

Article

Application of Liquid Hydrogen Carriers in Hydrogen Steelmaking

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Abstract: Steelmaking is responsible for approximately one third of total industrial carbon dioxide (CO₂) emissions. Hydrogen (H₂) direct reduction (H-DR) may be a feasible route towards the decarbonization of primary steelmaking if H₂ is produced via electrolysis using fossil-free electricity. However, electrolysis is an electricity-intensive process. Therefore, it is preferable that H₂ is predominantly produced during times of low electricity prices, which is enabled by the storage of H₂. This work compares the integration of H₂ storage in four liquid carriers, methanol (MeOH), formic acid (FA), ammonia (NH₃) and perhydro-dibenzyltoluene (H18-DBT), in H-DR processes. In contrast to conventional H₂ storage methods, these carriers allow for H₂ storage in liquid form at moderate overpressures, reducing the storage capacity cost. The main downside to liquid H₂ carriers is that thermochemical processes are necessary for both the storage and release processes, often with significant investment and operational costs. The carriers are compared using thermodynamic and economic data to estimate operational and capital costs in the H-DR context considering process integration options. It is concluded that the use of MeOH is promising compared to the other considered carriers. For large storage volumes, MeOH-based H₂ storage may also be an attractive option to the underground storage of compressed H₂. The other considered liquid H₂ carriers suffer from large thermodynamic barriers for hydrogenation (FA) or dehydrogenation (NH₃, H18-DBT) and higher investment costs. However, for the use of MeOH in an H-DR process to be practically feasible, questions regarding process flexibility and the optimal sourcing of CO₂ and heat must be answered.

Keywords: fossil-free steel; hydrogen storage; liquid hydrogen carriers; hydrogen direct reduction; industrial decarbonization



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1. Introduction

Steelmaking is responsible for approximately one third of industrial carbon dioxide (CO₂) emissions [1]. In order to meet the demands of the Paris Agreement and avoid the worst consequences of climate change, these emissions must be reduced drastically within the coming decades [2,3]. This is not achievable with the currently dominating steelmaking route based on blast furnace (BF) technology [4].

The most energy and emission-intensive step of BF steelmaking is the removal of oxygen from iron ore, i.e., the reduction in iron oxides (mainly hematite, Fe₂O₃) to produce iron (Fe). In the BF, this reduction is primarily achieved via reaction with coke, which is produced from fossil coal. As the iron oxides are reduced, the coke is oxidized to form CO₂ (either directly, or via the initial formation of carbon monoxide (CO) that is later combusted to provide heat). Consequently, as long as coke is the main reducing agent, CO₂ will be an unavoidable byproduct of BF steelmaking. At best, modern BF-based steelmaking results in around 1.6–1.9 tons of CO₂ per ton of steel produced [5,6].

In addition to iron ore, steel can also be produced from recycled steel scrap, most often using an electric arc furnace (EAF). This is referred to as secondary steelmaking. In the European Union (EU), 39% of all steel is produced via this secondary route [6]. As the recycled steel has already been reduced, secondary steelmaking requires significantly less

energy and produces far less CO₂ than production starting from iron ore in a BF. Therefore, increasing steel recycling is an effective route towards decreasing the CO₂ footprint of steel [7]. However, it is predicted that there will still be a substantial demand for iron ore-based steelmaking in 2050, even with increased steel recycling [8]. To meet this demand, it is necessary to develop new iron ore reduction processes that can achieve near-zero CO₂ emissions.

One promising way towards the decarbonization of iron ore-based steelmaking is hydrogen (H₂) direct reduction (H-DR). In H-DR, iron ore is reduced by H₂, yielding only water (H₂O) as a byproduct. This process is called direct reduction as the produced iron, referred to as direct reduced iron (DRI) or sponge iron, remains in the solid phase (direct reduction without melting). The main reducing reaction in H-DR can be summarized as



Note that reaction (1) is endothermic, which means that the incoming H₂ must be pre-heated to a high temperature (>800 °C) to provide sufficient heat for the reaction.

H-DR requires substantial supply of H₂. By the stoichiometry of reaction (1), approximately 54 kg of H₂ is needed to produce 1 t of pure Fe. In practice, some unreduced material remains in the product DRI due to thermodynamic limitations [9]. Typically, around 94% of incoming Fe₂O₃ is fully reduced in commercial DR processes based on natural gas; this yields a H₂ consumption of around 51 kg/t DRI [10–12]. Consequently, for the production of 2 Mt of steel per year, similar to the current production at the SSAB Luleå plant (a relatively small plant by European standards [13]), approximately 300 t of H₂ would be consumed per day [14].

Reduction of iron ore with pure H₂ is not an entirely novel concept. The world's first, and, to date, only, H-DR plant went into operation in 1998 in Point Lisas, Trinidad; however, that plant closed down in 2016 due to poor economic performance [5,15]. In recent years, interest in H₂ steelmaking is growing, with several industrial projects pursuing H-DR, including HYBRIT (SSAB, LKAB and Vattenfall, Sweden), H2FUTURE (voestalpine, Austria), and SALCOS (Salzgitter, Germany) [16,17]. In addition, both ArcelorMittal and thyssenkrupp are planning to implement H-DR at their Hamburg and Duisburg sites, respectively [18–20].

It should be noted that while no CO₂ is released during the reduction of iron ore with H₂ (per reaction (1)), the production of the fed H₂ may be associated with significant CO₂ emissions, in particular when starting from natural gas (as was the case for the Trinidad H-DR plant), oil or coal. Therefore, H-DR based on H₂ produced from fossil fuels is not attractive if the goal is to eliminate or heavily reduce the CO₂ emissions of steelmaking, at least as long as the byproduct CO₂ is not captured and stored. Currently, approximately 96% of global H₂ production is from fossil fuels [21].

The presently most feasible way to produce H₂ without emitting significant CO₂ is the electrolysis of H₂O. In electrolysis, H₂O is split into H₂ and oxygen (O₂) using electricity. If this electricity is produced from fossil-free sources, H₂ can be produced with near-zero CO₂ emissions. The principal downside of electrolysis is the large electricity demand: state-of-the-art electrolyzers require around 50 kWh of electricity to produce 1 kg of H₂. As a result, full-scale implementation of H-DR with electrolysis to replace existing BF capacity involves substantial amounts of electricity—complete conversion of the current EU steel capacity could require up to 18% of the current EU electricity consumption [8,22].

The high electricity demand of electrolysis means that the H₂ production cost depends heavily on the price of electricity. As the electricity price varies over time, in particular when a large share is generated from intermittent sources such as solar and wind, it is sensible to consider the use of H₂ storage. Such a storage allows for H₂ to be produced predominantly during times with lower electricity prices, yielding a lower average electricity cost, while still maintaining constant DRI production.

2. Hydrogen Storage in Hydrogen Direct Reduction Context

For investment into a H₂ storage as part of an H-DR process to be sensible, the prospective reduction in H₂ production electricity cost must at least make up for the capital expenditure (CAPEX) of the storage and the associated electrolyzer overcapacity as well as the average operational expenditure (OPEX) of the storage and release processes, e.g., the costs of any additional electricity and heat. Therefore, H₂ storage in the H-DR context should be:

- Low in investment cost (low CAPEX);
- Efficient, i.e., require little additional electricity and heat (low OPEX);
- Dynamic, i.e., it should be possible to change the operating mode of the storage (e.g., from filling to emptying) rapidly enough to respond to electricity price changes.

In terms of dynamics, it should be possible to empty the storage at a sufficient rate to be able to significantly turn down the electrolyzers when desired, i.e., during periods of high electricity prices. Ideally, the entire H-DR process would run on stored H₂ during electricity price peaks, allowing electrolyzers to operate at minimum load or be turned off (hot or cold standby) [23]. The minimum desired response time for storage operating mode changes is presently unclear. That said, significant day-to-day load changes would likely be required, at least, considering the dynamics of intermittent renewable energy sources.

The storage of H₂ is challenging due to its low density and high reactivity. Moreover, as H₂ has historically most often been produced from natural gas, oil, or coal, all more easily storable substances than H₂, there has been little incentive to develop H₂ storage technologies. Consequently, only a few large-scale storages of pure H₂ exist today. All of these are large underground man-made pockets in salt formations filled with compressed gaseous H₂ (up to around 230 bar) [24]. These facilities, referred to as salt cavern storages, are generally considered to be the most favorable large-scale H₂ storage option in terms of overall economics, resulting from their low-cost construction via leaching and the gas impermeability of the salt; examples of operating H₂ salt cavern storages are found in the UK and the USA [25–27]. Unfortunately, salt formations suitable for these storages are not ubiquitous [28]. For instance, no suitable salt formations exist in Sweden and many regions of the USA [29]. Therefore, other types of H₂ storage must be sought in certain regions. For instance, in the HYBRIT project, the pursued H₂ storage option is the lined rock cavern (LRC) technology [5]. An LRC is a type of underground storage made up of a steel- and concrete-lined cylindrical hard rock cavern [24,29,30]. The presence of the hard crystalline rock of the Baltic shield covering large parts of Sweden makes implementation of an LRC storage feasible in the HYBRIT project, although investment costs are significantly higher than for salt cavern storage [28]. In other words, certain geological conditions are also necessary to construct an LRC storage. There are also mechanical limits to H₂ withdrawal rates from underground storages that may limit their appeal in the H-DR context [24]. For salt cavern and LRC storages, allowable rates lie in the range of 6–15% of the maximum storage capacity per day [24,26,31,32].

The dependence on local geology and the limitations in the withdrawal rate of underground H₂ storage opens up the possibility of utilizing alternative H₂ storage technologies in H-DR processes. One such alternative technology is based on so-called liquid H₂ carriers, which will be explored in this work.

3. Liquid Hydrogen Carriers

3.1. Overview

By chemically reacting H₂ with a secondary chemical substance, it is possible to form so-called liquid H₂ carriers. Due to the high reactivity of H₂, these hydrogenation reactions tend to be exothermic, i.e., heat-producing. Liquid carriers allow for H₂ to be stored at a high volumetric density in liquid form, enabling compact storage and low-cost transportation. When H₂ is subsequently needed, the carriers may be dehydrogenated in thermochemical endothermic processes to produce H₂ and the original secondary substance. The low-cost storage and transportation of liquid H₂ carriers introduces a number

of opportunities for flexibility in the H-DR process that would not be possible, or at least as attractive, for a gaseous storage. A few examples are:

- Import and export of the liquid H₂ carrier to or from the H-DR site is readily achieved;
- Placement of the H₂ production and storage units becomes less geographically constrained;
- Very large H₂ storages are possible, covering, e.g., seasonal variations in electricity price.

The typical downsides of using liquid H₂ carriers are the high heat demand of the dehydrogenation process and the high investment costs of the necessary hydrogenation and dehydrogenation plants. In addition, the hydrogenation process typically involves the compression of gases (at least H₂), requiring an often-significant input of electricity. Dynamic operation of the hydrogenation and dehydrogenation facilities in response to electricity price changes is also often unknown, limited or, at least, unconfirmed.

Although all liquid H₂ carriers share the characteristics above, there are a number of additional factors to weigh when choosing the optimal carrier in the H-DR context. Numerous liquid H₂ carriers have been suggested in the scientific literature, but relatively few have been studied outside of gram-scale laboratory experiments and theoretical models [33]. In the coming sections, these most widely discussed liquid H₂ carriers will be described. They can be categorized into three groups:

- (1) Those based on a reaction between H₂ and CO₂ (e.g., methanol (CH₃OH, MeOH) and formic acid (CH₂O₂, FA));
- (2) Those based on a reaction between H₂ and nitrogen (N₂) (e.g., ammonia (NH₃));
- (3) Those based on a reaction between H₂ and unsaturated liquid hydrocarbons (liquid organic hydrogen carriers (LOHCs)).

Based on current technology, these carriers could be implemented for large-scale H₂ storage within the context of a fossil-free H-DR process, although no such storage has yet been demonstrated at an industrial scale. The main reasons for this are the generally significant similarities between such storage systems and existing large-scale industrial chemical processes.

3.2. Integration of Liquid Hydrogen Carriers in Hydrogen Direct Reduction Processes

The prospective integration of the considered liquid H₂ carriers in an H-DR process is seen in Figure 1.

As can be seen, the choice of liquid H₂ carrier affects the overall layout of the H-DR process somewhat, although the general principle is the same with all carriers: (mainly) electricity must be supplied for the hydrogenation process and (mainly) heat for the dehydrogenation process. The supply of dehydrogenation heat can be achieved in several ways, as shall be discussed below. In addition, the handling of the secondary material with which H₂ reacts differs depending on the chosen carrier, with CO₂-based carriers as particularly special cases.

3.2.1. Management of Secondary Material

For the non-CO₂-based carriers, management of the secondary material is relatively simple. In the case of NH₃, N₂ is sourced from the atmosphere via air separation (into O₂ and N₂), a well-established process [34]. After dehydrogenation, N₂ is returned to the atmosphere. For LOHCs, the dehydrogenated (“unloaded”) LOHC carrier must be stored. As this unloaded carrier is typically also a liquid, its separation from released H₂ and storage is relatively straightforward.

For CO₂-based storage, the situation is more complex. Sourcing CO₂ from the air is far less viable compared to N₂ due to its much lower concentration (around 0.04% vs. 78% by volume), although this is, in principle, possible and is a technology under development [35,36]. Therefore, all CO₂ released upon dehydrogenation of the CO₂-based carriers is preferably captured, instead of released to the atmosphere, and recycled to produce new H₂ carrier. However, in practice, such operation is unlikely due to losses

during the storage cycle and the cost of CO₂ storage. Therefore, additional CO₂ must be supplied to the storage process, although the recycling and storage of some amount of CO₂ may be attractive to reduce the demand for external carbon in certain cases.

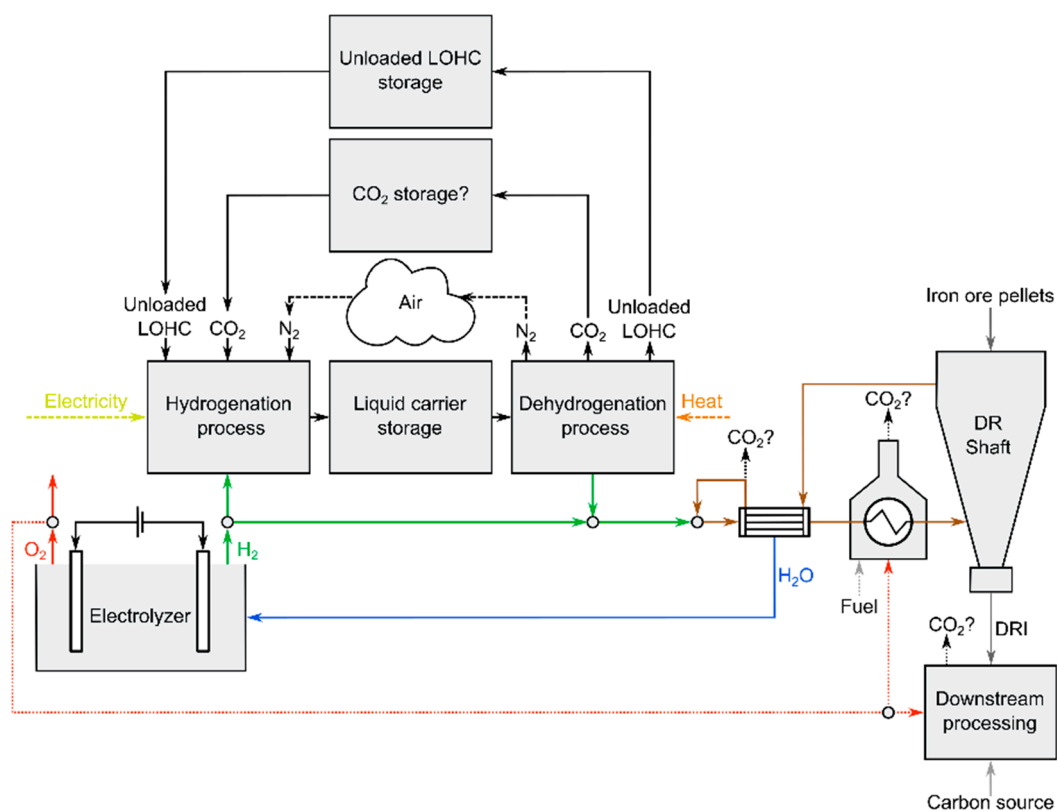


Figure 1. Schematic representation of the integration of various liquid hydrogen carriers in an H-DR process. Possible CO₂ sources are indicated (separation from DR process reducing gas, oxy-fuel combustion reducing gas pre-heating, separation from downstream processing steps).

Additional CO₂ for H₂ storage can be sourced in several ways. Within the H-DR process, one can imagine at least three sources, as seen in Figure 1:

- (1) the separation of CO₂ from the reducing gas in the case that in-shaft carburization would be applied;
- (2) the reducing gas pre-heating process;
- (3) the processing steps downstream of the DR shaft (e.g., the electric arc furnace (EAF)).

Out of these options, the pre-heating route appears the most attractive and generally applicable. Pre-heating via the use of biomass oxy-fuel combustion to co-produce CO₂ for MeOH production in an H-DR process was evaluated in a recent study [37]. In the case that oxy-fuel combustion of biomass is used to pre-heat the reducing gas to 700 °C, the CO₂ generated is sufficient to allow for a 41% electrolyzer overcapacity, with sufficient amounts of O₂ generated by electrolyzers to fully feed the combustion process. Compared to other CO₂-sourcing options, oxy-fuel combustion of biomass appears to be attractive in that it serves multiple functions within the H-DR process. It would also constitute a relatively constant source of biogenic CO₂. In contrast, capturing CO₂ from downstream processes would likely entail additional costs with few co-benefits. In the case that in-shaft carburization is applied, the capture of CO₂ from the top gas would be necessary to avoid its accumulation in the reducing gas loop. Therefore, utilizing this CO₂ to store H₂ could potentially also be an attractive option. However, the feasibility and general attractiveness of in-shaft carburization in a fossil-free H-DR process is currently unclear. While carbon is

an unavoidable part of steelmaking, it may also be viable to introduce this downstream of the reduction process, e.g., in the EAF, rendering in-shaft carburization unnecessary [38,39].

Finally, the import of CO₂ to the H-DR site may also be a feasible solution. The importance of the biogenic origin of such imported CO₂ must be emphasized. If the CO₂ is not biogenic in origin, the steelmaking process could not be considered fossil-free. The use of CO₂ captured from pulp mills or from biogas (upgrading) plants are possible options [40]. Naturally, one could also consider the decentralized production of a liquid H₂ carrier at the site with biogenic CO₂ in such cases, considering the relative ease of transporting these carriers by ship, truck or rail. Investigation of such schemes, while potentially interesting, is considered outside of the scope of the present work.

3.2.2. Management of Heat for Dehydrogenation

As mentioned previously, a general feature of all liquid H₂ carriers is the need to supply significant amounts of heat to the dehydrogenation process. The necessary heat amount and temperature level differs from carrier to carrier. For certain carriers, heat of different temperature levels is needed, e.g., for evaporation at a lower temperature followed by dehydrogenation in the gaseous phase at a higher temperature. Several heat supply options are conceivable. Ideally, surplus heat from the H-DR process would be used for dehydrogenation, as this is likely the lowest-cost option. Within the H-DR process there are several potential sources of such surplus heat. The most prominent examples include:

- Heat from electrolyzers;
- DRI product cooling in the case that cold DRI or hot-briquetted iron is produced [10];
- Excess heat from reduction gas pre-heating.

The amount of available heat from these sources can be approximated using basic thermodynamic data. Considering a H₂ demand of 51 kg H₂/t DRI, an electrolyzer efficiency of 50 kWh_{el}/kg H₂ yields approximately 560 kWh/t DRI of surplus heat from electrolyzers when at full load. Commercial alkaline and polymer electrolyte membrane (PEM) electrolyzers operate at 50–90 °C [41]. Upgrading this heat to higher temperatures using heat pumps could be an option [42,43]. Note that electrolyzers are predicted to operate at varying loads within a H-DR process, allowed for by the integration of the H₂ storage. Therefore, heat from electrolyzers will be intermittent and mainly available during times of low electricity prices, rendering heat integration between electrolyzers and the dehydrogenation process challenging.

The sensible heat available from DRI cooling can be significant in an industrial-scale H-DR process: assuming that the DRI exits the reduction shaft at 850 °C and has a specific heat capacity of 0.56 MJ/(t, K), around 0.1 MW/(t DRI/h) down to 200 °C [12,37]. However, it is not certain that this heat will be available as the direct transfer of hot DRI from the reduction shaft to the EAF reduces the electricity demand of the EAF [10]. A possibility that could enable the use of the DRI cooling heat is that EAF operation, which is electricity-intensive, is avoided during times of high electricity prices (when the dehydrogenation process is expected to be operated). However, the viability of such operation is presently unclear.

As the reduction of iron ore with H₂ is an endothermic reaction (reaction (1)), the incoming H₂ must be pre-heated to a high temperature before entering the reduction shaft. The heat required for this pre-heating is substantial in an industrial-scale H-DR process: approximately 10 kWh/kg H₂ of heat must be supplied if the reducing gas enters the reduction shaft at 900 °C [37]. The excess heat from reduction gas pre-heating depends on what heating technology is used. For instance, for electric heating, the amount of excess heat would be negligible. However, even if oxy-fuel pre-heating is applied, as described previously, the amount of excess heat is likely too small to be useful for integration with a dehydrogenation plant [37].

In summary, heat integration between the dehydrogenation and H-DR processes is complicated and context-dependent. A major challenge is the intermittency of the dehydrogenation process.

If heat integration with the H-DR process is not feasible or sufficient, other sources of heat for the dehydrogenation process are needed. Three alternatives are obvious: (1) combustion of part of the released H₂ (or the liquid H₂ carrier), (2) electric heating, and (3) external fuel. All these alternatives are associated with certain challenges or disadvantages.

Combustion of part of released H₂ is a straightforward approach, and is typically applied in fossil-fuel-based H₂ production. The combusted H₂ can often be sourced from the downstream separation step (e.g., pressure swing adsorption (PSA)), which generally results in one near-pure H₂ stream and one dilute H₂ stream suitable for combustion [44–46]. However, the conversion losses associated with electrolysis renders H₂ combustion an expensive source of heat. Furthermore, if only part of the stored H₂ can be delivered to the H-DR process upon dehydrogenation, the storage and the hydrogenation process must be oversized accordingly, adding investment and operational costs. The direct use of electric heating is potentially more efficient, but is, as of yet, not commercially available for the dehydrogenation processes of interest here (the main reason for this is that combustion of natural gas has historically been a lower-cost source of heat than direct use of electricity, rendering the development of such reactors uninteresting), although developments are underway [44,47]. A downside here is that the dehydrogenation process should ideally only run during times of high electricity prices, which could also render electrified dehydrogenation expensive, despite the higher efficiency compared to H₂ combustion. The third option, combustion of an external fuel, is potentially limited by the availability and cost of fossil-free fuels (biomass, biofuels) [48]. Only in certain regions, e.g., Sweden, is the direct use of forest residues potentially a low-cost option [49].

3.3. Carbon Dioxide-Based Carriers

Several reactions are possible between H₂ and CO₂. For H₂ storage purposes, the most useful products are those that are simultaneously liquids at room temperature and can be dehydrogenated at low cost. This limits the number of contenders significantly. Carbon monoxide (CO) and methane (CH₄) are both gaseous at room temperature and require large inputs of high-temperature heat to release H₂. Formaldehyde (CH₂O) is also a gas at room temperature (normal boiling point −19 °C), although formaldehyde–water solutions are stable. However, the direct synthesis of CH₂O from CO₂ and H₂ is challenging, mainly due to thermodynamics and selectivity issues, limiting its appeal as a H₂ carrier [50].

The two most investigated CO₂-based liquid H₂ carriers are methanol (CH₃OH, MeOH) and formic acid (CH₂O₂, FA). Out of these, MeOH is currently the most mature option, as both MeOH production from CO₂ and MeOH reforming may be considered established industrial processes. In contrast, converting H₂ and CO₂ to FA is rather complex. Several processes have been suggested in recent years, but industrial application has not yet occurred [51,52]. Nevertheless, FA remains a H₂ storage option with significant potential. In particular, it may prove feasible to release H₂ from FA at near-room temperature, given that viable catalysts are developed [51].

3.3.1. Methanol

Methanol (MeOH) is the simplest alcohol, containing 12.6% H₂ by weight. Its current production is nearly entirely based on natural gas or coal feedstocks. However, the direct production of MeOH from CO₂ and H₂ using a near-identical process is possible and has been commercialized, with the most notable example being the “George Olah Renewable Methanol Plant” operated by CRI (Carbon Recycling International) on Iceland, although that plant is relatively small at 4000 t MeOH/y [53,54]. The main economic barrier of CO₂-based MeOH production is the cost of producing H₂ via electrolysis [55].

The production of MeOH from CO₂ and H₂ is exothermic and endergonic at ambient conditions [50]. The only byproduct of the reaction is H₂O that may be separated via distillation.



The formation of MeOH is thermodynamically promoted by high pressures and low temperatures. However, due to kinetic reasons, elevated reactor temperatures of around 250 °C are typical [56]. As a result, complete conversion of the reactants is not achieved in a single pass through the reactor, necessitating recycling, as seen in Figure 2. To avoid the accumulation of inerts in the reactor loop, a purge stream is required. A 1 mol% purge has been reported, but the amount depends on the purity of the inlet CO₂ (electrolysis produces very pure H₂, >99.5% for all conventional technologies) [57,58].

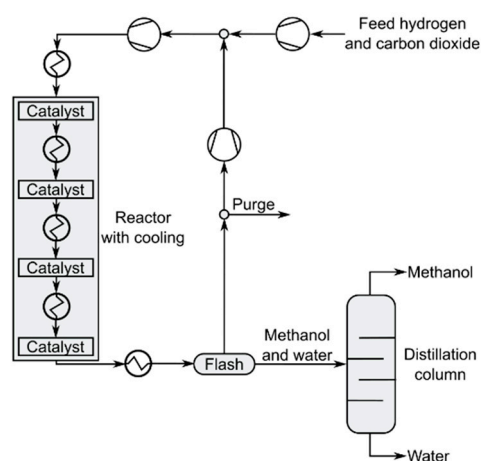


Figure 2. Generic CO₂-based MeOH production process [37].

The most commonly applied catalyst for CO₂-based MeOH production is based on copper (Cu): Cu/ZnO/Al₂O₃ [59–61]. This catalyst is relatively cheap and has been proven to be able to operate under fluctuating conditions [60–62]. Minimum loads down to 10% of the design capacity should be possible in CO₂-based MeOH production [63].

The production of MeOH from CO₂ is, as mentioned, an exothermic process. In practice, the heat generated via this reaction is more than sufficient to cover the heat demand of the rest of the storage process, i.e., the overall hot utility demand is negative [55,57]. This includes the separation of formed MeOH and H₂O via distillation. In an H-DR process, where MeOH would principally be produced to store H₂, this distillation step is unnecessary, as MeOH would be mixed with H₂O during the dehydrogenation step (the reverse reaction of (1)) anyway [64].

The electricity demand of a CO₂-based MeOH plant is rather low (excluding electrolysis). Compression of fed and recycled gases constitutes the main electricity consumption. In addition, a significant amount of electricity could theoretically also be generated via integration of steam turbines and organic Rankine cycles in the process [55,57,65]. Consequently, the net total electricity demand of the process is estimated at around −0.06 to 0.175 kWh/kg MeOH (−0.3 to 0.9 kWh/kg stored H₂) in the literature, indicating that the process can be self-sufficient or even export electricity [40,55,57,65]. Note that these values include distillation.

The dehydrogenation of MeOH may proceed via the reverse of reaction (2), which is called MeOH steam reforming (MSR). The basic layout of a MSR process is seen in Figure 3. The same kind of catalyst as in CO₂-based MeOH production may be used, i.e., Cu/ZnO/Al₂O₃; consequently, using a single reactor for both hydrogenation and dehydrogenation processes may be possible, although this concept is yet unproven [66]. Using these catalysts, a high selectivity towards CO₂, rather than CO, can be achieved in MSR [67–70].

As the production of MeOH from CO₂ and H₂ is exothermic, MSR is endothermic. In addition, since MSR typically takes place in the gas phase at elevated temperatures (200–300 °C), significant amounts of heat for the evaporation of MeOH and H₂O must also be supplied. However, evaporation of MeOH and H₂O can be achieved at a relatively low temperature (an equimolar mixture boils at 73 °C), which means that, e.g., electrolyzer

waste heat could be utilized. If MSR is to completely supply a 2 Mt DRI/y H-DR process with H_2 , around 50 MW of evaporation heat ($<100\text{ }^{\circ}\text{C}$) and 30 MW of reaction heat ($200\text{--}300\text{ }^{\circ}\text{C}$) must be supplied [37]. The separation of released H_2 and CO_2 is commonly achieved via PSA in existing MSR plants [71]. The energy demand of this separation process is low. PSA requires elevated inlet pressures, but the compression of gases can be avoided in MSR in favor of pumping of liquid MeOH and H_2O with typical pressures of 10–25 bar [72,73]. Typically, as seen in Figure 3, heat is supplied via combustion of the PSA off-gas in MSR. This off-gas contains a small concentration of H_2 . If the off-gas is combusted to provide the entire heat demand of MSR, around 8–10% of the stored H_2 would be consumed [33,68]. Supplying this heat via electricity, e.g., via inductive heating, which has recently been patented, may also be an attractive approach, but has not yet been demonstrated at scale [47]. To the best knowledge of the author, no large-scale ($>100\text{ t } H_2/\text{d}$) MSR plant exists today. However, scale-up should be straightforward considering the low process complexity and that only standard equipment is needed [74].

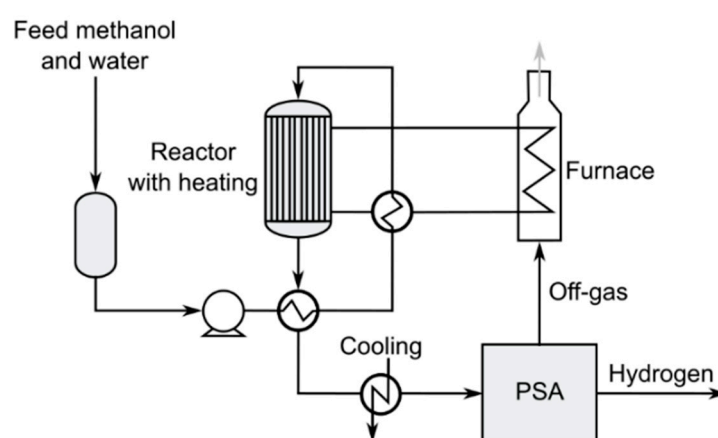
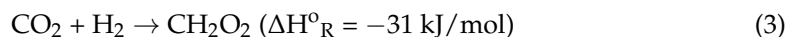


Figure 3. Conventional layout of a methanol steam reforming process [37].

3.3.2. Formic Acid

Formic acid (CH_2O_2 , FA) is the simplest carboxylic acid. It is a liquid at room temperature (normal melting point is $8\text{ }^{\circ}\text{C}$). Compared to MeOH, FA stores less H_2 by weight (4.4%), but the thermodynamic barrier for the release of H_2 (and CO_2) is significantly lower [50,75].

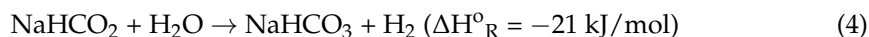
In practice, FA is facing several challenges as a liquid H_2 carrier, the most severe residing with the FA production step. FA can be formed via direct reaction between H_2 and CO_2



However, this reaction is strongly endergonic, and insignificant amounts of FA are formed, even at very high pressures [75–77]. This thermodynamic barrier can be overcome by performing the reaction in a basic solution, typically containing an amine, at high pressures ($>100\text{ bar}$) [64,78,79]. The amine scavenges any formed FA to produce formate salts. This salt formation pushes the equilibrium of reaction (2) towards FA. While this is advantageous in terms of the reaction equilibrium, other problems are created. Firstly, these formate salts are generally quite stable and, secondly, the acquired formate salt solutions tend to be very dilute [76]. Taken together, this means that the separation process becomes energy-intensive [79]. Estimates of the electricity and heat demand of CO_2 -based FA production are in the range of 3.6–6.7 and 16–63 (at $100\text{--}200\text{ }^{\circ}\text{C}$) kWh/kg H_2 stored, respectively [78,79]. This type of CO_2 -based FA production has not been demonstrated on a significant scale [80].

A way around the cumbersome separation is to not utilize FA as the H_2 storage medium but instead the formate salt solutions. Formate salts ($MHCO_2$, where $M = Na, K, Cs$ or NH_4) store H_2 at a lower density than FA, theoretically around $20\text{--}28\text{ kg } H_2/\text{m}^3$ [81].

However, the reversible storage of H₂ in these salts is far more thermodynamically advantageous (the hydrogenation reaction is mildly exergonic) [75]. In addition, there is, ideally, no release of CO₂ along with H₂ during dehydrogenation as a bicarbonate salt is formed instead, per reaction (4) (here the sodium-based system is shown as an example):

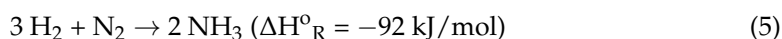


In practice, the achievable H₂ storage density in formate salt solutions is limited by the solubility of the byproduct bicarbonate salts [76]. This limited solubility is detrimental to the efficiency of the H₂ storage cycle, as large amounts of H₂O must be heated to the reaction temperature during both hydrogenation and dehydrogenation (the exothermic enthalpy of hydrogenation does help somewhat). That said, the heat that must be supplied is at a relatively low temperature but above 100 °C. The dehydrogenated bicarbonate salt solution must be stored, which would add some cost to the storage. While the use of formate salts for H₂ storage is potentially attractive in the H-DR context, mainly due to the hypothetically low energy demand, no thorough techno-economic analysis of these types of systems is currently available in the literature.

As for the other liquid H₂ carriers discussed herein, the dehydrogenation of FA or formate salt solutions requires an input of heat. However, unlike the other carriers considered in this work, the actual reaction enthalpy is not the most critical aspect [76]. Instead, pre-heating of FA or formate salt solutions to the reaction temperature dominates the overall heat demand. This means that the concentration of the FA or formate salt solutions is an important parameter. The total heat demand of FA or formate salt dehydrogenation can be estimated to be 2.8–9.1 (ranging from pure FA to aqueous FA at a concentration of 4 M) and 5.7 kWh/kg H₂, respectively [76]. Fortunately, the required temperature level of this heat is generally low (<100 °C), indicating that, e.g., waste heat from electrolyzers could be utilized. A disadvantage of FA compared to MeOH is the higher share of CO₂ released with H₂. This lower concentration of H₂ in the dehydrogenation product gas means that more CO₂ must be separated out per kg of H₂ sent to the H-DR process. However, the thermodynamics of FA dehydrogenation allow for high pressures (up to 700 bar), despite the co-release of gaseous CO₂, to be attained directly without compression, which may ease the separation [82]. Most often, Ru- or Rh-based catalysts have been applied for FA dehydrogenation, although many different catalysts have been investigated; a major challenge is achieving both high activity and high selectivity towards CO₂ [51,52,83–85].

3.4. Ammonia

N₂-based H₂ carriers, specifically NH₃, may be attractive for H₂ storage for a number of reasons. The H₂ storage density of liquid NH₃ is very high, at around 120 kg/m³, over 150% the density of liquid H₂ [86], although NH₃ condenses at around −33 °C, which necessitates storage in well-insulated refrigerated containers (pressurized storage at ambient temperature is also possible, but is more costly at large scales). NH₃ is formed via reaction between H₂ and N₂ in an exothermic reaction, typically as part of the well-known HaberBosch process



Similar to MeOH production, the formation of NH₃ is exergonic at ambient conditions and is favored by high pressures and low temperatures but is, in practice, operated at a high temperature [87]. The basic layout of the Haber-Bosch reactor loop is seen in Figure 4.

Typical reactor conditions are 150–250 bar and 400–450 °C, most often utilizing an iron-based catalyst [88]. Similarly to MeOH, complete conversion is not achieved in a single pass through the reactor and recycling of unreacted H₂ and N₂ is necessary, with part of the recycle loop purged to prevent the accumulation of inerts in the reactor. However, the amount of inerts introduced into an electrolysis-based Haber-Bosch process should be sufficiently low to dissolve in the produced NH₃, rendering a purge stream

unnecessary [88]. NH_3 is separated out from the recycle loop via condensation at -25 to -33 °C, which necessitates refrigeration [88,89]. The need for refrigeration provides another reason for the high reactor pressure in the Haber-Bosch process: a lower pressure would lead to unpractically low NH_3 condensation temperatures [90].

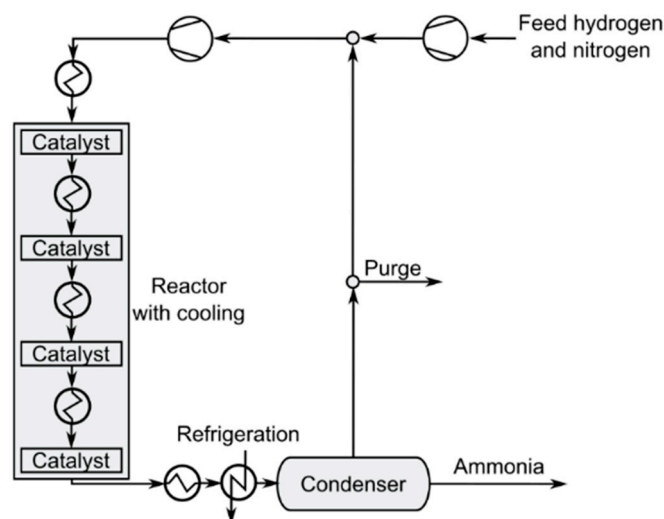


Figure 4. Generic layout of Haber-Bosch NH_3 synthesis loop.

Unlike the other considered liquid H_2 carriers, the atmosphere can be utilized as a vast reserve of relatively low-cost N_2 . Consequently, storage of N_2 is not necessary and this saves costs. However, although N_2 is plentiful in the atmosphere, air separation still requires a significant amount of energy. The most feasible process option at large scale is the use of cryogenic air separation units (ASUs). These require an electricity input of around 0.2–0.8 kWh/kg N_2 , mainly for compression of the incoming air [91–94]. Translated to electricity per H_2 stored in NH_3 , this is 2.3–3.7 kWh/kg H_2 . Considering the high pressure of NH_3 synthesis, it can be concluded that this is the most electricity-intensive hydrogenation process of the ones considered. Estimated total electricity demands of ASU operation and NH_3 production are in the range of 0.6–1.1 kWh/kg NH_3 in the literature, equivalent to 3.4–6.2 kWh/kg stored H_2 .

The dehydrogenation or “cracking” of NH_3 , the reverse reaction of (5), requires high temperatures due to both thermodynamic and kinetic reasons [95]. No large-scale NH_3 cracking plant exists today [96]. However, one can imagine a layout similar to current steam methane reformers (SMRs) that produce H_2 from natural gas. A recent report from the project “Ammonia to Green Hydrogen” investigated a hypothetical such large-scale NH_3 cracker capable of delivering 200 t H_2 /d [96]. The heat demand of the cracker was found to be 119 MW (in terms of fuel lower heating value, equivalent to 14.3 kWh/kg H_2). The combusted fuel is assumed to be a mixture of NH_3 and H_2 . Around 15 MW of electricity could also be co-produced from the generated steam (40 bar, 345 °C). The separation of H_2 from N_2 and any remaining NH_3 is achieved using a cryogenic process. This cryogenic process, which also produces liquid N_2 , requires an electricity input of 1.8 MW (approximately 0.2 kWh/kg H_2). It should be noted that the product of this model plant is fuel cell grade H_2 at 250 bar. In a future H-DR process, compression and purity demands would be significantly lower, leading to savings in both operational and investment costs. Nevertheless, the need for large amounts of high-temperature heat for NH_3 dehydrogenation remains a significant obstacle. Additionally, the NH_3 dehydrogenation process would have to be operated dynamically in the context of an H-DR process. The viability of such operation is currently unknown.

3.5. Liquid Organic Hydrogen Carriers

Unlike for the CO₂- and N₂-based carriers previously described, the dehydrogenated forms of liquid organic H₂ carriers (LOHCs) are liquid [97,98]. Consequently, H₂ is the only gaseous product of the dehydrogenation process and a gas separation step can be avoided (compared to the previously considered carriers, where the separation of CO₂ or N₂ is necessary) [98].

As with the previously discussed liquid H₂ carriers, the hydrogenation of LOHCs is exothermic, while dehydrogenation is endothermic. However, these energetic barriers tend to be larger for LOHCs. The most widely discussed LOHC is perhydro-dibenzyltoluene (H18-DBT, dehydrogenated form is dibenzyltoluene (DBT)). As H18-DBT/DBT is the LOHC that has received the most attention in the recent scientific literature, it will be the main LOHC investigated here. More thorough reviews of LOHC technology can be found elsewhere [99–103]. To supply the necessary heat for the dehydrogenation of H18-DBT, around 30% of released H₂ must be combusted [91,104]. This is a clear disadvantage of H18-DBT and LOHCs in general. Certainly, if surplus heat from a nearby process can be used for the dehydrogenation step, the attractiveness of LOHCs increases [99]. A full supply of H₂ via H18-DBT dehydrogenation to an industrial-scale H-DR process producing 2 Mt DRI/y would require approximately 100 MW of heat (>300 °C). The H18-DBT/DBT H₂ storage cycle is shown in Figure 5.

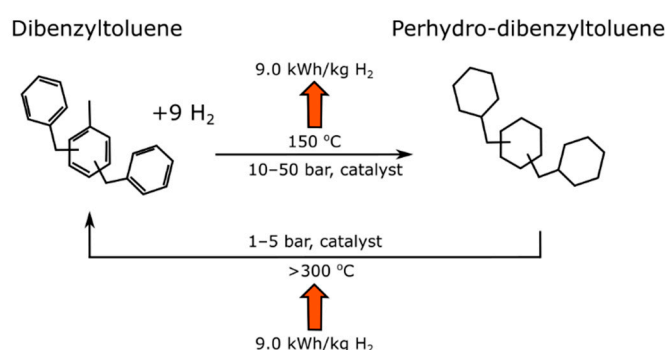


Figure 5. Hydrogen storage cycle for (perhydro-)dibenzyltoluene.

Unlike the other considered liquid H₂ carriers (with the exception of formate salts), the dehydrogenated form of LOHCs must be stored. This means that storage capacity is limited not by the size of the container, but by the amount of LOHC. The bulk price of DBT, which has a maximum H₂ storage capacity of 6.2% (by weight), is approximately 2–4 €/kg [91,105]. Consequently, the cost of DBT sufficient to store 1000 t of H₂ is around 30–60 M€, excluding the cost of any storage containers and associated equipment (e.g., pumps). Some LOHC material is also lost over time due to thermal degradation and must be replaced, adding further costs [106]; approximately 0.1% of DBT can be estimated to be lost per storage cycle [91,104]. The cost of storage capacity is substantially higher for LOHCs than for other liquid H₂ carriers (even for NH₃, which requires insulated tanks) and is more comparable to that of underground gaseous H₂ storage [24]. Among the LOHCs suggested in the literature, DBT is amongst the cheapest. Based on the simple calculation above, we conclude that while LOHCs with lower enthalpies of dehydrogenation do exist, the higher costs of these may prevent their implementation in an H-DR context.

The H18-DBT/DBT LOHC system has been investigated rather rigorously in recent years, including a successful demonstration of hydrogenation of DBT using “wet” H₂ and gas mixtures containing H₂ (e.g., syngas) [107,108]. The dynamic operation of both hydrogenation and dehydrogenation processes has also been examined. One recent innovation is the use of the same reactor for both DBT hydrogenation and H18-DBT dehydrogenation [105,109]. By altering the pressure, it is possible to release (low pressure) or store (high pressure) H₂ using a Pt-based catalyst in the same reactor. Using one reactor for both hydrogenation and dehydrogenation lowers the total investment cost and allows for more

dynamic operation as the reactor rarely has to be heated up from a cold stand-by mode. However, a large-scale reactor of this kind has not yet been demonstrated.

Commercial units for H₁₈-DBT/DBT-based H₂ storage, including hydrogenation, dehydrogenation and storage equipment, are available [110]. However, standardized units are relatively low-capacity in terms of steelmaking, with maximum rate capacities of 12 t H₂/d and 1.5 t H₂/d for hydrogenation and dehydrogenation units, respectively.

4. Comparison

Investment into a H₂ storage in the H-DR context is only sensible if the operational and investment costs of the storage do not outweigh savings in the electricity cost of H₂ production due to the dynamic operation of electrolyzers. With this in mind, available economic data for the considered H₂ carriers are compared in this section. It should be noted that none of these carriers have been used for the storage of H₂ at scales suitable for industrial-scale steelmaking. Therefore, the reported values should be regarded as approximate estimates only.

4.1. Investment Costs

Storage of H₂ in a liquid carrier requires three principal units: (1) a hydrogenation plant, where the carrier is produced; (2) a storage; (3) a dehydrogenation plant, where H₂ is released from the liquid carrier. For certain carriers (LOHCs, formate salts), a secondary storage unit for storage of the dehydrogenated carrier is also needed. At present, it is uncertain whether the one-reactor concept is industrially viable for H₁₈-DBT/DBT. Therefore, solutions featuring either one combined reactor or separate hydrogenation and dehydrogenation reactors are both considered.

For these calculations, a standard 0.6 scaling factor has been used for all hydrogenation and dehydrogenation facilities. Storage capacity costs have been assumed to scale linearly. The shown data represent only purchased equipment costs, thus excluding engineering, construction, and contingency costs.

4.1.1. Hydrogenation Plants

For most liquid H₂ carriers, the hydrogenation plant contributes to the best part of the overall investment cost. One reason for this is the typically high pressures, another is the quite common recycling of unconverted reactants after the reactor, which increases process complexity and size.

The investment cost of the hydrogenation plants depends on their rate capacity. The appropriate hydrogenation rate capacity in the H-DR context is presently uncertain. The choice of installed rate capacity will need to take the development of the electricity market until implementation into account, for instance. Such an optimization is not attempted here. However, hydrogenation rate capacities in excess of the H₂ demand of the full-scale H-DR process are unlikely due to the high investment costs of electrolyzers. It is also unlikely that the storage must be filled at such rates in order to feed the dehydrogenation process considering the electricity price dynamics.

In Figure 6, the investment costs of the considered hydrogenation plants are seen as a function of their hydrogenation rate capacity. Electrolyzer overcapacity, corresponding to the hydrogenation plant rate capacity, is necessary to feed the plant. Therefore, the investment costs of electrolyzers (or electrolyzer overcapacity) for three cases: 300, 500 and 700 €/kW (assumed to scale, linearly with capacity) are also shown. Electrolyzer investment costs at scales suitable for full-scale H-DR production are presently uncertain, as no such systems have been built. However, values in the range 300–700 €/kW may be feasible for scale-up of production volumes [111–114].

Again, it must be emphasized that the uncertainty of the investment costs of these hydrogenation plants is significant. This is particularly true for DBT and FA, where few literature values are available [104]. However, results indicate that the hydrogenation of N₂ via the Haber-Bosch process to produce NH₃ is the most capital-intensive option,

followed by FA. A reason for this is the high synthesis pressure and temperature of the Haber-Bosch process compared to the other carriers. The investment cost of a CO₂-based MeOH production plant and a DBT hydrogenation plant appears rather similar, although, again, the values for DBT are uncertain. Reuß et al. (2017) report much lower values, for instance, [115]. Here, we use the values by Hank et al. (2020) due to their recency, and since values are based on “... discussion with an industrial stakeholder and manufacturer of LOHC pilot plants”. This result seems to indicate that, while the MeOH production process is more complex, featuring, e.g., distillation, the higher catalyst cost of DBT hydrogenation more than makes up for this. The potential use of a single reactor for both dehydrogenation of H18-DBT/DBT and hydrogenation of DBT will be discussed in Section 4.1.4.

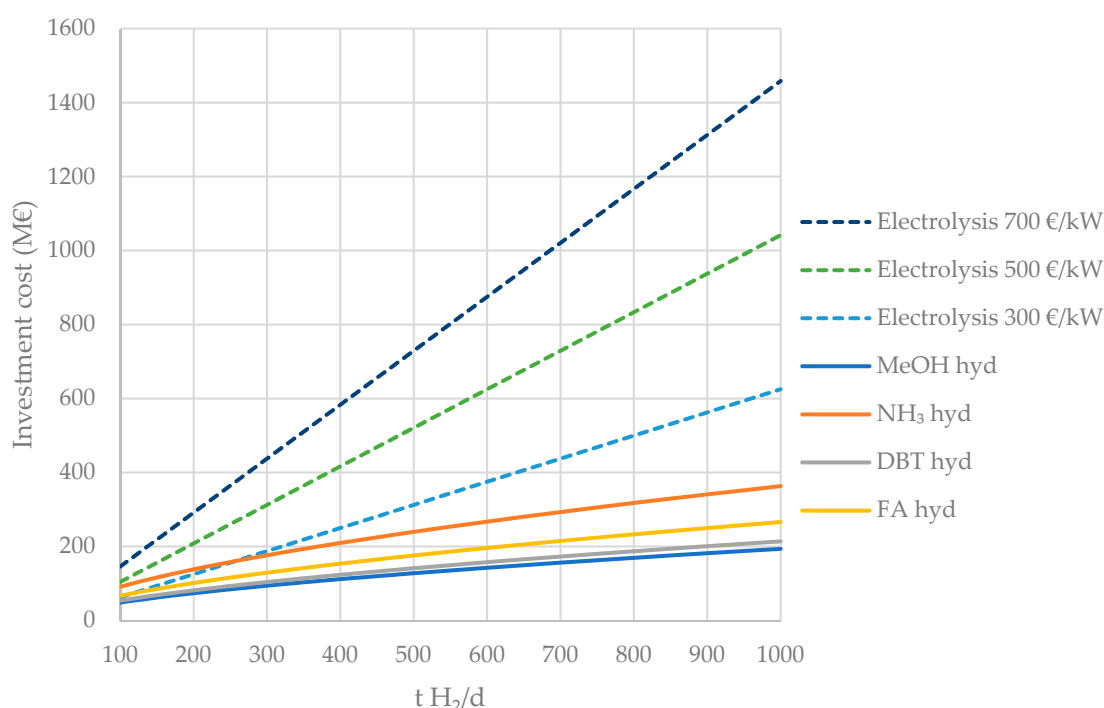


Figure 6. Investment costs of electrolyzer overcapacity and hydrogenation plants for different liquid H₂ carriers.

Comparing hydrogenation plant and electrolyzer overcapacity investment costs in Figure 6, it can be seen that electrolyzer overcapacity generally dominates. Generally, it can be concluded that the investment cost of electrolyzer overcapacity has a more significant effect on the overall investment cost than the choice of liquid H₂ carrier.

4.1.2. Dehydrogenation Plants

Economic data are scarce for large-scale liquid H₂ carrier dehydrogenation plants. For instance, no data were retrievable regarding the investment costs of a prospective FA dehydrogenation plant from the scientific literature. For MeOH, data come from a single paper written by employees at Lurgi in 2001. No other economic data were found for large-scale MeOH reforming plants. A similar lack of data is noted for NH₃ dehydrogenation. In that case, data come from the previously mentioned “Ammonia to Green Hydrogen Project” report [96], which, again, is the only identified comprehensive reference. For H18-DBT, the same uncertainty as with the investment cost of the DBT hydrogenation plant is noted. Values from Hank et al. (2020) are used for H18-DBT dehydrogenation [91]. Investment costs of dehydrogenation plants are plotted as a factor of their H₂ rate capacity in Figure 7.

Sizing of the dehydrogenation unit is more straightforward compared to the hydrogenation unit. To allow for minimum electrolyzer use during times of high electricity prices, the dehydrogenation plant should be sized to be able to deliver 100% of the H-DR H₂ demand, i.e., it should be possible to operate the entire H-DR process on H₂ from the

dehydrogenation plant. The generally lower investment costs of the dehydrogenation plants compared to hydrogenation (H18-DBT/DBT being the exception) also supports this sizing strategy. Necessary dehydrogenation plant rate capacities to fully supply H-DR processes at various scales is also indicated in Figure 7.

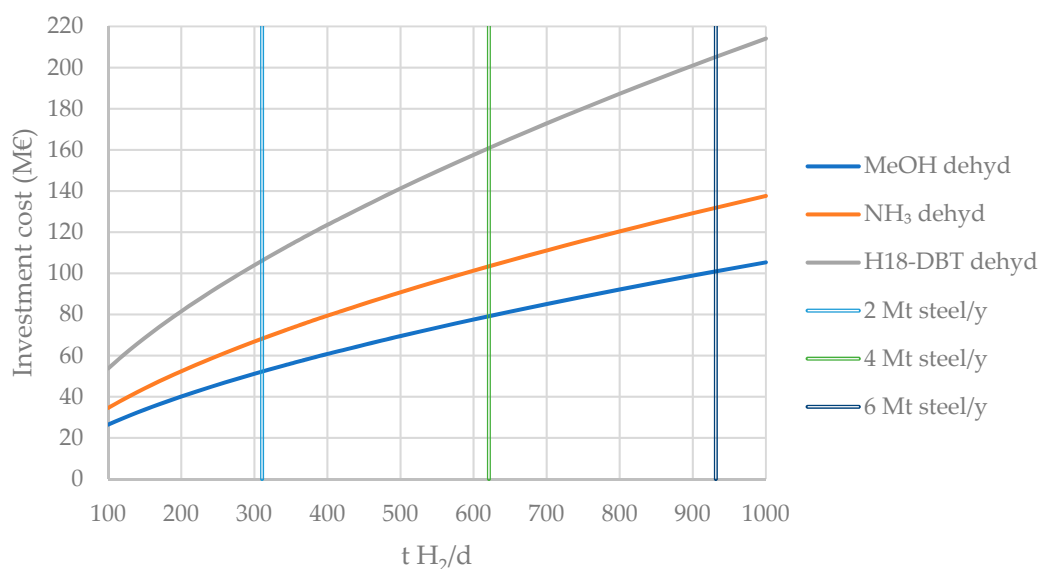


Figure 7. Dehydrogenation plant investment costs for different liquid H₂ carriers. H₂ demand of dehydrogenation plant to fully supply H-DR process at different production scales also indicated (assumed 0.9 capacity factor, 51 kg H₂/t steel).

All considered dehydrogenation plants consist of two subprocesses: the actual dehydrogenation reactor and then a separation step to produce near-pure H₂. In certain cases, the separation step can be achieved in multiple ways. There is also the question of H₂ purity. Fuel-cell-grade purity H₂ is not necessary in the H-DR process, but the minimum required H₂ purity is presently unknown. In the NH₃ dehydrogenation process described above, a cryogenic purification process is applied to generate fuel-cell-grade purity H₂. A less complex and lower-cost separation process may be feasible in the H-DR context, lowering the overall costs of the NH₃ dehydrogenation plant. For the other carriers, separation is more straightforward, either via simple condensation (H18-DBT/DBT), or PSA (MeOH) [98,116].

In terms of dehydrogenation, MeOH appears to be the lowest investment cost option by a significant margin. The reasons for this are foremost the relatively low process temperature (compared to NH₃), cheap catalyst (compared to H18-DBT) and process simplicity. H18-DBT dehydrogenation is found to be the most expensive option due to catalyst costs (noting, again, the uncertainty of H18-DBT/DBT economic data). The differences in investment costs are considerable: at 300 t H₂/d rate capacity, the MeOH dehydrogenation plant is approximately 30% and 100% less expensive than options based on NH₃ or H18-DBT, respectively.

4.1.3. Storage Units

The cost of H₂ storage capacity differs greatly among the considered liquid H₂ carriers. MeOH can be stored in conventional steel storage tanks, similar to those used for storing oil. FA is, in high concentrations, corrosive due to its acidity. This corrosiveness means that pure FA must be stored in stainless steel tanks, which increases material costs by roughly 30% compared to carbon steel (lower-concentration FA solutions can be stored in polyethylene, polypropylene or rubber-lined carbon steel vessels.) [79,117,118]. NH₃ is most commonly stored in liquid form in insulated tanks (boiling point −33 °C), which increases costs, although the volumetric H₂ storage density is high. The situation is most unique for H18-DBT/DBT. Firstly, both hydrogenated and dehydrogenated forms must

be stored, necessitating at least two storage tanks. Secondly, the LOHC material itself must also be purchased in sufficient amounts. As a result, H₂ storage capacity is relatively expensive for LOHCs, as can be seen in Table 1.

Table 1. Investment cost of storage for different liquid H₂ carriers [91].

Liquid H ₂ Carrier	€/t Carrier	€/t H ₂
MeOH	75 €/t MeOH	397
FA	63 €/t FA	1439 *
NH ₃	350 €/t NH ₃	1977
(H18-)DBT	68 €/t (H18-)DBT for storage tanks, 2 €/kg DBT material	34,452 #

* Based on MeOH storage cost, adapted for stainless steel (factor 1.3) and differences in liquid density compared to MeOH ($792/1220 = 0.65$). # Includes two storage tanks (both at 68 €/t (H18-)DBT) and DBT material (at 2 €/kg DBT).

4.1.4. Total Investment Costs

The overall investment costs for different liquid H₂ carriers as a function of storage capacity is seen in Figure 8. The comparison is based on an H-DR process producing 2 Mt of DRI per year. Two cases with different hydrogenation rate capacities, equivalent to electrolyzer overcapacities of 25% and 75%, are shown for each carrier. The only exception is for H18-DBT/DBT utilizing the same reactor for hydrogenation and dehydrogenation (the one reactor (OR) concept) where only one case (100% overcapacity) is shown. FA is not included, as no investment costs of its dehydrogenation process could be found in the literature.

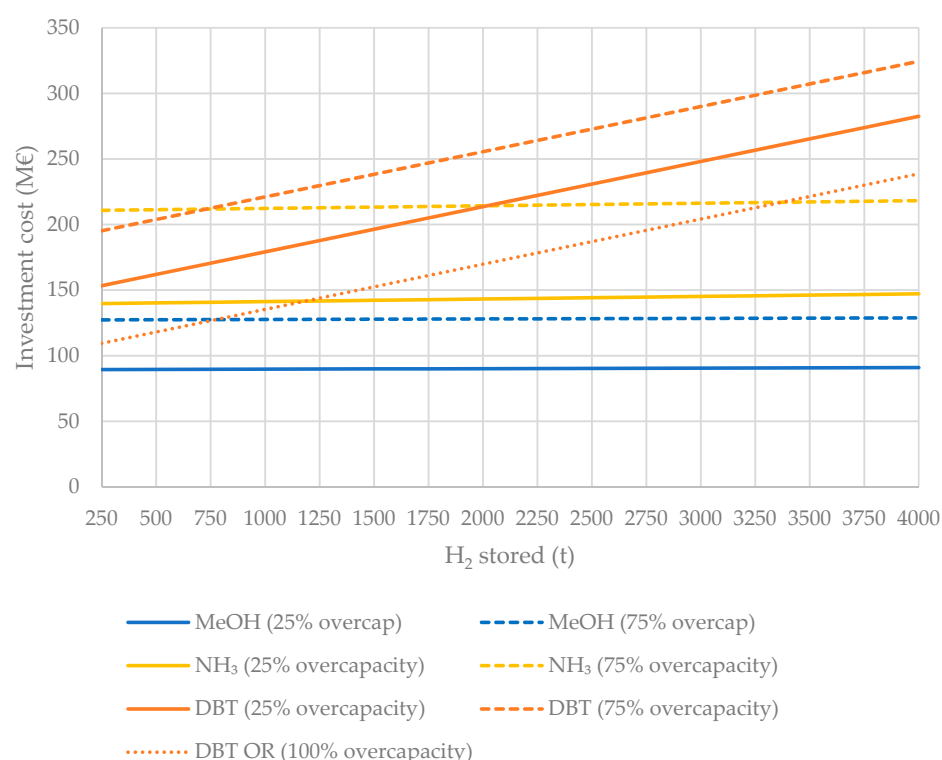


Figure 8. Total investment costs of liquid H₂ carrier-based H₂ storage systems (OR = one reactor concept).

Several conclusions can be drawn from Figure 8. Firstly, the cost of storage capacity is nearly negligible for MeOH and NH₃, but not for H18-DBT/DBT. Consequently, MeOH and NH₃ appear to become better options at larger storage capacities. Secondly, MeOH is, in nearly all cases, the lowest-cost liquid carrier option. The only exception is for the case

of low storage capacities, where the OR H18-DBT/DBT system potentially reaches lower investment costs due to use of a single facility for both hydrogenation and dehydrogenation.

4.2. Operational Costs

The purpose of a H₂ storage in the H-DR context is to lower the electricity cost of H₂ production via exploiting differences in electricity price over time, as more H₂ can be produced at lower electricity prices and less at high electricity prices. The operating costs of the storage, i.e., mainly costs of additional electricity and heat, determine how much the electricity price must increase between the storage and release of H₂ for storage to reach a positive contribution margin and become economically sensible. The capacity factor and overall profitability of the storage is then dependent on how often such sufficiently large electricity price differences appear, i.e., on the electricity market dynamics. In practice, additional factors such as electricity price forecast accuracy, storage capacity limitations, hydrogenation and dehydrogenation process dynamics, and electrolyzer degradation also come into play. Therefore, the profitability of investment into a H₂ storage can only be evaluated via simulation. Nevertheless, consideration of the operational costs of the storage along the historical electricity price duration curves can give an indication of how often and how profitably a storage can be operated.

As mentioned previously, the operational costs of H₂ storage in these liquid carriers is largely made up of the electricity demand of the hydrogenation process and the heat demand of the dehydrogenation process. Relevant values for these processes are seen in Table 2.

Table 2. Electricity and heat demands of dehydrogenation and hydrogenation processes.

Liquid H ₂ Carrier	Electricity Demand Hydrogenation (kWh/kg H ₂)	Heat Demand Dehydrogenation (kWh/kg H ₂)	Temperature Dehydrogenation
MeOH	<0.0–0.9	2.5–6.9 [#]	64% < 100 °C, rest > 200 °C
FA	3.6–6.7 (+16–63 heat)	2.8–9.1	<100 °C
NH ₃	3.4–6.2	14.3 (−1.6 electricity generated)	>500 °C
H18-DBT/DBT	0.4	11.5 [□]	>300 °C

[#] 64% of this heat is for evaporation of MeOH and H₂O at <100 °C. Reaction heat assumed to be supplied with 90% efficiency. Lower value (2.5 kWh/kg H₂) assumes that evaporation heat is freely available from the H-DR process. [□] Based on value by Eypasch et al., but corrected to use the proper heat of dehydrogenation of H18-DBT [119].

For hydrogenation, the use of NH₃, and especially FA, appears to be the most energy-intensive options. The large heat demand of FA production, mainly due to separation processes (as mentioned in Section 3.3.2), is also of note (all other hydrogenation processes have a heat surplus). Unfortunately, for low-temperature electrolyzers, the surplus heat would not be sufficient to power the FA production process, both in terms of amount and temperature level (100–200 °C). Therefore, it is likely that external heat must be supplied to an FA production process. In contrast, the H18-DBT/DBT and MeOH routes require relatively small amounts of electricity for hydrogenation. This is due to the relatively low reactor pressures. The heat generated via the exothermic hydrogenation reactions is assumed to be utilized within the overall hydrogenation processes, as heat integration is likely challenging considering the intermittent operation.

For dehydrogenation, FA is likely the least heat-intensive option, especially considering the low reaction temperature (<100 °C), followed by MeOH. In addition, a large part of the heat demand of MeOH dehydrogenation (around 64%) is at a relatively low temperature. The actual reaction heat of MSR (at >200 °C) could theoretically be covered by DRI cooling, which appears an attractive option. However, the supply of low-temperature heat in the cases of FA and MeOH may still constitute a challenge, especially considering the previously mentioned poor temporal match between FA or MeOH dehydrogenation and electrolyzer operation in the H-DR process.

The dehydrogenation of NH₃ or H18-DBT requires significant heat at elevated temperatures. Heat integration within the H-DR process appears unlikely to be sufficient in

these cases. Instead, this heat should preferably be supplied via combustion of part of the released H_2 , electricity or external fuels; if part of released H_2 is combusted to generate this heat, more than 35% of the released H_2 is consumed [44,47].

Using the data in Table 2, it is possible to estimate the added cost of storage ($\Delta C_{storage}$ (€/kg H_2)) in the liquid carriers due to additional OPEX compared to the case without storage, given an electrolysis efficiency (P_{elec}), a “low” electricity price ((€/MWh) P_{low}) for when H_2 is stored, and a heat price during hydrogenation ((€/MWh) Q , only applicable for the FA case).

$$\Delta C_{storage} = \left(\frac{(P_{elec} + P_{hyd}) \cdot \left(\frac{\text{€}}{\text{MWh}} \right) P_{low}}{1 - \frac{Q_{dehyd}}{LHV_{H_2}}} \right) + Q_{hyd} \cdot \left(\frac{\text{€}}{\text{MWh}} \right) Q - P_{elec} \cdot \left(\frac{\text{€}}{\text{MWh}} \right) P_{low} \quad (6)$$

Equation (6) assumes that the heat for the dehydrogenation process is supplied via combustion of part of the released H_2 (with no heat losses). This means that the electricity price during the hydrogenation process ((€/MWh) P_{low}) becomes a very important parameter, as the combustion of H_2 produced at a relatively high electricity price constitutes expensive heat. Note that the electricity supply for dehydrogenation processes is not included in Equation (6), as these are generally small. It is also assumed that it is not viable to generate electricity from an intermittently operated NH_3 dehydrogenation plant. An electrolysis efficiency of 50 kWh/kg H_2 and a hydrogenation heat price of 20 €/MWh yields the results in Figure 9. Two cases have been plotted for all carriers except DBT: one based on the most optimistic values in Table 2 (“LOW”) and one on the most pessimistic (“HIGH”). The difference between LOW and HIGH is particularly large for FA, reflecting the relative uncertainty of its application.

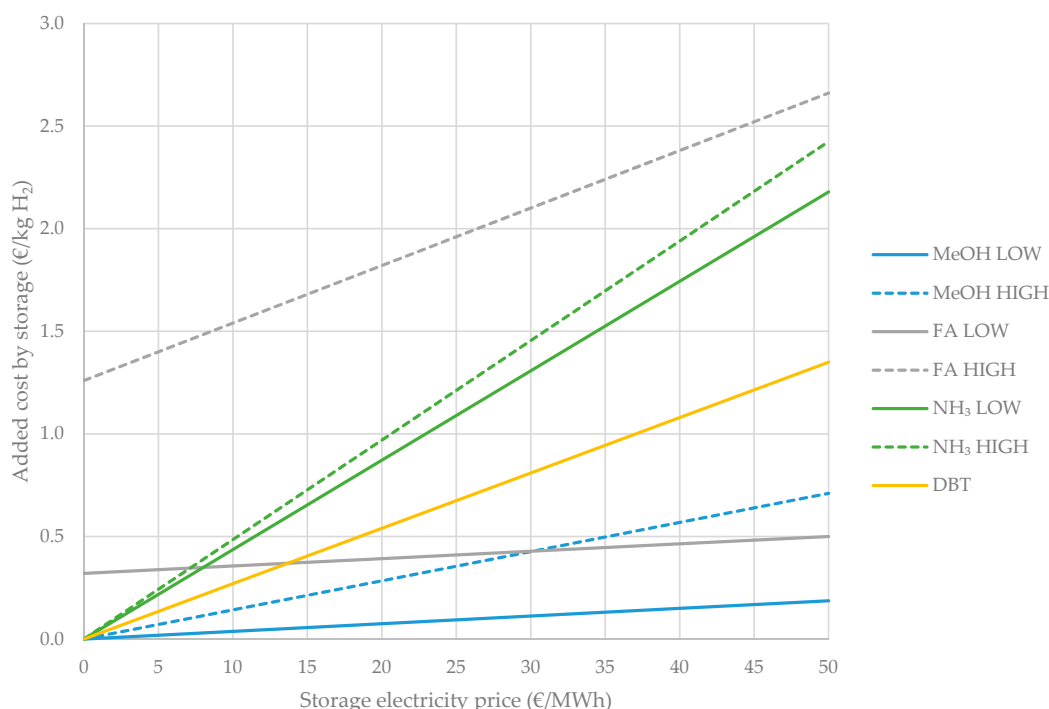


Figure 9. Added cost of storage for liquid H_2 carriers. Heat for dehydrogenation is supplied via combustion of part of released H_2 , heat price for FA hydrogenation 20 €/MWh (other hydrogenation processes are exothermic).

As can be seen, MeOH turns out to be the best-performing option for nearly the entire range of considered storage electricity prices due to its relatively low associated electricity demand of hydrogenation and heat demand of dehydrogenation (even in the worst-case scenario). The negative effect of the large heat demand of FA production,

particularly in the pessimistic case, can be clearly seen in Figure 8: even for a storage electricity price of 0 €/MWh, storage of H₂ in FA adds 0.3–1.3 €/kg to the cost of H₂. The large heat demand of NH₃ and H18-DBT dehydrogenation renders the use of these carriers particularly unattractive for higher storage electricity prices, as a large share of the stored H₂ must be combusted. Note that the results in Figure 9 do not include the investment cost of the storages or electrolyzer overcapacity. The effects of limited load flexibility are also excluded. Therefore, the real added costs of storage are larger.

4.3. Load Flexibility

For H₂ storage in liquid carriers to be practical, it must be possible to produce and dehydrogenate these in a dynamic manner. As seen in Figure 9, ideally, H₂ is overproduced and stored only when the electricity price is relatively low, while the stored H₂ is only utilized when the electricity price is relatively high (when it is expensive to produce “new” H₂ via electrolysis) [56]. Chemical processes have conventionally not been operated according to this logic. Indeed, as the prices of typical feedstocks, e.g., oil, coal and natural gas, varies slowly in comparison to that of electricity, there has been no strong incentive to maximize the load window and operational flexibility of industrial chemical processes. The focus has instead generally been on increasing the process efficiency at nominal load and to ensure that the process can operate at nominal load as regularly as possible [120,121]. Therefore, data on process flexibility are often scarce, uncertain or unknown for such processes. However, this has been changing in recent years with the increasing interest in large-scale chemical processes based on a feed of H₂ produced via electrolysis.

In an H-DR process, a low minimum load is important for both hydrogenation and dehydrogenation processes, as a high minimum load in either end necessitates the production of H₂ during times of relatively high electricity prices. However, as the nominal capacity of the dehydrogenation process will generally be higher than that of the hydrogenation process (due to the high investment cost of electrolyzers and electricity price dynamics), its minimum load becomes especially important. On the hydrogenation side, the adverse effects of a high minimum load may be partially managed via the integration of a buffer storage of gaseous H₂, although this adds investment costs. Such a buffer storage can be used to supply H₂ to the hydrogenation process during high electricity prices, allowing the electrolyzers to then be turned off (or operated at their minimum load).

Amongst the liquid H₂ carriers considered here, the largest body of process flexibility data exists for MeOH and NH₃. However, even here the reported values have generally not been demonstrated in practice, at least not consistently over extended periods in full-scale facilities. For MeOH production with H₂ and CO₂, minimum load values in the range of 10–20% of the nominal load have been reported [56,63,122]. Maximum ramp rates from 20%/h to up to minimum to full load within minutes appear possible [56,62,123]. Data on the dynamic operation of industrial-scale MeOH reformers are scarce. However, the possibilities for dynamic MeOH dehydrogenation appears to be good considering the relatively low required temperatures, the moderate heat demand and relative success in developing small-scale rapid-start-up MeOH reformers for automotive applications [67,124,125]. PSA units have short start-up times as well [89]. Electrically heated MeOH reformers should be able to achieve near-instantaneous start-up [47].

Dynamic operation of the Haber-Bosch is receiving increasing interest in the literature. Current Haber-Bosch processes typically operate with a minimum load of around 50–60% and a maximum ramp rate of 20%/h [126,127]. However, minimum loads of around 20–30% or lower should be achievable, e.g., via increasing the concentration of inert content in the reactor loop, although such methods do increase the specific electricity consumption of the NH₃ synthesis somewhat due to increased compression work [127–129]. One possibility to achieve this is via limiting the purge stream during operation at partial load (this method of controlling the Haber-Bosch process load has been patented [127]) [128]. Cold start-up of the Haber-Bosch process normally takes multiple days.

Large-scale NH_3 dehydrogenation has, as already mentioned, rarely been considered in the literature. However, the process is rather similar to conventional steam methane reforming (SMR) [96]. Industrial SMR plants typically operate continuously with minimum loads of at least 30%; start-up requires at least a couple of hours [130]. The subsequent cryogenic separation step is typically not very dynamic either [89]. As for MeOH, electric heating of the NH_3 dehydrogenation process may facilitate faster dynamics [44].

Commercial H18-DBT hydrogenation and DBT dehydrogenation processes can achieve minimum loads of 50% of the nominal rate per supplier data [131]. The one reactor DBT concept would, by its nature, allow for 0% minimum loads (as the reactor is completely switched over from hydrogenation to dehydrogenation or vice versa), although the minimum load of the reactor in either mode is presently uncertain [109].

No data on the dynamics of CO_2 -based FA production or FA dehydrogenation could be found in the literature. Nevertheless, low minimum loads and relatively fast startup could be realistic considering the relatively low temperatures involved, especially for FA dehydrogenation.

5. Conclusions

The application of liquid H_2 carriers in the context of large-scale H-DR processes has been investigated. The main advantage of storage of H_2 in such liquid carriers rather than gaseous underground storage is the far lower cost of storage capacity. Four of the most intensively investigated liquid H_2 carriers were considered: MeOH, FA, NH_3 and H18-DBT/DBT. The technological readiness of the application of these carriers differs in, e.g., an H-DR context. MeOH and NH_3 are the most developed carriers, in particular with regard to the hydrogenation process, as these are largely based on current conventional industrial processes. For H18-DBT/DBT, commercial equipment does exist, but only at small scales as of yet. The use of FA as a H_2 carrier at large scales remains to be demonstrated, in particular its direct production via the hydrogenation of CO_2 .

The application of a liquid H_2 carrier requires a hydrogenation plant, a carrier storage and a dehydrogenation plant. The investment and operational costs of these units differs significantly from carrier to carrier. Based on a review of the literature data, it is concluded that the MeOH-based system should achieve the lowest investment costs overall for a given electrolyzer overcapacity and H-DR process H_2 demand. The NH_3 route suffers from the high capital-intensity of the Haber-Bosch process, while the investment cost of the H18-DBT/DBT system is weighted down by the need to store the dehydrogenated carrier. For small storage capacities ($<750 \text{ t H}_2$), a version of the H18-DBT route utilizing the same reactor for both hydrogenation and dehydrogenation may be competitive at relatively low H_2 storage capacities. The overall investment cost of a FA-based system remains uncertain, especially for a large-scale dehydrogenation plant.

In terms of operational costs, MeOH again performs the best, particularly when low-temperature heat ($<100 \text{ }^\circ\text{C}$) is available from the H-DR process. NH_3 and H18-DBT require significantly more high-temperature heat for dehydrogenation, which limits their appeal in an H-DR process. Uniquely, the operational costs of the FA route are dominated by the potentially high heat demand of the hydrogenation process caused by the energy-intensive separation steps. If large amounts of heat at $<180 \text{ }^\circ\text{C}$ are available at low cost ($<5 \text{ €/MWh}$), FA may be competitive with MeOH in terms of operational costs. However, this scenario does not appear likely.

Beyond investment and operational costs, the economic viability of liquid H_2 carriers in the H-DR context depends on the load flexibility of the hydrogenation and dehydrogenation processes. This is a growing research field and the current available data are limited. Nevertheless, the dynamic operation of the MeOH and NH_3 production processes appears feasible, with minimum loads in the ranges of 10–20% and 20–30% for MeOH and NH_3 , respectively. MeOH dehydrogenation has been proven to be a flexible process at small scales, e.g., onboard vehicles, and operates at a relatively low temperature, which facilitates quick start-up. Nevertheless, the load flexibility of an industrial-scale MeOH reformer

remains to be determined. The high temperatures necessary for the NH_3 dehydrogenation process will limit its load window; the similar SMR process has a typical minimum load of 30%. Currently available DBT hydrogenation and H18-DBT dehydrogenation plants have minimum loads of 50% per supplier data. The main relative advantages and disadvantages of the considered liquid H_2 carriers, as well as the main questions to be answered before their commercialization is possible, are summarized in Table 3.

Table 3. Summary of advantages, disadvantages and main questions left to be answered before large-scale employment of the considered liquid H_2 carriers.

Liquid H_2 Carrier	Advantages	Disadvantages	Questions to Resolve before Large-Scale Deployment
MeOH	<ul style="list-style-type: none"> High H_2 storage density. Relatively low-temperature, low-heat demand dehydrogenation. Relatively low-pressure hydrogenation. 	<ul style="list-style-type: none"> Large heat demand of evaporation of MeOH and H_2O. CO_2 may be expensive from certain sources. 	<ul style="list-style-type: none"> Load flexibility. Optimal process design without distillation. Optimal supply of CO_2.
FA	<ul style="list-style-type: none"> Low-temperature dehydrogenation possible. High-pressure dehydrogenation possible. 	<ul style="list-style-type: none"> Low H_2 storage density. Hydrogenation is energy-intensive. CO_2 may be expensive from certain sources. 	<ul style="list-style-type: none"> Scale up of CO_2-based production process. Techno-economics of dehydrogenation process. Optimal supply of CO_2.
NH_3	<ul style="list-style-type: none"> High H_2 storage density. Practically endless supply of N_2. Well-established production process. 	<ul style="list-style-type: none"> Energy-intensive dehydrogenation. Must be liquefied, stored in insulated containers. Haber-Bosch process capital intensive, high pressures needed. 	<ul style="list-style-type: none"> Load flexibility. Optimal catalyst for and design of dehydrogenation process.
H18-DBT/DBT	<ul style="list-style-type: none"> Near-pure H_2 released. Low process complexity. Relatively low-pressure hydrogenation. 	<ul style="list-style-type: none"> Dehydrogenated LOHC must be stored. LOHC material is expensive. Large heat demand of dehydrogenation. 	<ul style="list-style-type: none"> Load flexibility Scale-up of processes Catalyst costs at larger scales.

We conclude that MeOH is the most attractive candidate for integration into a large-scale H-DR processes amongst the considered liquid H_2 carriers. MeOH is especially advantageous for large H_2 storage capacities. Nevertheless, significant hurdles for the implementation of this carrier remain, mainly related to the appropriate supply of heat for dehydrogenation and CO_2 for hydrogenation.

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