

Committee of Experts on the Transport of Dangerous Goods and on the Globally Harmonized System of Classification and Labelling of Chemicals

Sub-Committee of Experts on the Transport of Dangerous Goods

16 September 2024

Sixty-fifth session

Geneva, 25 November-3 December 2024

Item 3 of the provisional agenda

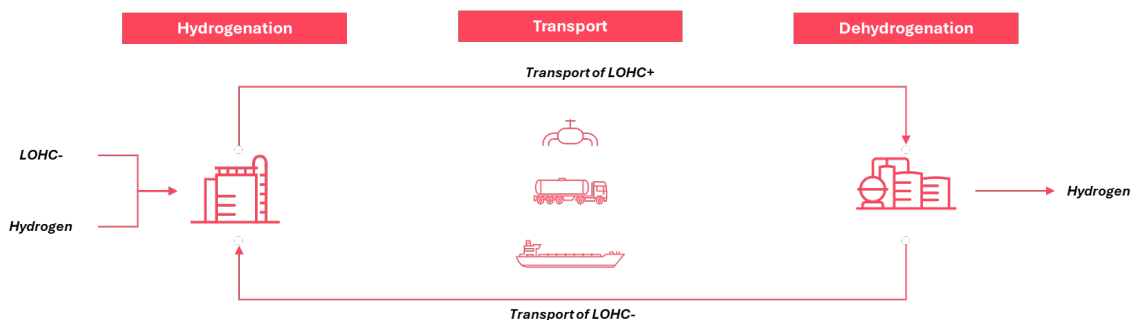
Listing, classification and packing

Transport of liquid organic hydrogen carriers - new special provision to UN 3082 – additional information

Submitted by the expert from Germany

I. Introduction

1. Document ST/SG/AC.10/C.3/2024/73 “Transport of liquid organic hydrogen carriers – new special provision to UN 3082” submitted for consideration of the Sub-Committee at the sixty-fifth session proposes a limit of 0,5 L(H₂)/kg(LOHC) for physically dissolved hydrogen, which is tolerable for a safe transport of liquid organic hydrogen carriers (LOHCs) listed under UN 3082.
2. With this informal document, Germany seeks to provide additional information to support the working paper submitted.
3. The general process for LOHC-based hydrogen transport is schematically illustrated and described below.
4. For the sake of clarity, the dehydrogenated, i.e. hydrogen-lean, form of the hydrogen carrier is abbreviated as “LOHC-“, while the hydrogenated, i.e. hydrogen-rich, form of the hydrogen carrier is referred to as “LOHC+”.



Hydrogenation

5. The chemical binding of hydrogen to another element or to double or triple bonds of another molecule is referred to as hydrogenation.
6. Hydrogenation is a common reaction in the chemical or food industry and has been in use for over 100 years. Examples of large-scale hydrogenation reactions include the production of ammonia via the Haber-Bosch process or the production of margarine from rapeseed oil.
7. Hydrogenation reactions are exothermic, i.e. energy is released in the form of heat during the hydrogenation process. Thermodynamically, exothermic reactions are favoured at

lower temperatures, e.g. ~250 °C for the hydrogenation of LOHC-. To lower the activation energy, hydrogenation catalysts are usually employed as well.

8. Additionally, hydrogenation reactions benefit from high pressures of hydrogen based on Le Chatelier's principle. Thus, pressures of > 10 bar are applied in the hydrogenation of LOHC- to achieve high conversion rates from LOHC- to LOHC+.

9. Higher gas pressures, however, affect the physical dissolution of a gas within a liquid according to Henry's law. In consequence, higher partial pressures of hydrogen will lead to a higher amount of physically dissolved hydrogen within the LOHC+. An analogous example from daily life is carbonated water, where CO₂ is injected into tap water under high pressures and is present as a physically dissolved gas in the carbonated water.

10. To reduce the amount of physically dissolved hydrogen, technologies such as vacuum degassing or nitrogen stripping or optimization of the process parameters can be applied. Germany wants to emphasize that these technologies are well-established on an industrial scale.

Transport

11. For the transport of both LOHC+ and LOHC-, existing infrastructure such as pipelines, tank trucks, rail tank cars or tankers can be used.

12. When dealing with the presence of physically dissolved hydrogen in a liquid organic hydrogen carrier, controlled degassing and/or equilibration with inert gases can help to maintain an inert atmosphere and prevent the uncontrolled, spontaneous degassing of the physically dissolved hydrogen. By establishing an equilibrium between the inert gas above the LOHC and the physically dissolved hydrogen in the LOHC within the closed tank, this ensures that a complete degassing of the remaining physically dissolved hydrogen from the LOHC in the tank cannot take place.

Dehydrogenation

13. The removal of previously chemically bound hydrogen from a molecule is considered as dehydrogenation, i.e. it is the reverse of a hydrogenation reaction.

14. Dehydrogenation reactions are essential for many chemical processes, e.g. conversion of alkanes to more reactive olefines or the production of styrene.

15. Thermodynamically, dehydrogenation is an endothermic reaction, i.e. an energy input is demanded for the reaction to occur. Thus, a combination of high temperatures (> 280 °C) and a dehydrogenation catalyst is required to release the chemically bound hydrogen again.

16. Consequently, it is impossible for chemically bound hydrogen to be released from the LOHC+ in the absence of high temperatures and a catalyst. The chemically bound hydrogen is thus stored safely during transport, as neither temperatures > 250 °C nor a dedicated dehydrogenation catalyst will be present.

17. Finally, low pressures during the dehydrogenation reaction are beneficial for a higher release rate of the chemically bound hydrogen based on Le Chatelier's principle.

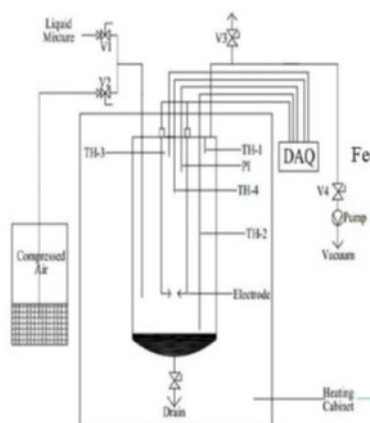
18. Germany wants to emphasize that physically dissolved hydrogen can be present after the dehydrogenation as well. To decrease the amount of physically dissolved hydrogen, the same principles apply as described for the hydrogenation. Thus, technologies such as vacuum degassing or nitrogen stripping can be applied prior to the transport of LOHC- as well.

II. Discussion

19. The Physikalisch-Technische Bundesanstalt (PTB, National Metrology Institute of Germany) conducted a risk assessment for the liquid organic hydrogen carrier benzyltoluene, which is assigned to UN 3082 as a dangerous good of Class 9.

20. The scope of the risk assessment was to evaluate whether physically dissolved hydrogen can degas from the LOHC, leading to the formation of explosive atmospheres.

21. The experimental tests were conducted using the following setup:



22. The tests were conducted using both BT+ (hydrogenated benzyltoluene) and BT- (dehydrogenated benzyltoluene) samples:

- Sample 1: Untreated BT- from a dehydrogenation plant (sample taken at 32 °C; pressure during dehydrogenation: 2.5 bar_a)
- Sample 2: BT- after storage under nitrogen for 16 h (sample taken at 22 °C; pressure during dehydrogenation: 2.5 bar_a)
- Sample 3: Untreated BT+ from a hydrogenation plant (sample taken at 20 °C; pressure during hydrogenation: 30 bar_a)

23. For the experimental tests, a dedicated procedure simulating worst case conditions was applied. The procedure was as follows:

- 90% of the reaction vessel at the PTB was filled with the respective sample under atmospheric conditions.
- While stirring, the samples were cooled down to -30 °C and subsequently heated up to +70 °C to ensure as much release of physically dissolved hydrogen as possible.
- Reaching +70 °C, sparks were generated for 0.5 seconds over a spark gap of 3 mm with an ignition transformer providing 14 kV.
- Via thermocouples, the temperature of the sample, the temperature above the ignition site, and the temperature axial to the ignition site were monitored.
- Additionally, the pressure in the reaction vessel was monitored.

III. Results

24. An ignition was considered to have taken place if an increase in temperature was accompanied by a simultaneous 5% increase in pressure.

25. Only for the untreated BT- sample under worst case conditions, both an increase in temperature and pressure was monitored in the experimental tests. Thus, only for this sample was an ignition observed based on the criteria defined.

26. For all other samples, no increase in pressure > 5% was monitored together with an increase in temperature. In consequence, no ignition of a flammable gas phase took place for the other samples.

27. The experimental tests conducted at the PTB demonstrated that under worst case conditions, there might be a risk of formation of an explosive atmosphere based on a degassing of physically dissolved hydrogen.

28. Thus, Germany is convinced that a defined limit for physically dissolved hydrogen will improve the safety of LOHC-based hydrogen transport.

29. However, LOHCs show different hazard potentials due to their different properties. Thus, Germany is hesitant to propose one unique UN number for all LOHCs. Instead, Germany proposes a limit of physically dissolved hydrogen of 0.5 l(H₂)/kg(LOHC), for all substances assigned to UN 3082 when used as liquid organic hydrogen carriers.
