it remains unclear if the identified substances are used or if they are only potential candidates. Similarly, it cannot be concluded which substances are used as hydrogen release initiators, if by-products are formed in substantial amounts and to what extent they are reused in the synthesis process, and if solvents are used as they are indicated as optional. Overall, there are too many uncertainties to derive the ZZS-status of the individual substances within this system. Few general remarks can be made.

With regard to the hydrogen-lean carriers, if they are present as respirable dust, they can be carcinogenic. The group 'respirable crystalline silica dust', with group members Cristobalite (CAS 14464-46-1), Tridymite (CAS 15468-32-3) and Quartz (SiO<sub>2</sub>) (CAS 14808-60-7) is listed on the Dutch ZZS-list, as Directive (EU) (2017/2398) concludes that there is sufficient evidence of the carcinogenicity of respirable crystalline silica dust.

The hydrogen-rich carriers contain no carbon atoms in their structures, and it remains to be seen to what extent their properties (e.g. physicochemical, PBT, CMR) can be estimated using existing models. For estimates to be meaningful, comparable substances should be part of the training set of the model. For example, running the SMILES codes of several cyclic siloxanes shows that the models within EPIsuite give a warning that the substance is inorganic and that the estimate is outside the estimation domain.

## 8 Discussion, conclusions and recommendations

A transition towards a hydrogen economy is being stimulated in the EU and the Netherlands, with ambitious goals set for domestic production of renewable hydrogen as well as imports into the EU. To enable these ambitions large scale transport and storage of renewable hydrogen will be needed. Many options are currently on the table with none of them ticking all the boxes. Transport of gaseous hydrogen via pipelines seems the most favourable option in the long run, but the appropriate infrastructure needs to be put in place by repurposing existing natural gas pipelines and extending the network. Pipelines also have their limitations, especially when considering import from far away regions that might become important suppliers of renewable hydrogen, such as Chile and Australia. In analogy to the current practice for petroleum and its derivatives, transport using tankers seems particularly suitable in those situations. But in which form the hydrogen will be shipped is yet to be determined. Liquid hydrogen needs complex infrastructure that is not yet in place and has the disadvantage that efficiency decreases with the distance travelled and time spent. Hydrogen carriers that are liquid under ambient conditions or that become liquid under relatively mild conditions seem at this stage more suitable to kick start the transition as existing transport and storage infrastructure can be used. Various liquid hydrogen carriers have been proposed, some of which are close to large-scale implementation.

To facilitate informed decision making regarding the use of liquid hydrogen carriers, this report elaborated on the underlying concept, provided an overview of the field and investigated ten relevant liquid hydrogen carriers in more detail. Particular attention was given to the hazardous properties in terms of ZZS (the Dutch term for SVHC)<sup>7</sup>. ZZS are substances that can be harmful to humans and the environment, and they can be carcinogens, mutagens, reproduction toxicants, persistent and bioaccumulative substances, or substances with properties that lead to an equivalent level of concern, such as endocrine disruptors. Dutch national policy is to keep ZZS out of the living environment where possible. The knowledge generated in this report on the ZZS properties of liquid hydrogen carriers can be considered complementary to the existing external safety risk assessments (Arcadis & Berenschot, 2021; Berenschot, Arcadis, & TNO, 2023), as the two approaches focus on different safety aspects. For a complete picture, the risks to workers, public and the environment should also be assessed, taking thereby all relevant substances that have been identified, into account. This will require the modelling of emissions and the retrieving of exposure data from the REACH registration dossiers, both of which were outside the scope of this study.

<sup>7</sup> ZZS is an abbreviation of the Dutch term for Substances of Very High Concern, i.e. '*Zeer Zorgwekkende Stoffen*'. ZZS identification is based on exactly the same criteria as SVHC identification, i.e. Article 57 of the REACH regulation. Still the Dutch ZZS list is broader than the Candidate List of SVHCs for Authorisation. This is because the Dutch ZZS list includes formally identified SVHC's, but also substances that comply with the SVHC criteria regardless of their formal SVHC status under the REACH regulation (see section 6.3 for more details).

Our inventory of liquid hydrogen carriers shows that the field is broader than anticipated, that developments are speeding up with several liquid hydrogen carriers being close to large-scale implementation, and that for certain candidates applications are developed that are beyond bulk transport and storage of hydrogen, making them *de facto* energy carriers. Liquid hydrogen carriers can be carbon based (LOHC) or without carbon (LIHC). Some require a return transport to repeat the process (reversible type). Others start each cycle by capturing the hydrogen-lean carrier from the atmosphere (circular type). The circular LIHC ammonia and the reversible aromatic LOHCs toluene and benzyltoluene appear to be the closest to large scale implementation for the transport of renewable hydrogen, while the interest for the circular LOHC methanol is increasing. Drawback of the circular candidates is that the hydrogenation step is rather energy intensive. An additional bottleneck for methanol is that capturing of carbon dioxide from the atmosphere (DAC) is still costly and needs upscaling to operational scale. Temporary solution could be the use of carbon dioxide captured from emission sources (CCU), but this is not a carbon dioxide neutral process. Drawback of the reversible candidates is the return transport which adds up to costs and logistics. We note that the production of the aromatic substances (biobased or fossil) was not considered in this study, but should also be taken into account. Our research further identified a trend where the use of particularly ammonia, methanol, formic acid and benzyltoluene is extended beyond the use as hydrogen carrier to act as an energy carrier that can directly power ships, heavy transport or off-grid energy systems. In those cases the hydrogen-rich carriers are dehydrogenated in end-devices with integrated fuel cells that convert the released hydrogen to electricity. These potentially wide dispersive uses should be considered in the discussions on liquid hydrogen carriers, as they can result in increased and diffused emissions.

The ZZS statuses derived show that all LOHCs investigated in this report have one or more substances with ZZS properties. Still differences were observed between the different types of LOHCs. For three of the four reversible aromatic LOHCs (benzyltoluene, dibenzyltoluene and naphthalene) and the reversible heteroaromatic LOHC (*n*-ethylcarbazole), at least the hydrogen-lean carrier has ZZS properties, often supplemented with ZZS by-products. The remaining reversible aromatic LOHC toluene had no ZZS carriers, but was shown to form three ZZS by-products. The primary by-product was benzene whose concentration increased with the degree of dehydrogenation. Generally, it can be expected that under operational conditions, where numerous hydrogenation-dehydrogenation cycles are performed at high temperatures, the amount of by-products formed will increase. From a ZZS point of view, where minimalization of ZZS emissions is pursued, preferentially by substituting ZZS with safer alternatives, large-scale introduction of (hetero)aromatic LOHCs might not be the obvious choice. The remaining LOHCs, being the reversible coupled LOHC ethylene glycol and the two circular LOHCs formic acid and methanol, all three formed the by-product carbon monoxide, which is a ZZS. Ethylene glycol formed an additional by-product with ZZS properties. In the case of formic acid and methanol it is relevant to note that the by-product carbon monoxide can react with water to form carbon dioxide during

dehydrogenation, thus removing the ZZS and increasing the hydrogen yield. From a ZZS point of view, the circular LOHCs seem a more favourable option than the investigated (hetero)aromatic and coupled LOHCs.

This study also investigated two LIHCs. The hydrogen carriers of the circular LIHC ammonia are not ZZS, and no solvent or by-products were identified. From a ZZS point of view, ammonia is an acceptable liquid hydrogen carrier. For the reversible LIHC silicone hydrate derivatives no conclusions could be drawn as it could not be determined which substances are used as carriers, if solvents are used, and if by-products are formed. We note that even if the hydrogen-rich substances were specified, it is likely that no conclusions could be drawn with regard to their ZZS properties due to their specific molecular structures. To our knowledge there are no halogen-terminated carbon-free siloxanes registered under REACH and existing models do not have similar substances in their training sets, preventing them to reliably estimate their properties. From a ZZS point of view, it would be recommendable to generate for these substances (eco)toxicological and environmental fate data prior to large scale implementation, so their ZZS statuses can be derived. A full overview of the derived ZZS statuses for each of the investigated liquid hydrogen carriers is provided in Table 15.

The methodology applied in this report foresees in four ZZS categories. These categories correspond to a ZZS concern with an increasing level of uncertainty when going from left to right in Table 15. Ideally, reliable (eco)toxicological and environmental fate data are available for a ZZS conclusion, which is drawn in one of the frameworks/regulations that allow a formal ZZS status to be determined. These substance are assigned the category 'ZZS' (i). In reality, it takes time to formally determine a ZZS status even when the necessary data are available yielding the category 'Consider as ZZS' (ii). The latter category also applies when substances are self-classified as CMR<sup>8</sup> category 1A/B, or when a substance contains a ZZS constituent. When there is substantial ZZS concern for a substance, and actions are taken under the REACH regulation to further investigate this concern (e.g. substance evaluation (preceded by CoRAP<sup>8</sup> listing), PBT<sup>8</sup> or ED<sup>8</sup> assessments) or the substance is in the process of being regulated with regard to ZZS properties (ARN<sup>8</sup> or ROI<sup>8</sup> for restrictions, SVHC<sup>8</sup> and CLH<sup>8</sup>) the substance is placed on the Dutch potential ZZS list, yielding the category 'Potential ZZS' (iii). The last category 'of equivalent concern as potential ZZS' (iv) is applied when there is a ZZS concern, but the substance has not been placed on the potential ZZS list, as there are no actions running under REACH. For substances in the latter category there is generally limited data available, often lacking essential data. Models are used to estimate relevant substance properties, which adds to the uncertainty. Substances falling in the latter category should, if prioritized, be further investigated.

<sup>8</sup> CMR: carcinogens, mutagens or reproduction toxicants; PBT: persistent, bioaccumulative and toxic substances; ED: endocrine disruptors; CoRAP: Community Rolling Action Plan; ARN: Assessment of Regulatory Needs, previously termed RMOA (Regulatory Management Option Analyses); RoI: Registry of Intentions.

Table 14 Overview of the derived ZZS statuses of the selected liquid hydrogen carriers.

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

\* Recently, LOHCs based on substituted naphthalene have been proposed. These systems were not extensively reviewed. We do note, however, that the hydrogen-lean carriers are substituted PAHs that belong to the ZZS group of PAHs.

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<sub>2</sub>: carbon dioxide; NH<sub>3</sub>: ammonia; N<sub>2</sub>: nitrogen; SHD: silicon hydride derivative; SS: silica and/or silicate compounds.

Another aspect that adds to the uncertainty of this research is data availability. For some liquid hydrogen carriers, e.g. toluene, a lot of data can be found regarding the substances used as well as those formed during (de)hydrogenation, while for others, e.g. silicone hydrate derivatives, no data were available at all. The lack of data can be interpreted as a lack of hazard, but that would be a wrong assumption. It is key that for substances that are intended to be used on a large scale data becomes available before implementation. This brings us to the point that when the application of a substance is altered, e.g. heat transfer oil use under closed conditions becoming used as a large scale liquid hydrogen carrier or even used as energy carrier that directly powers end-devices, with accompanying widespread use, its REACH registration dossier should be updated accordingly. The update should reflect the changes both with respect to the tonnage and accompanying (eco)toxicological and environmental data, as well as to the exposure scenarios foreseen. Other substances that have no REACH registrations should become registered which would disclose data necessary to determine their ZS properties.

This study showed that only one of the investigated liquid hydrogen carriers had no substances with ZS properties, i.e. the circular LIHC ammonia, and that the circular LOHCs methanol and formic acid do form the ZS by-product carbon monoxide, but also that that by-product can react during dehydrogenation to carbon dioxide. The other investigated LOHCs had two or more ZS by-products (toluene, esters of ethylene glycol) or used at least a hydrogen-lean carrier with ZS properties (benzyltoluene, dibenzyltoluene, naphthalene, *n*-ethylcarbazole). Application of the latter category for bulk transport of renewable hydrogen would appear especially troublesome from a ZS point of view, as it would mean that large quantities of ZS will be handled and shipped. Measures can be taken on an EU, national and local level to restrict/ban certain substances and/or applications after their introduction to improve safety, but the dynamics of this process is not in line with a Safe-and-Sustainable by Design (SSbD) approach. The energy transition is an ideal opportunity to get off to a good start, not hampered by legacy uses, aiming at a maximized safety and sustainability. Early on in the design process attention should be given to the identification of substances of concern within the liquid hydrogen carrier technology, thereby also considering the impact of these substances on health, climate and the environment during the entire lifecycle. These investigations should include the substances investigated in this study (carriers, solvents and by-products), but also the catalysts, which fell outside the scope of this study. For example, dehydrogenation of the LIHC ammonia is currently mainly conducted by a nickel supported on aluminum oxide as catalyst (Lucentini et al., 2021), with nickel being on the Dutch ZS list. Other hazardous aspects should be considered too. For example, the circular LIHC ammonia, which contains no ZS, is highly toxic and from an external safety point of view is not an obvious choice especially when used as energy carrier that can lead to widespread use. Comparing these different hazardous properties, as well as economic and practical aspects of liquid hydrogen carriers would allow for balanced decisions steering towards an energy transition that is green, sustainable and safe.

## 8.1 Recommendations

Innovation is an iterative process in which it is desirable to make well-directed choices as early as possible or to encourage such choices. Against this background, and considering that the systematic consideration of ZZS properties is lagging behind in the research and development of liquid hydrogen carriers, we recommend the following:

### *Recommendations for industry*

- Include ZZS screening as a standard part of the development process. This should be done as early as possible in the process thereby using the SSbD framework as proposed by the European Commission.
- Keep the registration of liquid hydrogen carriers under the REACH regulation up to date with regard to substance identity of the carriers, the tonnages used (and accompanying (eco)toxicological and environmental data), as well as to the exposure scenarios foreseen.

### *Recommendations for research institutes*

- Continue mapping of the rapidly evolving field of liquid hydrogen carriers to identify new candidates and/or altered uses.
- Develop assessment tools that allow weighing of liquid hydrogen carriers based on their ZZS properties, but also other relevant aspects such as sustainability, efficiency and realizability of the systems.
- Develop models and/or scenarios to estimate the exposure of humans and the environment to these substances and products.

### *Recommendations for authorities*

- Ascertain that this type of safety analysis is on the agenda of developers, financiers and policy makers.

## 9 Acknowledgments

This report is an extended and updated English version of an advice to the province of South Holland dated December 2022 that focused on LOHCs. We would like to thank C. van Driel (Province of South Holland), L. Louwerse (Province of South Holland), F. Meijer (Province of North Holland), R. van Ieperen (Province of North Holland), P.A. Pel (Environmental Protection Agency of the Rijnmond area) and M. Touber (Environmental Service of the Region Noordzee kanaal), for their participation in the advisory group of that project. We would like to thank J. van der Ree (RIVM) and the ministry of Economic Affairs and Climate Policy for enabling the publishing of this report within the framework of the project Strengthening the RIVM knowledge base on energy transition and environmental impacts. In addition, we would like to thank the various RIVM experts for their valuable input on this report: C.W.M. Bodar, M.E.J. Pronk, E. Rorije, A.G. Schuur, R. van Herwijnen and E.M.J. Verbruggen.



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## 11 Annex

### 11.1 Sources and data used for ZZS status derivation

*(English translation of section 3.6 of the Dutch guidance document 'Werkwijze stofadviezen ZZS in de vergunningverlening' (RIVM, 2020b)).* The following steps describe how information is collected to arrive at a substance recommendation and associated category. If sufficient data is found for a conclusion at a step, it is not necessary to continue. If nothing is found in a source, this is not explicitly stated in the substance advice.

- a. Check whether the substance is on the ZZS list. If so, it is indicated why this substance is on the ZZS list; reference is made to the sources for identification as ZZS. Even if the substance belongs to a group on the ZZS list, the substance is a ZZS.
- b. Check whether the substance is on the list of potential ZZS. If so, the reason for placement is stated.
- c. Check whether the Committee for Risk Assessment (RAC) or the Member State Committee (MSC) has already agreed an advice for a substance within the EU on harmonized CLP classification or PBT/vPvB status of the substance. This is particularly important if this advice has not yet been converted into an official harmonized CLP classification or inclusion in the REACH candidate list, respectively.
- d. Check the SDS and the website of the European Chemicals Agency (ECHA: [echa.europa.eu](http://echa.europa.eu)) whether there is a CLP self-classification according to the European CLP regulation (EC 1272/2008) as CMR cat. 1A/1B. This also happens if there is already a harmonized CLP classification. This involves examining why a CLP self-classification on the ECHA website may deviate from the harmonized CLP classification or classification on the SDS (for example, a contamination). RIVM can advise on how to interpret these differences.
- e. ECHA's website also checks whether the substance is classified as CMR cat. 2 and whether this classification is based on a lack of data.
- f. See if there is a positive PBT/vPvB (persistent, bioaccumulative and toxic/very persistent and very bioaccumulative) conclusion in the REACH dossier or if the SDS indicates that the substance is PBT/vPvB. In addition, check whether the dossier indicates that there were too few data for a PBT/vPvB conclusion.
- g. Check whether the substance has been included in the most recent lists of CMR substances of the Ministry of Social Affairs and Employment due to a classification as CMR cat. 1A/B or 1B by the Health Council. These lists are updated twice a year. NB According to the AB/AR, the SZW lists are not a source for inclusion on the ZZS list. However, the presence of a substance on one of these SZW lists may have prompted a company to identify this substance as ZZS (also known as ZZS self-classification).
- h. Search European dossiers as available under the REACH, plant protection products, biocides and (veterinary) medicines

regulations for additional data and assessments, which will be taken into account in the advice.

- i. Look for structural analogues that can serve as an indicator of environmental behaviour or toxicity of the substance. Check whether there are similarities in structure between the substance in the application and substances already on the ZZS list or on the list of potential ZZS. To this end, we use the recently developed similarity tool, see also (Wassenaar et al., 2019).
- j. Consult QSARs (models that can predict substance properties) such as the RIVM PB(t) tool (Rorije et al., 2011) and alerts from the OECD QSAR Toolbox and use the indications from the inventory for Annex III of REACH<sup>9</sup> to estimate whether the substance may have ZZS properties.
- k. Check whether the substance has an Occupational Toxicological Limit Value (ATG) on the SER website, or whether a Maximum Permissible Risk Level (MPR) is available for the substance on the Risks of Substances website. These values can be used as an indication of the degree of toxicity of the substance.

The inclusion of data from the public literature or sources other than those described above is not excluded.

## 11.2 Elaboration on the derivation of ZZS statuses

*(English translation of section 3.7 of the Dutch guidance document 'Werkwijze stofadviezen ZZS in de vergunningverlening' (RIVM, 2020b)).*

To ensure clarity between different recommendations, a number of additional guidelines are given below on how the information collected from a source as described in section 6.1 can be taken into account in the advice. The letters below (a, b, c etc.) are related to the letter from Section 6.1, additional items are at the bottom of the list with new letters l and m:

- a. The conclusion 'ZZS' follows for substances on the ZZS list or substances that belong to a substance group on the ZZS list.
- b. A further estimate of the ZZS status can be made for substances on the potential ZZS list. It can be concluded that the substance can be regarded as ZZS, but also that the care for the substance is probably not equivalent to ZZS or potential ZZS.
- c. For substances that have been identified as SVHC by the Committee for Risk Assessment (RAC), which deals with the harmonized CLP classifications, but for which no final formal decision has yet been taken by the European Commission, it is advised that this is a SVHC and is therefore placed on the ZZS list<sup>10</sup>. In only very exceptional cases, a RAC decision is not adopted by the European Commission. In the procedure we check whether something is going on at the RAC. In other cases where identification as ZZS is likely in the future, but which have not yet been treated by MSC or RAC, for example, it is advised to consider the substance as ZZS.
- d. If a notification has been submitted in the ECHA database that a substance is CMR cat. 1A/B (self-classification), then this substance must be treated as ZZS in the permit granting

<sup>9</sup> <https://echa.europa.eu/en/information-on-chemicals/annex-iii-inventory>

<sup>10</sup> This is due to the longer lead time within CLH before the decision is formal. This is indicated in the ZZS list with a footnote.

process. This CLP self-classification is still assessed within the substance advice. An example could be that there are many different notifications. The advice may then be based on the majority of the CLP self-classifications, but this will be assessed separately in each case. The notification can also be the result of pollution.

- e. A harmonized CLP classification as CMR cat. 2 may also have been given because there is insufficient data for CLP classification as CMR cat. 1A/B. Using this method, we can estimate whether a CMR cat. 2 substance can still be placed in the category of equivalent care as a potential ZS. In this case, we recommend the care of this CMR cat. 2 substance as equivalent to that of potential ZS<sup>11</sup>.
- f. If it is indicated in the REACH dossier or on the SDS that the substance is PBT or vPvB, it is recommended to consider the substance as ZS. If the dossier indicates that there are insufficient data for a PBT conclusion, a substance is a potential PBT/vPvB according to the REACH framework. On this basis, in combination with other PBT indications (see j), it can be concluded that the substance has an equivalent concern as a potential ZS.
- g. For substances for which the Health Council has recommended a CMR at. 1A/B classification and substantive substantiation is available for this advice, it can be advised to regard the substance as ZS. However, if a harmonized CLP classification is also available, then this is generally leading, see also e.
- h. The REACH dossier may contain data indicating that a substance may meet the SVHC criteria. The concern of the substance is then equivalent to that of potential ZS. The activities regulation states that substances with endocrine-disrupting properties are also ZS according to the criteria in the European regulation for biocides and plant protection products. Assessments in these frameworks can therefore also lead to the conclusion that a substance is a ZS.
- i. In addition to applying the RIVM similarity tool (see 3.6.i), an expert judgment will still be applied.
- j. The information from QSARs will have to be weighed separately for each substance. It is preferable if a conclusion is substantiated by several (relevant) QSARs.
- k. An ATG lower than 25 mg/m<sup>3</sup> is an indication that the substance has an equivalent concern to potential ZS.
- l. If it is estimated that a degradation product may be formed in sufficient quantities that may meet the ZS criteria, the advice will be based on the degradation product.
- m. For substances with several known components (UVCBs and multi-constituents<sup>12</sup>), the properties of the individual components are examined. This is usually done up to a lower concentration limit of 0.1% by weight, but this can also be lower, such as for benzo[a]pyrene, for which a concentration limit of 0.01% by weight is used under CLP. If one of these components of the

<sup>11</sup> Carrying out additional studies is not (yet) always possible under REACH (Woutersen et al., 2018). This has not been taken into account when drawing up the list of potential ZS because the classification proposal for each CMR 2 substance then has to be reviewed.

<sup>12</sup> See: <https://echa.europa.eu/nl/support/substance-identification/what-is-a-substance>

UVCB or multiconstituent is a (potential) ZZS, then this applies to the entire substance (van Herwijnen, 2019).

- n. Polymers are often multi-component substances but are exempt from REACH registration. This limits the amount of data and available assessments. A possible assessment step is to check whether the monomers and other components are permitted as raw materials for food contact materials. This may be an indication that a polymer does not meet the SVHC criteria. Other criteria can be used ad hoc to advise something about the (potential) concern of polymers.



Published by:

**National Institute for Public Health  
and the Environment, RIVM**

P.O. Box 1 | 3720 BA Bilthoven

The Netherlands

[www.rivm.nl/en](http://www.rivm.nl/en)

February 2024

Committed to  
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