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Hydrogen technologies — Methodology for determining the greenhouse gas emissions associated with the production, conditioning and transport of hydrogen to consumption gate

Annex J

Hydrogen Conversion Pathway – LOHCs as Hydrogen Carriers

Contents

Annex J
(informative)

Hydrogen Conversion Pathway – LOHCs as Hydrogen Carriers

J.1 Process description and overview

Sections J.1.1 and J.1.2 provide a description and an overview for LOHCs as hydrogen carriers.

J.1.1 Description

Liquid organic hydrogen carriers (LOHC) are easily transportable materials that can undergo relatively facile hydrogenation and subsequent dehydrogenation to be utilized as an alternative to high pressure or cryogenic hydrogen delivery. While LOHCs are still in the early stages of commercialization, their potential advantages include their compatibility with existing gasoline infrastructure (e.g., existing pipelines), high density of hydrogen compared to gaseous storage vessels, high boiling point relative to liquid hydrogen, and, depending on the compound, low toxicity.

LOHC hydrogenation involves hydrogenating a chemical feedstock, such as toluene, benzyltoluene (BT) or dibenzyltoluene (DBT), over catalyst beds. In the current guidance, the term “Initial LOHC” refers to the initial toluene, BT or DBT entering from outside the supply chain, “Hydrogenated LOHC” refers to the hydrogenated compound exiting the hydrogenation process, such as methylcyclohexane, perhydro-BT or perhydro-DBT, and “Dehydrogenated LOHC” refers to the toluene, BT or DBT exiting the dehydrogenation process. LOHCs are intended to be transported long distances and then dehydrogenated near the point of use to release hydrogen.

Many different feedstocks have been explored for use in LOHCs in RD&D efforts worldwide, including toluene, benzyltoluene (BT), dibenzyltouene (DBT), benzene, and N-ethylcarbazole. The current guidance focuses specifically on systems based on toluene, BT or DBT. Future guidance may address other LOHC systems.

J.1.2 Overview

Section J.1.2.1 and J.1.2.2 provide output metrics, system boundary and details for the process of LOHC hydrogenation and dehydrogenation.

J.1.2.1 Output Metrics and System boundary

Key sources of emissions in the LOHC pathway can be categorized into modules, described in Figure J.1 —. While the design and configurations of hydrogenation/dehydrogenation facilities can vary widely, they generally entail exothermic hydrogenation, endothermic dehydrogenation, recycling of the feedstock chemical (e.g., toluene, BT or DBT) between the point of dehydrogenation and hydrogenation, and use of “makeup” LOHC in the hydrogenation step to account for losses during the hydrogenation/dehydrogenation cycles. As shown in Figure J.3 —, LOHC can also be directly produced, bypassing hydrogen production and delivery in a process called Direct MCH production (DMCH).

The guidance below in Section J.1.2.2 describes the mechanisms to characterize emissions of Modules 3, 4, and 6. The emissions associated with Module 1 should be calculated per ISO/TS 19870,” with one exception regarding the reporting unit.

Transportation Annexes describe the methodology for calculating the emissions associated with modules 2, 5, and 7.

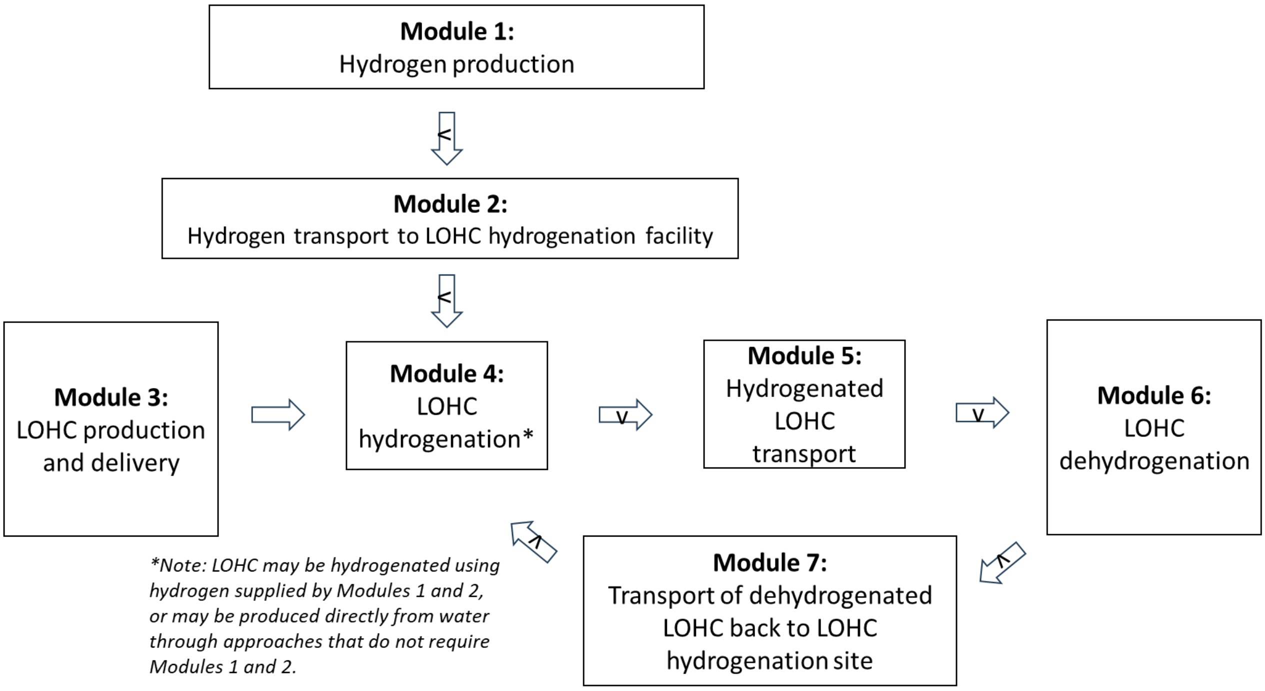

Figure J.1 — Modules for Life Cycle Analysis of LOHCs

The current guidance recommends the use of the following reporting metric for life cycle analysis:

- Kilograms of carbon dioxide equivalent per kilogram of hydrogen (i.e. $kgCO_2e/kgH_2$). The numerator corresponds to the sum of emissions associated with Modules 1-7. In a given deployment, if a Module does not occur (e.g., if hydrogen is not separately produced in delivered, in the case of the direct MCH pathway), then its emissions associated with that module can be treated as zero.

The current guidance recommends that the functional unit (kgH_2) reflect the mass of hydrogen produced by the LOHC dehydrogenation facility at the end of Module 6.

J.1.2.2 LOHC hydrogenation and dehydrogenation

As shown in Figure J.2 —, the production of MCH, PBT or PDBT commonly entails passing the Initial LOHC (toluene, BT or DBT) through a heat exchange, mixing the Initial LOHC with hydrogen, and then passing the mixture through a reactor with catalyst beds. Facilities can vary concerning heat integration, and the temperature and pressure of the Initial LOHC mixed with hydrogen will determine the amount of Hydrogenated LOHC produced.[1,2] An emerging alternative is the direct use of water and electricity without a separate hydrogen supply. This pathway, depicted in Figure J.3 — is currently in the early stages of commercialization.

The toluene feedstock used in MCH production is typically produced during the petroleum refining process.[3] BT and DBT are made from toluene and benzyl chloride. Once the toluene, BT or DBT is

[1] https://www.mdpi.com/1996-1944/13/2/277
[2] https://www.sciencedirect.com/science/article/abs/pii/S0360319921016815
[3] https://www.euro.who.int/__data/assets/pdf_file/0020/123068/AQG2ndEd_5_14Toluene.PDF

produced, it would be delivered to a LOHC hydrogenation facility (unless the LOHC system was onsite) for hydrogenation.[4]

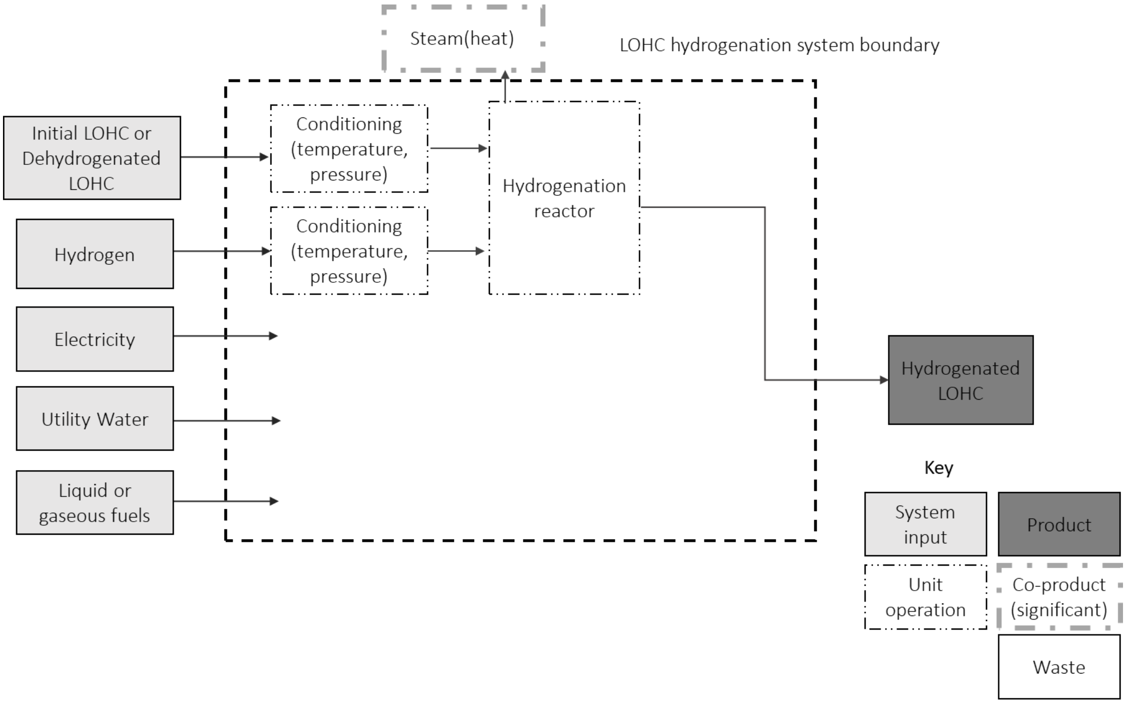

Figure J.2 — Example configuration of common LOHC hydrogenation pathways

Key attributes of facilities that will commonly vary include the degree of condensation, the manner of heat integration, and whether purge gases are disposed of as waste products (e.g., vented) or burned for heat generation. Figure adapted[2].

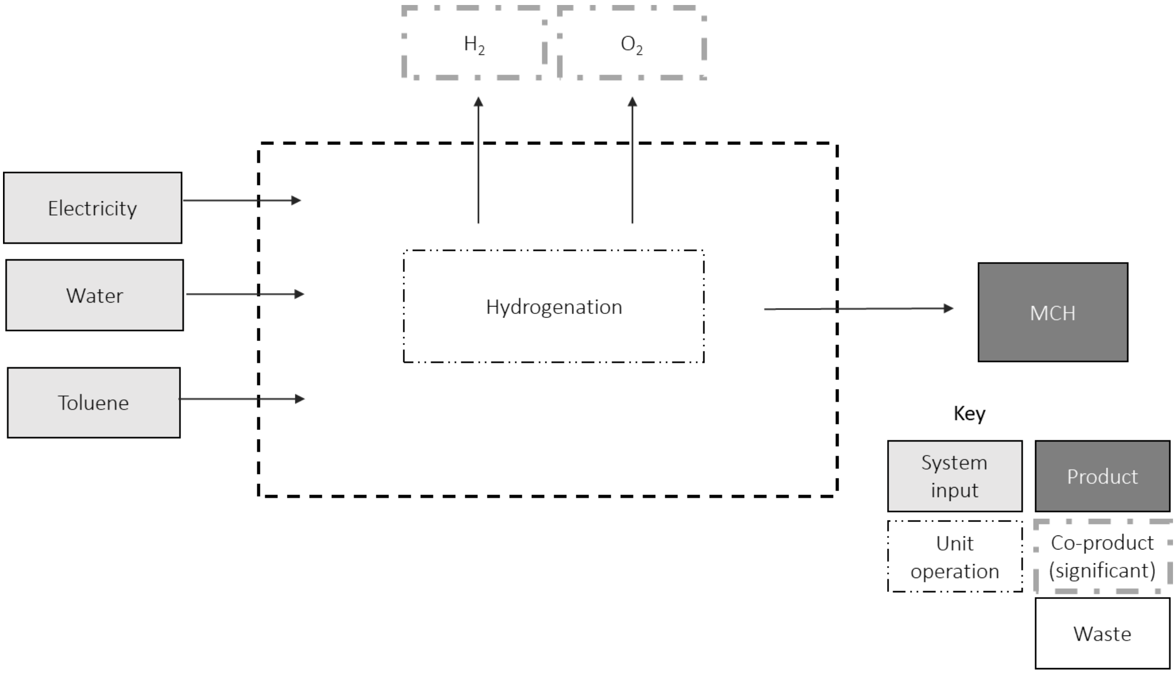

Figure J.3 — Example configuration of Direct MCH Pathway

4 https://ec.europa.eu/research/participants/documents/downloadPublic?documentIds=080166e5c551f4c2&appId=PPGMS

The pathway is currently in the early stages of commercialization.

Once a Hydrogenated LOHC is delivered to a Dehydrogenation facility, the dehydrogenation process releases the original toluene, BT or DBT and hydrogen. If carriers are used for large-scale commercial transport, it is expected that, in most cases, most Dehydrogenated LOHC will be sent back to the original hydrogenation facility for reuse or valorized regionally for other purposes (e.g., chemicals production) and that the remainder will be lost to the atmosphere. To produce a new batch of Hydrogenated LOHC, the original hydrogenation facility will typically utilize any Dehydrogenated LOHCs returned to the facility and supplement this with "makeup" LOHC. This "makeup" LOHC refers to new Initial LOHC produced to compensate for Dehydrogenated LOHC that was not returned (e.g., due to losses at the dehydrogenation facility). In scenarios where dehydrogenation losses are low, and most Dehydrogenated LOHC is returned from the dehydrogenation facility to the site of hydrogenation, the contribution of the emissions associated with the makeup LOHC production to the carbon intensity of hydrogen is expected to be low. However, in scenarios where losses during dehydrogenation or transport are high, the emissions associated with makeup LOHC production may become substantial.

To account for this variability, the document recommends that emissions associated with the production of makeup toluene, BT or DBT are accounted for in evaluating the emissions of LOHC. The emissions associated with producing the original batch of Initial LOHC for a facility of a given capacity may be excluded from the system boundary, as this Initial LOHC is expected to be levelized throughout hydrogen production over many years and ultimately represent a small share of life cycle emissions for hydrogen delivery from LOHCs considered in the current document.[5] Across this document, emissions associated with manufacturing the equipment used in hydrogen production (e.g., renewable or fossil generators, electrolyzers) are currently similarly excluded from the scope of analysis.

To distinguish the emissions associated with producing makeup LOHCs from those associated with producing an original batch, this document proposes two approaches to quantifying the amount of makeup LOHC:

1. Stakeholders engaged in producing LOHCs may report the total amount of toluene, BT or DBT used for LOHC hydrogenation within a specified analysis period (e.g., one year), as well as the amount returned by LOHC dehydrogenation facilities to the LOHC hydrogenation facility. The balance of LOHC represents the makeup, and emissions associated with this makeup must be reported.

$$\textit{Makeup LOHC} = \textit{Total LOHC delivered to the LOHC hydrogenation facility for hydrogenation} - \textit{Dehydrogenated LOHC received from LOHC dehydrogenation facilities} \quad \text{(J1)}$$

Equation 1: Quantity of makeup LOHC manufactured for LOHC hydrogenation over analysis period.

2. Stakeholders may meter the amount of makeup LOHCs produced and use the measured value instead of the estimate above.

[5] The life cycle emissions of toluene production are estimated at ~1.22 kgCO2e/kg-toluene. (Source: Plastics Europe. "Benzene, Toluene, and Xylenes (Aromatics, BTX)". February 2013. http://gabi-documentation-2014.gabi-software.com/xml-data/external_docs/PlasticsEurope%20Eco-profile%20BTX%202013-02.pdf). About 20 kg toluene are expected to be needed for each kg of hydrogen in the production of MCH. (Source: Argonne National Laboratory. "Toluene-Methylcyclohexane as Two-Way Carrier for Hydrogen Transmission and Storage". https://publications.anl.gov/anlpubs/2021/11/171777.pdf)

As noted above, toluene is commonly manufactured at petroleum refineries along with other petroleum products, and BT/DBT are manufactured from toluene and benzyl chloride.[6,7] Estimates of the emissions intensity of each Initial LOHC should account for direct and indirect emissions (excluding emissions associated with construction, manufacturing, and decommissioning of capital goods, business travel, employee commuting, and upstream leased assets). Since producing processes for each Initial LOHC are not expected to vary widely within each region, stakeholders may use region-specific emissions factors in the life cycle analysis of LOHCs. As the market for LOHCs develops, it is expected that such region-specific analysis will be documented, and standardized databases and guidance documents will be developed to inform LCA.

The configuration of dehydrogenation facilities is described in Figure J.4.

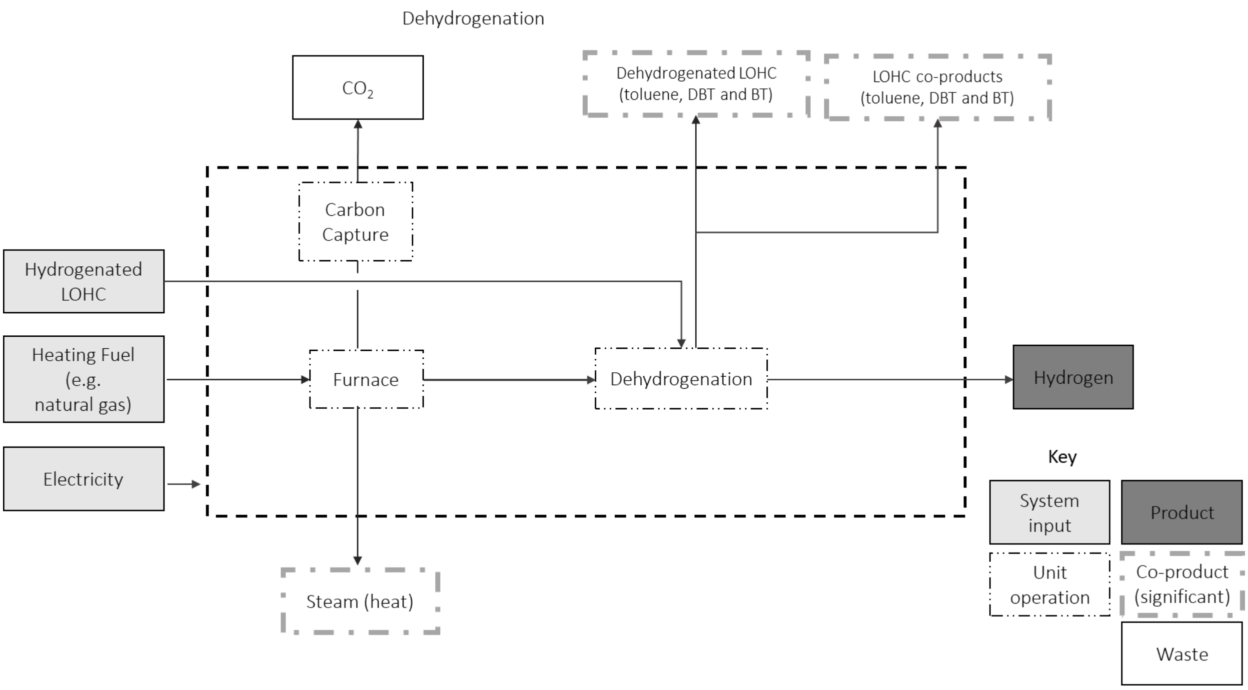

Figure J.4 — Example of configuration for LOHC dehydrogenation plant.

Attributes of facilities that may vary include whether or not the facility contains a PSA, whether the facility contains CCS, and the degree of condensation.

J.2 Emission sources and inventory

Table J.1 — and Table J.2 — provide emission sources and inventory for, respectively, LOHC production and hydrogenation and LOHC dehydrogenation.

Table J.1 — **Key Life Cycle GHG Emission Sources in LOHC Production and Hydrogenation**

Process unit/stage	Key emissions sources	Secondary emissions sources

[6] PlasticsEurope Eco-profile BTX Final 2013-03-05.doc (gabi-software.com)

[7] https://ec.europa.eu/research/participants/documents/downloadPublic?documentIds=080166e5c551f4c2&appId=PPGMS

Toluene production	• Extraction of petroleum feedstock • Delivery of petroleum to the refinery • Emissions allocated to toluene at the petroleum refinery, e.g., due to fuel combustion or electricity consumption	Toluene losses onsite
BT production	• Emissions intensity of toluene producing • Emissions intensity of chlorine production and subsequent benzyl chloride producing • Electricity consumption at the BT producing facility • Emissions at point of BT manufacture due to fuel combustion	BT losses onsite
DBT production	• Emissions intensity of toluene production • Emissions intensity of chlorine production and subsequent benzyl chloride producing • Electricity consumption at the DBT production facility • Emissions at point of DBT production due to fuel combustion	DBT losses onsite
Hydrogenation facility	• Emissions of electricity consumption • Potential fuel combustion. [8] Emissions should reflect CO_2 emissions onsite as well as emissions intensity of upstream fuel extraction, processing, and delivery. Emissions intensity of fuel extraction, processing, and delivery should include emissions of all associated electricity consumption, fuel combustion, and fugitive releases.	
Water supply and treatment to Direct MCH pathway	• Electricity for purification and treatment of water	

Table J.2 — **Key Life Cycle GHG Emission Sources in LOHC Dehydrogenation**

Process unit/stage	**Key emissions sources**	**Secondary emissions sources**
Furnace	• Production of heating fuel (e.g., natural gas)[9] • Delivery of heating fuel to dehydrogenation facility, including fugitive emissions and electricity or fuel consumed in transport (e.g., via pipelines or trucks) • Fugitive GHG emissions of heating fuel at dehydrogenation facility • CO_2 released by the furnace	
Dehydrogenation reactor	• Electricity consumption	

[8] Fuel combustion is not expected at all facilities, and will be negligible in many cases.

[9] In some cases, the heating fuel used may not be a fossil fuel. For instance, waste heat from nearby industrial processes may be used, or some of the hydrogen released via dehydrogenation may be used. If waste heat (that would otherwise be rejected to the atmosphere) is utilized, its emissions intensity may be treated as 0. If hydrogen is utilized, its emissions should be represented using ISO/TS 9870.

J.3 Emission Allocation

Potential co-products from hydrogenation are described in Table J.3 —.

Table J.3 — **Potential Co-Products and Emissions Accounting Framework for Hydrogenation**

Step	Potential Co-Products	Recommended Approaches to Emissions Accounting
Hydrogenation Reactor	Heat or steam generation for export	Allocation based on energy basis. (Attributional approach) System expansion. (Consequential approach)
Hydrogenation for Direct MCH pathway	Oxygen	System expansion (consequential approach)
Hydrogenation for Direct MCH pathway	Hydrogen	System expansion (consequential approach)

Table J.4 — **Potential Co-Products and Emissions Accounting Framework for Dehydrogenation**

Step	Potential Co-Products	Recommended Approach to Emissions Accounting
Furnace/dehydrogenation reactor	steam	Subdivision and Allocation based on physical causality (energy basis) (attributional approach) System expansion (consequential approach)
Dehydrogenation Reactor	Toluene, BT or DBT that is not returned to the hydrogenation facility but valorized in other markets	System expansion (consequential approach), using a region-specific emissions factor developed to include parameters described in Table J.1 —

J.4 Information to be reported

Table J.5 — describes reporting requirements for LOHC producers.

Table J.5 — **Information to be Reported for LOHC Hydrogenation Facilities**

Category	Parameters to Report
Facility details	• Facility identity • Facility location • Facility capacity [t/year] • Commencement of facility operation
Product specification	• Quantity of hydrogenated LOHC produced [tonnes]
Batch details	• Beginning and end of batch dates • Batch quantity [tons]

Electricity	Location-based emissions accounting: • Quantity of purchased grid electricity [kWh] • Location based emission factor used [gCO_2e/kWh] Market-based emissions accounting • Quantity of purchased grid electricity [kWh] • Quantity of contracted electricity [kWh] and/or quantity of associated GOs or RECs • Type of Gos or RECs • Residual electricity • Residual mix emission factor [gCO_2e/kWh] On-site electricity generation • Quantity of on-site generation [kWh] • Emission factor for on-site generation (as applicable) [gCO_2e/kWh]
Feedstock	• Total amount of toluene, BT and/or DBT consumed to produce hydrogenated LOHCs within the analysis period, including makeup LOHC and dehydrogenated LOHC (tonnes) • Total amount of dehydrogenated LOHC received from LOHC dehydrogenation facilities [tons] • Total amount of “makeup” LOHC consumed (calculated based on Equation 1 or directly measured as indicated in the description) [tonnes] • Emissions factor used to determine emissions intensity of toluene, BT and/or DBT [kgCO2e/kg-toluene or $kgCO_2e$/kg-DBT] • Total amount of water consumed for the Direct MCH pathway [L]
Waste and other co-products	• Quantity of steam produced [kg] • Quantity of steam sold [kg] • Emissions allocated to steam [$kgCO_2e$] • Quantity of hydrogen produced and sold in case of Direct MCH pathway[tons] • Quantity of O_2 produced and sold in Direct MCH pathway [tonnes]

Table J.6 — **Information to be reported for LOHC Dehydrogenation Facilities**

Category	**Parameters to Report**
Facility details	• Facility identity • Facility location • Facility capacity [tonnes/year] • Commencement of facility operation
Product specification	• Quantity of hydrogen produced [tonnes] • Quantity of dehydrogenated LOHC produced [tonnes] • Purity (%) and pressure (MPa) of hydrogen produced
Batch details	• Beginning and end of batch dates
Electricity	Location-based emissions accounting: • Quantity of purchased grid electricity [kWh] • Location based emission factor used [gCO_2e/kWh] Market-based emissions accounting • Quantity of purchased grid electricity [kWh] • Quantity of contracted electricity [kWh] and/or quantity of associated GOs or RECs • Type of GOs or RECs • Residual electricity • Residual mix emission factor [gCO_2e/kWh]

	On-site electricity generation • Quantity of on-site generation [kWh] • Emission factor for on-site generation (as applicable) [gCO_2e/kWh]
Fuel used in furnace	• Type of fuel used (e.g., natural gas) • Quantity of fuel used to produce heat [e.g. MJ] • Emissions intensity of fuel used, including all emissions associated with fuel extraction, transporting to a processing plant, and processing [e.g. kgCO_2e/MJ]
Products	• Total amount of dehydrogenated LOHC produced [tonnes] • Total amount of dehydrogenated LOHC returned to hydrogenation facility [tonnes] • Total amount of dehydrogenated LOHC valorized as a co-product in other industries [tonnes] • Total amount of hydrogen produced [tonnes]
Steam	• Quantity of steam produced [kg] • Quantity of steam sold [kg] • Emissions allocated to steam [kgCO_2e]
Other co-products	• LOHC co-production during dehydrogenation[10] [kg]
CO_2 capture	• Amount of electricity and/or heat used in CO_2 capture
Compression for transport of CO_2	• Amount of electricity used and/or fuel combusted for compression and pipeline transport of CO_2 • Amount of electricity used and/or fuel combusted to load CO_2 into trucks • Amount of fuel burned for truck transport of CO_2 [L] • Fugitive CO_2 emissions [kgCO_2e]

[10] Estimates of losses may be valuable in the context of other sustainability metrics, as toluene is a volatile organic compound.