Hydrogen Storage Technologies for Future Energy Systems

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Abstract

Future energy systems will be determined by the increasing relevance of solar and wind energy. Crude oil and gas prices are expected to increase in the long run, and penalties for CO_2 emissions will become a relevant economic factor. Solar- and wind-powered electricity will become significantly cheaper, such that hydrogen produced from electrolysis will be competitively priced against hydrogen manufactured from natural gas. However, to handle the unsteadiness of system input from fluctuating energy sources, energy storage technologies that cover the full scale of power (in megawatts) and energy storage amounts (in megawatt hours) are required. Hydrogen, in particular, is a promising secondary energy vector for storing, transporting, and distributing large and very large amounts of energy at the gigawatt-hour and terawatt-hour scales. However, we also discuss energy storage at the 120–200-kWh scale, for example, for onboard hydrogen storage in fuel cell vehicles using compressed hydrogen storage. This article focuses on the characteristics and development potential of hydrogen storage technologies in light of such a changing energy system and its related challenges. Technological factors that influence the dynamics, flexibility, and operating costs of unsteady operation are therefore highlighted in particular. Moreover, the potential for using renewable hydrogen in the mobility sector, industrial production, and the heat market is discussed, as this potential may determine to a significant extent the future economic value of hydrogen storage technology as it applies to other industries. This evaluation elucidates known and well-established options for hydrogen storage and may guide the development and direction of newer, less developed technologies.

INTRODUCTION

The key to a future, sustainable energy system lies in the increasing implementation and usage of renewable energies (1). Many countries have ambitious targets to substantially increase solar, wind, geothermal, hydro, and biomass energy production in the next few years. In Europe, this development is particularly dynamic. The European Union has announced a target in which 30–40% of electricity is produced from renewable energy by 2020. Germany's target, with its *Energiewende*, is even more ambitious. It aims to close all nuclear power plants in the country by 2022, accompanied by a strong growth in solar power plants and wind parks to produce 50% of its electricity from renewable energy by 2030 and 80% by 2050 (2).

Such a high contribution from renewable energy can be reached only if wind and solar power plants with massive storage capacities are installed. These plants must overproduce energy during energy-rich times (times when the sun is shining and the wind is blowing). Extra energy must be stored to compensate for energy shortages due to unfavorable weather conditions, or energy-lean times. The type of energy storage required must manage not only the natural day-night cycle for photovoltaic electricity production but also seasonal differences in the energy harvested from wind and the sun. The estimation of the necessary total storage capacity is a sophisticated and complex calculation. The arrival of such an estimation depends strongly on political, economic, and infrastructure developments; i.e., it depends on the development of a capacity market for energy storage or on future expansions of the electrical grid.

However, the mere substitution of fossil fuels in electricity generation is insufficient to meet the far-reaching, long-term goal of decarbonizing the whole energy sector claimed by the 2015 United Nations Climate Change Conference in Paris. To reach this ambitious goal, efficient links between renewable electricity production and energy generation via fuels for mobility and heat production are mandatory. **Figure 1** gives an overview of today's technology options for this kind of energy sector coupling. Of course, all these options build on further expanding the capacity to produce electricity from renewable energy sources. Moreover, the technologies shown in **Figure 1** will become more relevant if long-term storage of electricity in the gigawatt-hour (GWh) or terawatt-hour (TWh) range remains technologically problematic in electrochemical devices (e.g., batteries and redox flow systems). Under this assumption, the large amount of intermittent electricity produced from wind and the sun will be significantly below average market prices during sunny or windy times and at sunny or windy locations.

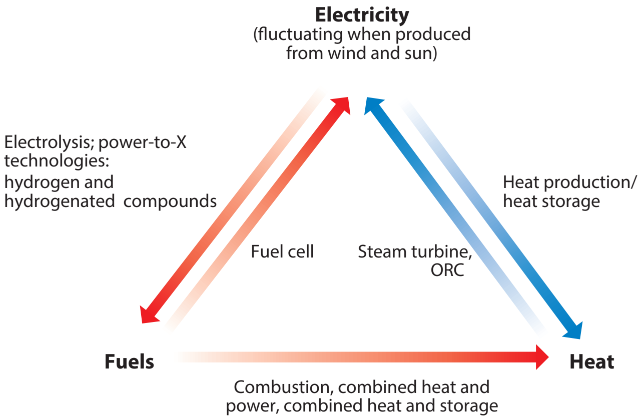

Figure 1

Options to apply renewable excess energies to other sectors in a future energy system. Abbreviation: ORC, Organic Rankine Cycle.

In this review we focus on the use of hydrogen from renewable electricity in either elemental form or chemically bound form as an energy vector. Hydrogen generation from electricity involves water electrolysis as a key technology. Although modern electrolysis research has progressed significantly (3), today 1 kg of hydrogen produced from electrolysis based on a realistic electricity price (accounting for the existing balance between full-load hours of the electrolyzer and the price of electricity) costs approximately €3 (4), which is based largely on the high investment cost of current electrolyzer technologies. This fact is important because it restricts some of the power-to-X options described below, especially power-to-methane, from today's economic standpoint. Because hydrogen produced by electrolysis is significantly more expensive than its heating-value equivalent for methane (which in Germany is approximately €1.20/kg H_2 and in the United States is approximately \$0.40/kg H_2), the addition of hydrogen from electrolysis to the natural gas grid, and moreover, hydrogenation of CO_2 to methane, is currently not economical. Other options to convert electricity to hydrogen without electrolysis involve thermochemical water splitting (5) and the use of strongly endothermic, high-temperature, electrically heated processes such as methane decomposition to carbon and hydrogen (6). These alternative pathways can also be free of CO_2 emissions but they are less technologically mature than electrolysis.

As a consequence of the current market, technologies that convert electrolysis hydrogen to high-value chemical products (e.g., ethylene from CO_2 and hydrogen) by direct catalytic or electrocatalytic conversion are of special interest (7). Another attractive option is the direct use of elemental hydrogen in the energy sector to produce clean electricity during energy-lean times or in the mobility sector as a future fuel. Provided that hydrogen from renewables is supplied in the right place, at the right time, in the right quantity, and at the right purity, these applications offer attractive business opportunities. However, they all require efficient hydrogen storage and transport technologies as the key step for their technical implementation. Therefore, it is likely that the changing energy system will create additional need for hydrogen infrastructure and that these developments will bring us closer to a future hydrogen economy. The hydrogen economy has been discussed since 1976, when Jones (8) postulated that a fully hydrogen-based energy system would be not only desirable but inevitable in the long term (9).

Currently, the strong interest in hydrogen technologies is reflected in the high number of publications on hydrogen storage options (10), compared with that for other gases such as nitrogen, oxygen, argon, helium, or natural gas. This interest is in sharp contrast to the technical reality. The total global hydrogen storage capacity is much smaller than, for example, the total global natural gas storage capacity. However, integrated hydrogen technologies offer new avenues to ultimate sustainability in future energy systems: Hydrogen produced from water by using renewable electricity, efficiently stored and transported, would emit in its combustion in a fuel cell or combustion chamber water as the only by-product. This closed cycle is expected to form the basis of a future CO_2-free energy system. In other words, the vast amount of literature on hydrogen storage reflects the high interest in a hydrogen economy that offers "a high degree of sustainability, which is vital for survival," according to E. von Weizsäcker (11, p. V).

Academic scientists are strongly attracted to the fact that efficient hydrogen storage is a veritable technological challenge: The volumetric storage density of hydrogen is poor. At ambient conditions its lower heating value is only 3 Wh/L, compared with 8,600 Wh/L for Otto fuel and 9,800 Wh/L for diesel. The critical temperature of hydrogen is only 33 K and its density is extremely low (0.0898 g/L at 0°C). Still, the gravimetric energy density of hydrogen is fascinating: 33,000 Wh/kg, which is approximately three times higher than that of traditional fossil fuels.

Introducing a hydrogen economy based on renewable electricity production comes with some new challenges for the hydrogen storage and transport technologies involved. In this review we discuss established and recently developed technologies in light of these new challenges. Our article is based on a future energy scenario in which CO_2 emissions are strongly restricted and therefore the use of fossil fuels is expensive. Moreover, electricity prices are anticipated to strongly fluctuate over time, with low prices during sunny and windy times.

Owing to the irregular nature of the sun and wind, the amount of hydrogen produced from these renewable energy sources will be irregular as well. This irregularity necessitates optimized transient processes and dynamic operation. Not only is dynamic operation a challenge for plant operations, it is also demanding with respect to economics. Although the investment in a continuously producing plant depreciates over more than 8,000 h of annual operation, the hours of sufficient or even excess renewable energy production from sun and wind are far lower. Thus, the chemical plant has to generate a sufficient return on investment in only a fraction of the traditional operation time. The economic considerations increase the share of investment cost in the calculated hydrogen price. Thus, it is important to target high-value hydrogen applications to create an economic case for pursuing them. Typically, hydrogen is most valuable when it is provided at high pressure and in high quality at specific locations in small to medium quantities. Examples of such applications include filling stations for hydrogen mobility applications (e.g., cars, buses, trains) or smaller industrial consumers.

We chose a scenario approach for this article and aim to highlight special aspects of hydrogen storage and transport technologies linked to these scenarios. Thus, we try to emphasize aspects that have been not been discussed in detail or that require additional attention. A hydrogen infrastructure (if introduced) would exist and compete with the conventional power supply infrastructure for a relative long period. Therefore, an interesting dimension to evaluate is the depth at which hydrogen can penetrate the power market (from 0 to 100%). This depth not only estimates the total market value and investment required but also differentiates the technological options according to their potential for stepwise and infrastructure-compatible introduction and application. For example, large single-hub applications are certainly preferred in a fully developed hydrogen economy simply because of economies of scale. However, this scenario requires a large single investment and is therefore risky, particularly during the transition toward a potential future hydrogen economy. In contrast, small-scale applications, although they are less efficient and have high specific investment costs, have a better chance of being implemented because their investment risk is more manageable.

PHYSICAL HYDROGEN STORAGE

Supplemental Material

Physical hydrogen storage methods are based primarily on the compression and cooling/liquefaction of hydrogen and sorption (mainly adsorption) or sorption-like methods such as molecular inclusion of hydrogen on nanostructured carbon, clathrate hydrates, and the like (see **Supplemental Figure 1**).

This section focuses mainly on compressed and liquefied hydrogen. Both of these technologies require a corresponding infrastructure—a compressor system for pressurization and cryogenics for liquefaction. The literature on compressed hydrogen does not usually discuss compression technology, which creates the assumption that this technology is available. In contrast, the literature on liquefied hydrogen deals mainly with liquefaction processes, as it is assumed that storage methods are largely available.

COMPRESSED HYDROGEN

Compressed hydrogen is an option considered in all future scenarios, from bulk cavern storage to compact storage methods for automotive applications.

Storage

The most commonly used standard gas cylinder has a volume of 50 L. New cylinders are designed for a pressure of 300 bar (the standard for more than 15 years). However, many cylinders with a pressure of 200 bar (the previous standard) are still in use (see **Supplemental Table 1** for details). Cylinders are usually delivered in bundles of 12, 15, or 16 pieces. The price for a 50 L (300 bar) cylinder of hydrogen ranges from €100 to €200 depending on delivery/transport considerations.

Supplemental Material

Supplemental Table 2 shows several typical values for automotive applications published by the US Department of Energy (DOE) (12). The values are given for the Type IV vessel, i.e., a tank made of composite materials such as carbon fiber with a polymer liner. All costs are in 2007 dollars and are stated for a relatively high production volume of 500,000 units per year. The costs in 2017 dollars are considerably higher (by 22%, accounting for the annuity factor of 2%) and further increase by a factor of 2 to 10 for production volumes lower than 10,000 units per year.

Reference 13 describes the requirements for the approval of hydrogen-powered vehicles and installation of components and subsystems, including the hydrogen tank, and provides a compact overview of possible problems and malfunctions such as corrosion, permeation, and temperature cycling.

An innovative storage device for compressed hydrogen is based on glass capillary arrays with a honeycomb-like structure and a diameter of approximately 100 μm. This structure is mechanically stable and can manage pressures over 1,000 bar, even with thin capillary walls (14). The experimental work described in Reference 15 reports that volumetric and gravimetric capacities of the investigated structures can exceed the DOE target (**Supplemental Table 2**), at least in the investigated microscale device, which has a volume of 8.5 cm^3. Similar work has been performed on glass microspheres (16), but the results are less spectacular.

At the other end of the scale, we find large compressed hydrogen storage facilities based on conventional underground caverns, mainly salt domes. Depleted oil/gas fields can also be used theoretically for these purposes. **Supplemental Table 3** lists the main parameters, such as pressure, volume, and capacity, of four known bulk hydrogen storage caverns.

CAPEX. The total construction cost of roughly €15 million (Mio) for the Moss Bluff system (17) corresponds to approximately €26.5/m^3 or €0.19/kWh (€15 Mio/80 GWh) specific capital expenditure (CAPEX), which amounts to approximately €7.9/kg H_2. The cost of hydrogen for initial filling (required for further operation) is usually included in this value. This figure is two orders of magnitude lower than the storage cost for automotive applications.

OPEX. It is difficult to estimate the operational expenditure (OPEX), because it depends on operation conditions. Prieur et al. (18) estimate a value of €0.06/kg H_2 in (the year) 2000 euros.

Levelized cost. Lord et al. (19) estimate the levelized cost (or net present value of unit cost over asset lifetime) of H_2 storage for salt caverns to be $1.61/kg, including piping and compressors. This evaluation is valid only for assumed conditions, but it gives an idea of the total storage cost in salt caverns. Generally, cost estimation is complex and perplexing because it depends on factors such as amortization parameters, financing conditions, and scope of supply.

Hydrogen quality. Hydrogen storage in caverns may alter hydrogen quality. Depending on the geological formation, impurities may include water vapor, hydrogen sulfide, or other hydrogenation products of rock ingredients. The corresponding systems for conditioning (drying and purification before hydrogen is injected into a pipeline for consumer use) are necessary.

Compression

Currently, only positive displacement machines, consisting mainly of reciprocating (classic piston or membrane) compressors with maximum pressures of 1,000 bar, are used for hydrogen compression. Rotary positive displacement machines (scroll or screw) may theoretically be used as well. Dynamic compressors (centrifugal and axial) are not yet available for hydrogen because of the high number of compressor stages required (in comparison to positive displacement machines), owing to the low density of hydrogen gas, and the corresponding complexity and cost. Further development in this field is necessary.

The so-called ionic compressor, a special kind of reciprocating compressor with a liquid piston based on ionic liquids (20, 21), is commercially available. Its hydraulic drive allows the system to reduce the dead volume to an absolute minimum. The stroke of every compressing stage can be controlled individually; therefore, the compressor is highly flexible and can be used as a feed compressor for relative low pressures and as a booster compressor for high-pressure upstream processes. The ionic compressor is highly efficient. Because hydrogen is compressed at nearly isothermal conditions, the outlet temperature of each compressor stage is much lower than that for conventional compressors (130–150°C at an inlet temperature of 50°C for a relative high compression ratio of 3). The specific energy consumption of an ionic compressor of 90 MPa (see **Supplemental Figure 2**) for 375 Nm^3/h from 5 bar inlet pressure to 900 bar outlet pressure is 2.9 kWh/kg.

Supplemental Material

One important issue is compressor lubrication. Systems based on mineral oil are not a suitable option because of hydrogenation, a chemical reaction between molecular hydrogen and some hydrocarbon components of the mineral oil. Therefore, only two options are feasible at present: dry compression or a compression system that uses an appropriate chemically inert lubrication substance.

Basically, all the compressors described above are multistage machines using single isentropic compressor stages; therefore, intercooling between compressor stages is generally necessary. The exergy of the compression heat is usually transferred to ambient (cooling water or cooling air) and is therefore lost for compression. The ionic compressor theoretically presents an exception to this rule. All compressors with extensive liquid lubrication (screw compressors and the like) may be exceptions as well, as a process close to isothermal compression with minimized losses can be accomplished with such devices.

The power P required for multistage compression can be calculated by the following equation: P [kWh/kg] $=$ 1.2 log (pressure ratio). This equation is applicable for isothermal efficiency of roughly 70% and a cooling water temperature of 15°C to 20°C. According to this rule, pressurization from 1 to 100 bar requires a power of approximately 2.4 kWh/kg [since log(100) $=$ 2], and a power of 3.6 kWh/kg is required for compression from 1 to 1,000 bar.

Compression Inside Vessels and Dynamics

Another thermodynamic aspect of compression often not discussed in the literature is compression of gas inside charged devices/vessels during filling. Here, compression is close to adiabatic (because of limited heat exchange with ambient) and isentropic (no entropy removal). It leads to heating inside the vessel and to corresponding exergy loss. It considerably reduces pressure in the vessel after cooling to normal storage temperature.

A similar but reversed process, cooling of the gas inside the vessel, occurs during gas withdrawal owing to corresponding adiabatic and isentropic expansion inside the vessel. The effect is also negative because the pressure in the cylinder falls more quickly than expected. The thermodynamics behind both of these processes is commonly described as the Joule effect in books on thermodynamics (to be distinguished from the Joule-Thomson effect), but real

Table 1 **Liquid hydrogen properties**

Property	Liquid	Gas, 300 bar (for comparison)
Density	70.85 g/L	20.77 g/L
Volumetric energy density	2.36 kWh/L	0.69 kWh/L
Mass energy density	33.3 kWh/kg	33.3 kWh/kg

simulation is challenging because of the nonsteady-state process. Reference 22 is a good starting point for discussions on this topic because it summarizes the available information and includes its own investigation into nonuniform temperature distribution inside the vessel. The Joule effect has an impact on efficiency because of exergy losses, but it primarily limits the charging (and discharging) rate and reduces the dynamics of application.

Recovery of Compression Energy

Partial recovery of compression energy on the user side is a topic more appropriate for pipeline projects and can be achieved with processes used today for natural gas pipelines (23). However, it will require a complete redesign of expanders because of the low molecular weight of hydrogen, as opposed to that of natural gas, and the corresponding large investment. In our opinion this is not an option for small-sized devices because of high specific costs.

LIQUID HYDROGEN

The use of liquefied hydrogen (LH_2) has a number of advantages such as high hydrogen and energy density, as shown in **Table 1**.

Boil-off losses (the evaporation of liquid hydrogen due mainly to heat leakage through the thermal insulation and connecting/supporting elements) are cited as the main disadvantage of LH_2 storage. We do not fully agree with this opinion. Of course, it can become a limiting factor, especially in regard to safety issues, but the real limiting factors are still the availability and cost of the liquefaction infrastructure. The energy demand for hydrogen liquefaction [10 kWh/kg H_2 for existing 5 tonne per day (tpd) plants] is relatively high, and therefore the losses during liquefaction are considerable. Owing to economies of scale, a large system can achieve considerably better efficiency and specific costs, and a better chance of beating out the competition. Therefore, further development of hydrogen liquefaction should focus primarily on large-scale systems.

Storage and Distribution

Cryogenic LH_2 tanks are well described in the literature on cryogenics (24–26). LH_2 tanks vary in size, from several liters to 3,800 m^3 (27). Typical boil-off losses vary from 0.1% to 1% per day, depending on tank size. The technology has not really changed since the 1990s, although several innovations were launched, for example, magnetic suspension of the inner vessel based on high-temperature superconductors, as demonstrated by Messer Griesheim in the late 1990s (28), or the free-form cryogenic tank based on composite materials announced by BMW in 2009 (29). Liquid loss during the distribution is typical for infrastructure based on LH_2 supply because of irreversibilities during refilling, pumping, cooling of transfer lines, etc. Liquid loss is estimated to be approximately 7 kg/day for a 725-kg tank (30), which corresponds to roughly 1% per day by using a relatively simple procedure. Liquid loss can theoretically be reduced by 50% by using more intelligent solutions for liquid helium handling (31) such as implementation of an internal Joule-Thomson heat exchanger.

Liquefaction

The basic refrigeration principles (e.g., hydrogen thermodynamic properties; Joule-Thomson, Claude, and Brayton processes; precooling options including mixed-gas processes) and the main hardware components are described in Reference 32. The reference contains a section on potential routes for medium- to long-term technology development and improvement. This kind of information is rare.

Theoretically, the process design itself is not complex and could be accomplished with any conventional process simulation tool, such as, for example, ASPEN, UNISIM, or PROVision, if the corresponding thermodynamic properties packages were available—but they are not. In reality, only data for normal hydrogen, pure orthohydrogen, and pure parahydrogen are available (see References 33 and 34). The calculation of properties for equilibrium hydrogen and for mixtures of four hydrogens (equilibrium, normal, ortho, and para) remains a challenging proposition. All modern liquefaction processes include an integrated ortho-to-para conversion step with somewhat imprecise kinetics (35). Therefore, the correct integration of the conversion process is still a challenge and a source of mistakes and errors in process design calculations.

A list of commercially available hydrogen liquefiers with capacities up to nearly 35 tpd is given in Reference 36. References 37–40 present a view of hydrogen liquefaction from the perspective of an industrial company. These contributions are valuable because they reflect the experience, expertise, and competence of industrial plant manufacturers.

Conventional hydrogen liquefaction follows a three-step process (**Figure 2**):

1. Compress (process 1 → 2 in **Figure 2**) pure and dry hydrogen (sometimes called feed stream or feed) in a compressor at a pressure higher than the critical pressure of hydrogen.

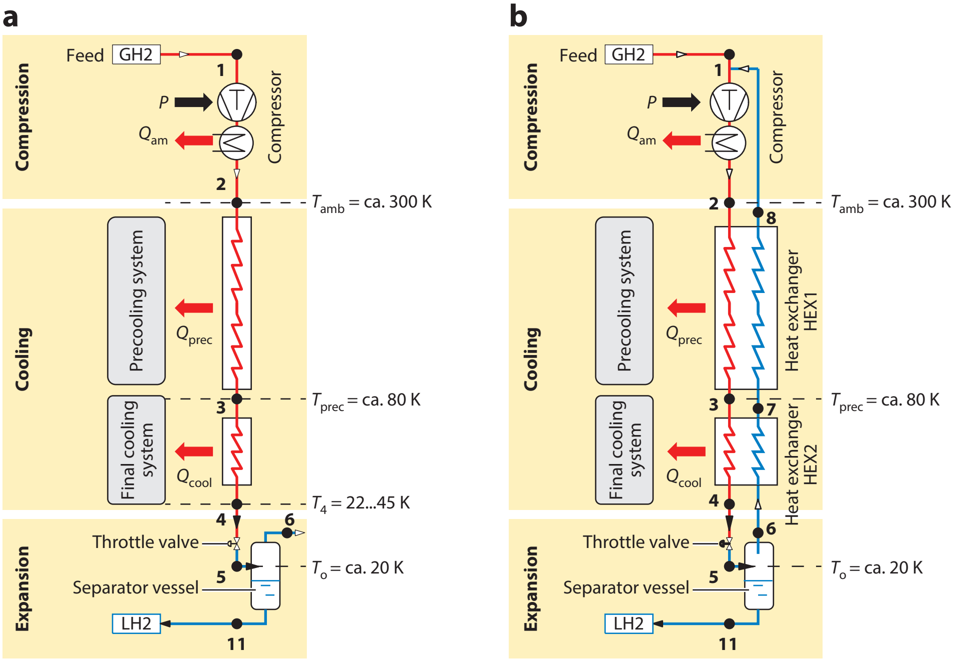

Figure 2

Hydrogen liquefaction: (*a*) general principle, (*b*) utilization of the flash gas cold.

2. Cool (processes 2 → 4 in **Figure 2**) to low temperatures in two steps. (*a*) In the precooling step (process 2 → 3) hydrogen is cooled from ambient temperature $T_{\mathrm{amb}} \approx 300$ K to temperatures close to $T_{\mathrm{prec}} = 80 \pm 15$ K, the so-called liquid nitrogen temperature level. The heat flow Q_{prec} is removed from the hydrogen feed during this step. (*b*) In the final cooling step (process 3 → 4), hydrogen is cooled to temperature $T_4 = 22$–45 K. The heat flow Q_{cool} is removed from the hydrogen feed in this step.
3. Expand (process 4 → 5 in **Figure 2**) the hydrogen from high pressure to low pressure (a pressure slightly above ambient pressure), usually by means of a simple valve, here shown as throttle valve.

Note that the ortho-to-para conversion and the corresponding removal of the conversion heat are integrated parts of the cooling procedure.

During expansion, the cooled, pressurized hydrogen becomes colder and partially liquefies. The liquid hydrogen is separated from the remaining vapor in a simple vessel (called a phase separator). The liquid is collected in this vessel or it can be removed from the liquefier.

Further, the vapor fraction (the so-called flash gas) is heated to temperatures close to ambient temperature in heat exchangers, whereas the valuable cold of this cold vapor stream is used to cool the hydrogen feed stream. This vapor stream is then injected into the feed stream prior to compression as shown in **Figure 2**.

An overview of conceptual designs from the literature is given in References 36 and 41. These concepts are designed for capacities ranging from 50 to 900 tpd LH_2. A classic process consisting of nitrogen precooling and expansion in an expander for the final cooling was analyzed, compared with pure helium and a pure-neon Brayton process, and recommended by Ohira (42). Quack (43) suggested a 170-tpd propane precooled liquefier with a feed compression of 80 bar and a helium-neon mixture Brayton process as the refrigerant for the main cooling; this design includes a virtual compressor with 16 compression stages. Berstad et al. (44) investigated a mixed-refrigerant cycle with a complex and "virtual" nine-component mixture of hydrocarbons, nitrogen, neon, and R14 for precooling. Ohlig & Decker (37) apply a pragmatic approach, using external chillers and a nitrogen expander cycle instead of liquid nitrogen precooling. An advanced process design can be found in References 40 and 45.

Cost Requirements

IDEALHY (41) was used as a benchmark for hydrogen liquefaction in recent years and has an estimated liquefaction cost of €1.72/(kg LH_2). Cost estimates and main assumptions are well described in this study. Therefore, they can be used for establishing a standardized cost and performance baseline to fairly compare different liquefaction concepts. The scope of supply, inefficiencies of main hardware components, gas losses, and auxiliaries [similar to procedures used by the DOE or NETL (46) for coal power plants] are drawbacks of the IDEALHY design. This task is a formal one, but its results would be immensely valuable if it could be implemented in the near future. Cardella et al. (40, 45) compare the energy and liquefaction costs of the IDEALHY and Linde Kryotechnik designs. Unfortunately, the authors describe the cost-estimating procedure schematically.

Power Requirements

According to Peschka (27), the theoretical minimum power required for hydrogen liquefaction is 3.9 kWh/(kg LH_2). With a power demand of 10 to 13 kWh/kg, today's hydrogen liquefaction plants require considerably more energy, corresponding to an overall thermodynamic efficiency of 30% to 40%. For comparison, the most efficient thermodynamic devices known today for converting heat to power are combined cycle power plants, which have a maximum efficiency of approximately 60%. Applying a similar level of plant complexity to a hydrogen liquefier, and hence assuming comparably high efficiency, a future hydrogen liquefier may reach power consumption values of 6.5 kWh/(kg H_2). We recommend this value as a target for long-term development.

A similar value of 6.76 kWh/kg is theoretically achieved for IDEALHY (41), but this value is calculated for precompressed (20-bar) hydrogen at the system inlet. Cardella et al. discuss (40) a more ambitious value of 6 kWh/kg, but for a 25-bar hydrogen feed. This number corresponds to an efficiency of approximately 45%, which is still far from 60%.

Utilizing Cold During Evaporation

Energy-saving potential is available if we consider not only liquefaction, but the entire LH_2-logistic chain. Utilizing the cold and para-to-ortho conversion cold during evaporation and warming of LH_2 could help minimize the amount of energy required. The theoretical maximum exergy content of LH_2 corresponds to the minimum power demand for hydrogen liquefaction, 3.9 kWh/kg. Using today's technology, which has an efficiency rate of 30% to 40%, it is possible to recover 1.2–1.6 kWh/kg. A value of 2.3 kWh/kg is achievable with a system efficiency of close to 60%. These values amount to 20–30% of the energy demand for future hydrogen liquefiers.

Discussion: Liquid Hydrogen

The general impression is that the potential for improvement is well understood. Therefore, somewhat conventional engineering routes concerning process optimization should be pursued in the next decade (short-term and middle-term development), as described in Reference 32. In the long term (from 2030 onward), further development of hardware components is necessary. This concerns primarily rotating equipment such as compressors (which have the largest potential for improvement) and expanders.

CRYO-COMPRESSED HYDROGEN

Cryo-compression technology (47) was launched by BMW (48) in 2012. Ahluwalia et al. (49) present a technoeconomic assessment. Thermodynamically, it can be considered a combination of compression and cooling/liquefaction. All other combinations—such as compression and sorption, cooling/liquefaction and sorption, and compression and cooling/liquefaction and sorption—are possible as well. A combination makes sense only if some disadvantages of individual technologies are eliminated or if advantages are increased. Cryo-compression allows a relative high volumetric density but does not solve the main problem of LH_2 storage (i.e., the availability and cost of infrastructure); therefore, it is as viable as compression and liquefaction.

HYDROGEN STORAGE BY PHYSISORPTION

An extended review of hydrogen storage in nanostructured carbon materials by Yürüm et al. (50) includes materials such as microporous activated carbon, carbon nanotubes/nanohorns, metal-organics frameworks, graphite nanofibers, and graphitic carbon inverse opal. The authors briefly discuss the kinetics aspects as well as theoretical approaches. Experimental approaches are described in greater detail.

The capture of hydrogen in a clathrate hydrate in combination with extremely high pressure was first reported in 1993 (51). In 2004, Florusse et al. (52) reduced the required pressure essentially by adding small amounts of promoting substances such as tetrahydrofuran, predicting approximately 5 wt% and 40 kg/m^3 for achievable hydrogen densities. Veluswamy et al. (53) present an extended overview of clathrate hydrates, including a simplified energy analysis of the overall process and an outlook for further investigations.

Current physisorption technologies are still far from being commercialized. The experimental studies are executed for small samples less than 100 g. The described technologies require high pressure and/or low temperatures as a rule. Therefore, we consider these techniques at their current state of the art not as a separate novel technology but as a type of valuable add-on to current compression and liquefaction methods.

CHEMICAL HYDROGEN STORAGE

Binding to Solids

Metal hydrides are solid materials that enable safe hydrogen storage at moderate temperatures and pressures. Many metal hydrides reach volumetric energy densities that approximate those of liquefied hydrogen. Metal hydrides consist of metal ions that form a lattice structure. Hydrogen adsorbs at a metal center, dissociates to form atomic hydrogen, and is finally inserted into the metal lattice. The total process is exothermic. Thus, when the carrier is loaded, heat must be removed. In contrast, the unloading is endothermic (54, 55).

The metals Li, Be, Na, B, and Al have been considered for hydrogen storage. Mg in particular has been the focus of different research groups. Researchers (56) have attempted to use heavier metals such as Ti or La. $LaNi_5$ and TiFe are of special interest because of their low release temperatures at low pressures (57, 58).

In the context of this review we discuss in detail magnesium hydride, as this material shows an attractive gravimetric hydrogen uptake of approximately 7.6 wt%. Upon uptake of each mole of hydrogen, 75 kJ of heat is released. This heat must be removed during charging; otherwise, equilibrium temperature would be reached quickly and the reverse reaction would set in (59).

To circumvent this limitation, magnesium must be ground to very fine particles with a high surface area. Zaluska et al. (60) first introduced this procedure in 1999 for magnesium nanoparticles. The authors have shown that hydrogen uptake depends mainly on particle size. Reducing particle size from 30 to 1 μm enables full conversion and reduces the loading time to a few hours. Meanwhile, manufacturing magnesium hydride nanoparticles in ball mills is well established (54, 57). Norberg et al. (61) have followed an alternative approach by first synthesizing stabilized nanoparticles from solution and then hydrogenating the particles.

In addition to surface modification, magnesium hydride carriers have been further optimized by additives. Johnson et al. (62) have described activation by adding the complex hydride $LiBH_4$ (lithium borohydride). The authors used a magnesium hydride–to–lithium borohydride ratio of 10:1 and demonstrated that at 300°C the resulting mixture releases hydrogen faster than the ground sample does. A similar approach by Li et al. (63) used TiH_2 as additive. Further, by adding graphite to magnesium hydride, heat removal is improved, such that loading can be carried out at temperatures as low as 200°C (63).

Because metal hydride nanoparticles often degenerate upon contact with air and moisture, practical methods to keep them viable for hydrogen storage under inert conditions are needed. Liu et al. (64) have coated, for example, Pd-Mg nanoparticles with a thin film of Parylene. The film acts like a protective membrane, rejecting oxygen and water from the metal hydride surface. The material was loaded at 50°C and a hydrogen pressure of 1 bar. However, the authors describe somewhat deteriorated release kinetics, probably due to the additional diffusion barrier (64).

In addition to chemical modification, other approaches adapt the storage tank and improve process design to make magnesium hydride–based hydrogen storage more efficient. Garrier et al. (65) have developed a special tank that is filled with metal hydride and a phase change material

(PCM). With this tank, reaction heat generated during hydrogen uptake can be stored by the applied Mg-Zn-PCM material and subsequently made available for endothermic hydrogen release. However, a hydrogen storage density of only 0.32 wt% (0.06 kWh/L) could be achieved with this approach. Delhomme et al. (66) have suggested an alternative approach to provide heat for hydrogen release from magnesium hydride. The authors propose to couple the heat generated by solid oxide fuel cells (SOFCs) into the hydrogen-release step. At the expense of some of the fuel cells' efficiency, hydrogen release from magnesium hydride can indeed be driven in this manner.

For large-scale storage, the sensitivity of metal hydrides is problematic. Moreover, their solid nature in combination with the considerable enthalpy of dehydrogenation creates challenges concerning heat transfer for fast hydrogen release. Whereas heat transfer onto liquids and gases is comparatively simple, uniform heat distribution into a large mass of solid is possible only when complex and expensive devices are used. For small- and very-small-scale applications, however, hydrogen storage in the form of metal hydrides is certainly more appropriate and the potential for economic success is significantly higher.

Pasini et al. (67) studied the requirements of metal hydrides for automobiles, developed from scenario-specific performance requirements, and compared them to requirements for existing metal hydride systems. The authors claim that a suitable metal hydride system would have to provide a minimum storage capacity of 11 wt% at low desorption enthalpies to reach the anticipated system-storage density. At present, no metal hydride comes close to meeting these requirements. Currently, metal hydrides seem to be most promising for supplying power to small consumer electronics, such as mobile charging units for USB devices.

Complex Hydrides

In addition to classic metal hydrides, which form a lattice structure with only one metallic element, are complex hydrides. Complex hydrides typically result from a reaction of boron, nitrogen, or aluminum hydrides with alkali metal hydrides. Typical examples include $LiBH_4$, $NaAlH_4$, and $LiNH_2$. In contrast to metal hydrides, hydrogen binds to complex hydrides via covalent bonding. The alkali ion forms a salt together with the hydride metalate ion (68, 69). Complex hydrides that have boron as the central atom present particularly high storage densities (e.g., $LiBH_4$ has 18.5 wt% and 121 g H_2/L). A survey of different boron hydrides was recently prepared by Ley et al. (69).

With respect to reversibility of hydrogen charging, alanates are particularly promising candidates. Initially, these systems were not considered rechargeable. However, Bogdanović & Schwickardi (70) reloaded the hydride by doping it with titanium, which acts as a catalyst in the lattice for the loading and unloading reactions. In total, $NaAlH_4$ offers a storage density of 7.4 wt%, but only 5.6 wt% is releasable in a reversible manner. Hydrogen loading is achieved at 170°C and at pressures between 120 and 150 bar (71). The stepwise hydrogen release is represented by the following equations:

$$3NaAlH_4 \leftrightharpoons Na_3AlH_6 + 3H_2 + 2Al \qquad 1.$$

$$Na_3AlH_6 \leftrightharpoons 3NaH + Al + \tfrac{3}{2}H_2. \qquad 2.$$

Na_3AlH_6 is formed in the first step, thereby releasing one mole of hydrogen per mole of $NaAlH_4$. This equals to 3.7 wt% of the stored hydrogen with respect to the weight of the initial compound. Another 1.9 wt% of hydrogen is released upon formation of the sodium hydride (71, 72). Doped alanate can be unloaded at significantly lower temperatures than undoped material can. This makes heat integration with fuel cells attractive, as the waste heat of the fuel cells can be used to release hydrogen from the alanate. Ahluwalia (72) studied such an energy supply system for mobile applications. His system reached a specific energy content of 0.59 kWh/kg and a storage density of 0.71 kWh/L.

After examining the specific strengths and weaknesses of hydrogen storage using complex hydrides, we can fairly state that hydrogen release at mild conditions is a strong point of this approach. However, recharging is still linked to considerable effort and costs. Moreover, handling large quantities of hydrides is not compatible with today's energy infrastructure. Therefore, using complex hydrides in a distribution network for hydrogen is probably not practical.

Binding Hydrogen to Gases

Hydrogen can be chemically converted to other chemicals. These chemicals may be other gases or liquids and typically offer advantages with respect to energy-dense storage options.

Ammonia. One example of a gaseous hydrogen storage compound is ammonia, which is formed by nitrogen hydrogenation. The storage cycle involves creating ammonia via the classic Haber-Bosch process (73), storing the ammonia in compressed form, and releasing the hydrogen by catalytic ammonia decomposition (74). Note that ammonia decomposition provides only mixtures of nitrogen and hydrogen. To produce clean hydrogen from ammonia, additional purification steps are necessary. Ammonia offers a storage capacity of 17.5 wt% hydrogen. Ammonia production is exothermic (−60.5 kJ/mol H_2), and ammonia decomposition consumes the same amount of heat. Ammonia is a toxic gas with low exposure limits, which is a major disadvantage of this hydrogen storage method, at least for the smaller, decentralized applications in which untrained people could directly contact the so-stored hydrogen. For long-range and large-scale transportation of hydrogen (e.g., shipping hydropower from Canada to Europe), ammonia could be a promising option in the future.

Methane. An alternative gaseous product for hydrogen storage and transportation is methane. Methane is the simplest alkane and the major component of natural gas. Having four hydrogen atoms per carbon atom, it is the carbon-based carrier with the highest storage capacity (25 wt%). One intriguing idea is to use the existing storage and pipeline capacity for natural gas to handle hydrogen after it is transformed to methane. For example, Germany's natural gas storage capacity is 24.5 billion Nm^3 (75, 76); compare that to the country's natural gas consumption in 2013: 97.9 billion Nm^3. This difference demonstrates that the transformation of hydrogen to methane makes the significant, existing volume of storage available for hydrogen storage. Note that direct feeding of hydrogen into the natural gas grid is difficult because at no location in the grid should certain maximum amounts be exceeded. Typical maximum amounts are 2–5% (75).

The reaction of hydrogen with CO_2, the so-called Sabatier reaction, was discovered in 1904 (77). Hydrogen reacts with CO_2, yielding water, methane, and heat. The reaction typically operates between 250°C and 400°C. Effective heat removal is important for managing the strongly exothermic reaction.

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \qquad \Delta H^0 = -165\,\text{kJ/mol}. \tag{3}$$

To produce methane, high-quality CO_2 has to be supplied. This can be achieved in power plants, for instance, by absorption of CO_2 from flue gas. However, capturing CO_2 from flue gas is associated with a large energetic effort (78). Therefore, the use of point sources that deliver relatively pure CO_2, e.g., from cement or ammonia production, is considered. Note that these CO_2 sources do not fulfill the requirements of decentralized or small-scale hydrogen storage. In the course of a total transition toward a renewable energy economy, CO_2 has to originate from renewable sources such as biomass or it has to be separated directly from air (79–81). For example, Mohseni et al. (82) have hydrogenated biogas-derived CO_2 after the necessary CO_2 purification. Another method is to combine methane synthesis with high-temperature electrolysis. Water evaporation and compensation of thermal losses during electrolysis result from the exothermicity of methane synthesis, yielding an overall power-to-methane efficiency of up to 85% (83).

However, there are limits to using methane for hydrogen storage. First, hydrogen from electrolysis, which is expensive (typical production costs are approximately €3/kg H_2) (84), is converted to a cheap commodity energy carrier. Under the unrealistic assumption of a 100% effective, stoichiometric conversion of hydrogen to methane, 1 kg of hydrogen (500 mol) would convert to 2 kg of methane (125 mol). With a lower heating value of 15.5 kWh per kilogram of methane and an assumed heat value of €0.04 per kilowatt hour, the resulting methane would have a value of €0.62 from the kilogram of hydrogen. This simplified calculation does not take into account the cost of CO_2, operating costs, or any depreciation of the plant. Some positive contributions will result from export of heat from methane synthesis. Note that on the level of this rough estimation, the addition of hydrogen to the gas grid is slightly more economical. Still, hydrogen is sold at the heating-value price of methane. One kilogram of hydrogen has a lower heating value, 33.3 kWh, which would result in an economic value of €1.33. In today's market scenarios, this still costs significantly less than producing hydrogen from electrolysis.

A second important limitation of methane as a hydrogen storage system is that it is difficult and costly to recover hydrogen from methane. In fact, the complete methane-reforming process chain (i.e., reforming, water-gas-shift reaction, CO_2 removal, CO hydrogenation or selective oxidation, pressure swing absorption) has to be established to recover good-quality hydrogen from methane. This is why in all real scenarios where hydrogen is stored in the form of methane no reconversion to hydrogen is considered but a direct energetic use of methane is envisaged (85). Strictly speaking, methane should therefore not be regarded as a hydrogen storage system but rather as an alternative energy carrier produced from hydrogen.

Methanol. Having a storage capacity of 12.5 wt% and a volumetric energy density of 3.3 kWh/L, methanol is another hydrogen storage compound and energy carrier. Using CO_2 as a hydrogen-lean storage molecule, its hydrogenation over copper–zinc oxide catalysts leads to methanol production with attractive reaction rates. Note that the reaction is limited by thermodynamic constraints, so that full conversion of CO_2 to methanol is not possible under realistic reaction conditions (86). In contrast to the aforementioned hydrogen-rich carriers, methanol is liquid at ambient conditions, thus enabling one kind of power-to-liquid technology for energy storage. Methanol can be directly used as a fuel in combustion engines. Higher efficiencies are expected, however, if a direct methanol fuel cell (DMFC) is applied (87). The use of DMFCs has reached commercial level on a small scale. Still, a number of research groups around the world are addressing the challenge of leaching methanol across the membrane. Methanol crossover affects the efficiency of the fuel cell as well as the long-term stability by swelling of the membrane. Compared with classic hydrogen PEM (polymer electrolyte membrane) fuel cells, the DMFC catalyst is less active (88–92).

Methanol is an attractive compound for hydrogen storage not only because direct applications are accessible (e.g., it can be used as fuel in fuel cells or as a source of C1 in chemical processes) but also because hydrogen can be liberated from methanol in a fairly straightforward manner by methanol steam reforming (93). A key parameter in methanol catalysis is to obtain the hydrogen in an almost completely CO-free manner to avoid the necessity of CO hydrogenation or partial CO oxidation prior to its use, e.g., in hydrogen vehicles (94).

Formic acid production. In a similar way, regenerative hydrogen can also be used to produce formic acid (FA) and formaldehyde derivatives. Although FA is caustic and corrosive, it is nontoxic and even registered as a food additive. Its gravimetric hydrogen storage capacity is only 4.4 wt%, but because of its relatively high density (1.22 g/cm^3), its volumetric hydrogen storage is 53.7 g H_2/L or 1.79 kWh of bound hydrogen (based on LHV) per liter.

FA can be readily reconverted to hydrogen and CO_2 at low temperatures (below 100°C) in a catalytic process. Boddien et al. (95, 96) have reported homogeneously catalyzed FA decomposition systems operating at room temperature. Under these conditions the released gas mixture is free of carbon monoxide and is ready for direct application in a PEM fuel cell (89, 97, 98). The equimolar mixture of CO_2 and hydrogen that is released from catalytic FA decomposition has to be separated to obtain pure hydrogen.

However, whereas hydrogen produced from FA is accessible, CO_2 hydrogenation to FA is not as straightforward. The thermodynamics of the CO_2 hydrogenation reaction to FA is much less favorable than the formation of methanol. Therefore, multistep processes are required to produce pure FA from CO_2, and bases, auxiliary solvents [e.g., dimethyl sulfoxide (99)], and special reaction media [e.g., ionic liquids (100)] are needed to produce FA at relevant efficiencies. Because of these complications, Schmidt et al. (101) considered FA to be a niche application. A further survey of processes and approaches to producing and decomposing FA is given by Yadav et al. (102). From the available information we conclude that FA may become a hydrogen storage system for small, off-grid energy applications. A new fueling infrastructure that can withstand the corrosive nature of FA would be necessary for mobile applications. Such a huge infrastructural investment for FA-powered vehicles is highly unlikely at the present state of the technology.

Fischer-Tropsch syncrude production. Longer-chain hydrocarbons can be produced from CO_2 and hydrogen by Fischer-Tropsch (FT) synthesis. The necessary reaction sequence essentially consists of three reactions (103): (*a*) The reverse water-gas shift reaction converts CO_2 and hydrogen to CO and water in an endothermic high-temperature process; (*b*) the actual FT reaction (reaction of CO and H_2) is a surface polymerization reaction of catalyst-bound methylene groups leading to a product distribution determined by the probability of chain growth; and (*c*) mild hydrocracking of waxes adjusts the product chain lengths. With a typical Co-based FT catalyst, typical reaction conditions of the actual FT reaction are 200–250°C and 10–40 bar syngas. The reaction is carried out in multitubular or slurry phase reactors (73).

FT synthesis converts hydrogen into a product mixture that has some similarity to crude oil (syncrude). Further refining and processing can provide finished products similar to existing fuels, such that the complete storage and transport infrastructure used for today's fuels becomes available for hydrogen transport and storage. With that, the FT method for hydrogen storage in principle gives access to applications ranging from strategic storage options to the mobility sector.

Drawbacks are similar to those mentioned above. Syncrude competes with crude oil–based hydrocarbon cuts and has a relatively low value in today's market. In fact, hydrogen from electrolysis, although expensive, is converted to a relatively cheap product by a complex process. Moreover, the FT synthesis reaction has not yet been optimized for intermittent and dynamic operation. Thus, a steady source of CO_2 and hydrogen is needed to operate the described sequence in a steady-state mode. The lack of dynamic operation in current FT synthesis processes makes the direct link to hydrogen derived from fluctuating, renewable electricity questionable at the very least. Albert et al. (104) recently suggested a solution to the latter problem. The authors used biomass-derived FA as a carbon source in FT synthesis. Depending on whether renewable hydrogen is available, the FT unit operates on FA-based CO and electrolysis hydrogen or on pure FA that can be thermally converted to CO (and water) and catalytically converted to hydrogen (and CO_2).

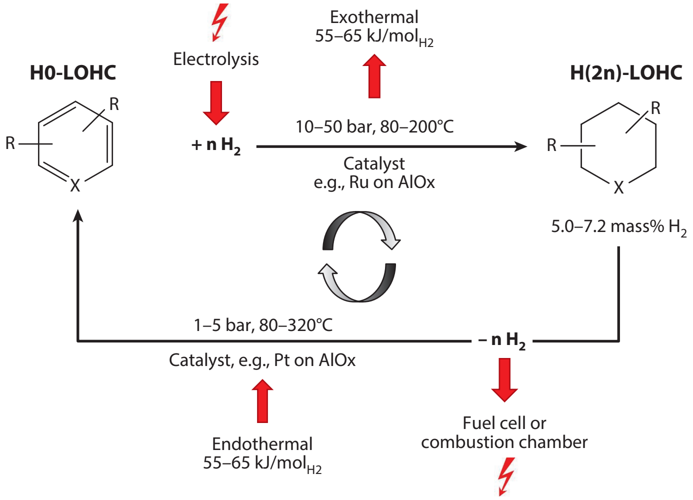

Figure 3

Reversible LOHC cycle of an aromatic or heteroaromatic hydrogen-lean LOHC compound. Abbreviation: LOHC, liquid organic hydrogen carrier.

Binding Hydrogen to Liquid Organic Hydrogen Carrier Systems

Hydrogen storage and transport in the form of liquid organic hydrogen carriers (LOHCs) is different from the aforementioned technologies because a liquid rather than a gas is used as the hydrogen-lean carrier. The advantage of using LOHC systems is that, after the hydrogen-release step and suitable condensation, high-quality pure hydrogen can be obtained. Moreover, the hydrogen-lean form of the storage system as well as the hydrogen-rich form can be handled in the infrastructure for today's fuels. Thus, the extraction of compounds from the atmosphere or exhaust gas streams and the release of compounds into the atmosphere are entirely avoided in hydrogen storage.

As the name suggests, LOHC systems are organic compounds that are liquid at typical ambient storage conditions. These systems always consist of pairs of molecules, at least one hydrogen-lean compound and one hydrogen-rich compound. To store hydrogen, the hydrogen-lean compound is contacted with hydrogen in the presence of a suitable heterogeneous catalyst and thereby converted exothermally to the hydrogen-rich compound of the LOHC system (**Figure 3**). At times or places of hydrogen or energy need, the hydrogen-rich form releases hydrogen in the presence of a suitable dehydrogenation catalyst via an endothermic reaction. All compounds of a suitable LOHC system are selected to ensure perfect compatibility with the existing infrastructure for fuels. Therefore, suitable LOHC systems should be characterized by a wide liquid range (low melting point, high boiling point). Other requirements for suitable LOHC systems are reversible thermodynamics and fast kinetics (in almost perfect selectivity) of the hydrogenation and dehydrogenation reactions and favorable toxicity and ecotoxicity properties (105).

The concept of LOHC-based hydrogen storage is based on reversible hydrogenation and dehydrogenation of double bonds (106, 107). The position of the hydrogenation/dehydrogenation equilibrium is therefore important when selecting the correct storage compounds and suitable reaction conditions for the charging and release processes. Using thermodynamic calculations, Müller et al. (108) studied the suitability of various material systems as LOHC systems. An optimum reaction enthalpy of approximately 40 kJ per mole of hydrogen has been derived from their calculations. At this value, the reaction heat is easy to handle and no thermodynamic limitations of note exist.

Historically, research activities toward hydrogen storage via reversible hydrogenation/dehydrogenation cycles date back to the 1980s. The first oil crises prompted researchers from the Paul Scherrer Institute in Switzerland to investigate the use of nuclear power for water electrolysis, hydrogen storage, and onboard hydrogen generation for fuel cell vehicles. The advantages of LOHC systems versus battery technologies (e.g., higher energy storage capacities, shorter refueling times) were recognized early on (109, 110).

Research on LOHC systems has substantially increased since 2010. This is due to the growing importance of renewable and fluctuating energy production in many countries. Consequently, a new focus of hydrogen storage research has been decentralized energy storage as well as the transportation of large amounts of hydrogen over long distances (111, 112). Still, attempts have been made to apply LOHC technology to the mobility sector (113). Technoeconomic analyses of LOHC technology have been recently published (114, 115). Pradhan et al. (115) compared, for example, the economic efficiency and the CO_2 balance of LOHC systems. The authors compared hydrogen supply via LOHC using existing fossil fuel logistics with hydrogen pipeline transport. They concluded that transporting hydrogen in the form of LOHCs with conventional trucks is more economical than hydrogen logistics via new pipelines. Additionally, the authors state that the entire LOHC process chain, including diesel consumption for LOHC transport, emits only one-third of the CO_2 emitted when using fossil fuels. The Chiyoda Corporation (Japan) is about to complete a pilot plant for large-scale hydrogenation and dehydrogenation of LOHCs within the next few years. After successful demonstration, the plant should be used to develop global hydrogen and energy logistics based on the LOHC concept (116).

A range of different LOHC systems have been proposed thus far in the literature. Their properties, their availability, and their toxicities/ecotoxicities indicate these systems are somewhat suitable for large- or small-scale hydrogen storage applications. Therefore, we present the most relevant LOHC systems and their characteristic differences to guide system selection for future applications at different scales. Additional information concerning the use of homocyclic LOHC systems is provided by Shukla et al. (117).

***N*-ethylcarbazole/perhydro-*N*-ethylcarbazole.** Nitrogen-containing aromatics are promising materials for use in LOHC systems. When a nitrogen atom is inserted into the aromatic systems, the reaction enthalpy and consequently the reaction temperature for hydrogen release are decreased (118–120). Depending on the position of nitrogen within the ring or ring system, different electronic effects occur. Clot et al. (121) and Cui et al. (122) have investigated the effect of different nitrogen atom positions. According to Pez et al. (123), *N*-ethylcarbazole can be dehydrogenated at temperatures as low as 120°C. Other alternatives, such as indole derivatives (e.g., 3-methylindole), allow dehydrogenation at similarly low temperatures but can suffer from side reactions and consequently low selectivities (124).

Supplemental Material

As shown in **Supplemental Table 4** (data taken from Reference 125), few details are available for perhydro-*N*-ethylcarbazole (H12-NEC), the hydrogen-rich form of the system. One reason is that H12-NEC is a mixture of isomers and its composition depends on the hydrogenation catalyst and conditions. Another reason is that H12-NEC thus far has no industrial use. The key advantage of the NEC/H12-NEC system compared with all pure hydrocarbon LOHC systems is its low hydrogenation enthalpy, which ranges between 50 and 55 kJ per mole of hydrogen. This value is 25–30% lower than the hydrogenation enthalpy for pure hydrocarbon LOHC systems (108, 120, 123). However, a number of problematic aspects are linked to the NEC/H12-NEC LOHC system: (*a*) The current technical availability of NEC is only approximately 10,000 tons/year (the compound is isolated from coal tar by distillation), such that the quality of technical samples varies and costs are high, typically around €40/kg; (*b*) pure NEC is a solid with a melting point of 68°C, which either limits the degree of dehydrogenation and thus the hydrogen capacity or makes heated tanks necessary; (*c*) thermal stability of NEC is limited, such that at temperatures above 270°C there are clear indications for dealkylation reactions even with optimized catalyst systems; and (*d*) toxicity and ecotoxicity of NEC and H12-NEC are not well investigated. The few indications that are available suggest that the different compounds and intermediates of the storage cycles NEC, H8-NEC, and H12-NEC behave differently in persistence, bioaccumulation, and toxicity tests. Much more work is necessary for characterization (126). Preferred applications of the NEC/H12-NEC LOHC system include small-scale dynamic applications with low LOHC hold-up that constantly remain at elevated temperatures. For large- and medium-scale storage the carrier price is too high and the storage capacity is too low. For onboard dehydrogenation in mobile applications the solid nature of pure NEC is a relevant problem.

Toluene/methylcyclohexane. The toluene/methylcyclohexane LOHC system is the most studied and most frequently applied LOHC system. With the exception of benzene (which is not feasible because it is carcinogenic), toluene is the structurally simplest aromatic LOHC compound. The toluene/methylcyclohexane system can store up to 6.1 wt% of hydrogen. With the associated density of methylcyclohexane (see **Supplemental Table 5** for details), this value corresponds to a volumetric storage density of 1.55 kWh/L. To fully dehydrogenate methylcyclohexane, 205 kJ of energy per mole of methylcyclohexane are needed, corresponding to a value of 68.3 kJ per mole of hydrogen (127, 128). Owing to this relatively high value, the dehydrogenation reaction has to occur at elevated temperatures to shift the equilibrium fully to the product side (128). According to the literature, a reaction temperature of 320°C is required for a methylcyclohexane-to-toluene conversion rate of 99% at a hydrogen partial pressure of 1 bar (129). At this temperature, all reactants and products are gaseous. To separate the formed hydrogen from organic vapor, condensation at low temperature is required.

Supplemental Material

Other properties of the toluene/methylcyclohexane system are summarized in **Supplemental Table 5**. The excellent technical availability and the cheap price of toluene are the strong points of the toluene/methylcyclohexane LOHC system. Hydrogen capacity is good, but volumetric storage density is harmed by the low density of methylcyclohexane. Toxicity is not optimal, but today large quantities of toluene and methylcyclohexane are handled in fuels. Owing to high hydrogenation enthalpy and high temperatures, dynamic and flexible applications are less suitable for this system but large-scale storage and transport are relatively attractive, as demonstrated by the Chiyoda Corporation hydrogen transport project in Japan (116).

Naphthalene/decalin. The pair naphthalene/decalin has also been investigated as a hydrogen carrier (130). By means of hydrogenation of naphthalene, up to 7.3 wt% hydrogen can be stored. Polycyclic aromatic compounds such as naphthalene are particularly suited as hydrogen carriers because of their high hydrogen storage capacity. However, naphthalene, one of the simplest polycyclic aromatics, is a solid at room temperature. Different strategies can be applied to overcome the melting point problem, such as mixing with a lower-melting LOHC or with solvents. Another option is to limit the degree of dehydrogenation to avoid forming pure naphthalene. However, all these options would negatively influence the overall storage capacity. Both the hydrogen-rich and the hydrogen-lean forms of the naphthalene/decalin LOHC system are significantly more toxic than diesel fuel and even more toxic than the methylcyclohexane and *N*-ethylcarbazole systems. **Supplemental Table 6** summarizes the relevant properties of the system. Although some aspects of this system are critical (e.g., melting point, toxicology), the high hydrogen storage capacity is a strong point that could most likely be used in large-scale storage and transportation scenarios where containment can be assured by expert handling and dedicated infrastructures. Still, whether the problematic nature of the compounds would justify such large-scale applications in light of better alternatives is doubtful (see below).

Benzyltoluene/perhydro-benzyltoluene and dibenzyltoluene/perhydro-dibenzyltoluene. The use of commercial heat transfer oils as LOHC compounds has been recently proposed (125). This approach has a number of natural advantages, as heat transfer oils are technically available substances with well-characterized physicochemical properties and toxicity/ecotoxicity. Moreover, these substances are optimized for low melting points (typically by applying mixtures of isomers), thermal robustness, and excellent high-temperature safety properties (e.g., flash point, ignition point). Among the commercial heat transfer oils, the LOHC pairs benzyltoluene/perhydro-benzyltoluene and dibenzyltoluene/perhydro-dibenzyltoluene, known under the trade names Marlotherm LH and Marlotherm SH, respectively, are particularly promising. Relevant data for both systems are summarized in **Supplemental Tables 7** and **8** (data taken from Reference 131).

Supplemental Material

As seen from **Supplemental Tables 7** and **8**, the two heat transfer fluids exhibit excellent physical properties for their application as LOHCs. Both dibenzyltoluene and benzyltoluene can take up 6.2 wt% of hydrogen. In particular, the wide liquid range of these isomer mixtures makes them attractive hydrogen carriers. Unlike NEC or naphthalene, no additives or solvents have to be added to keep the storage medium liquid and the discharge is not limited by crystallization. Only 65 kJ/mol of heat per mole of hydrogen are required to release hydrogen from the respective perhydro compounds (132). This heat is somewhat lower than the enthalpy for methylcyclohexane dehydrogenation to toluene (68 kJ/mol) (108). Another important advantage over the toluene/methylcyclohexane system arises from the higher density of the perhydro compound (910 g/L versus 770 g/L). This leads to a volumetric storage density that is 20% higher despite the chemically similar nature of these LOHC systems.

The hydrogen-lean forms, benzyltoluene and dibenzyltoluene, are well characterized with regard to toxicology, which is not surprising given their longstanding industrial use as high-temperature heat transfer fluids. These substances are described as nontoxic, nonmutagenic, and noncarcinogenic, which represents a potential labeling advantage relative to diesel and Otto fuel (125, 133). The registration process for perhydro-dibenzyltoluene has recently been completed and confirms that the hydrogen-rich carrier also falls under the same, favorable category with respect to toxicology (**http://www.hydrogenious.net/en/home/**). Benzyltoluene or dibenzyltoluene costs between €2 and €8/kg depending on the quantity of purchase, quality, and the actual price of oil.

The hydrogenation of dibenzyltoluene and benzyltoluene isomers for the purpose of hydrogen storage was first described by Brückner et al. in 2014 (125). Both LOHCs can be hydrogenated at 80–180°C and 20–50 bar hydrogen using a Ru catalyst, for example. Catalytic dehydrogenation is promoted by Pt/alumina catalysts at temperatures above 260°C. In long-term applications, temperatures above 330°C should be avoided with today's commercial Pt/alumina catalysts to prevent decomposition rates above 0.05% per hydrogenation/dehydrogenation cycle. Decomposition can lead to the formation of both light and heavy by-products. Both by-products can be removed in distillative cleaning processes that could be applied to clean up the LOHC carrier after multiple charging and discharging cycles.

Comparative evaluation of different LOHC systems. Depending on the application scenario, various properties of LOHC systems may be particularly relevant. **Figure 4** compares various hydrogen-lean forms of LOHC systems and their relevant properties of reaction enthalpy, boiling

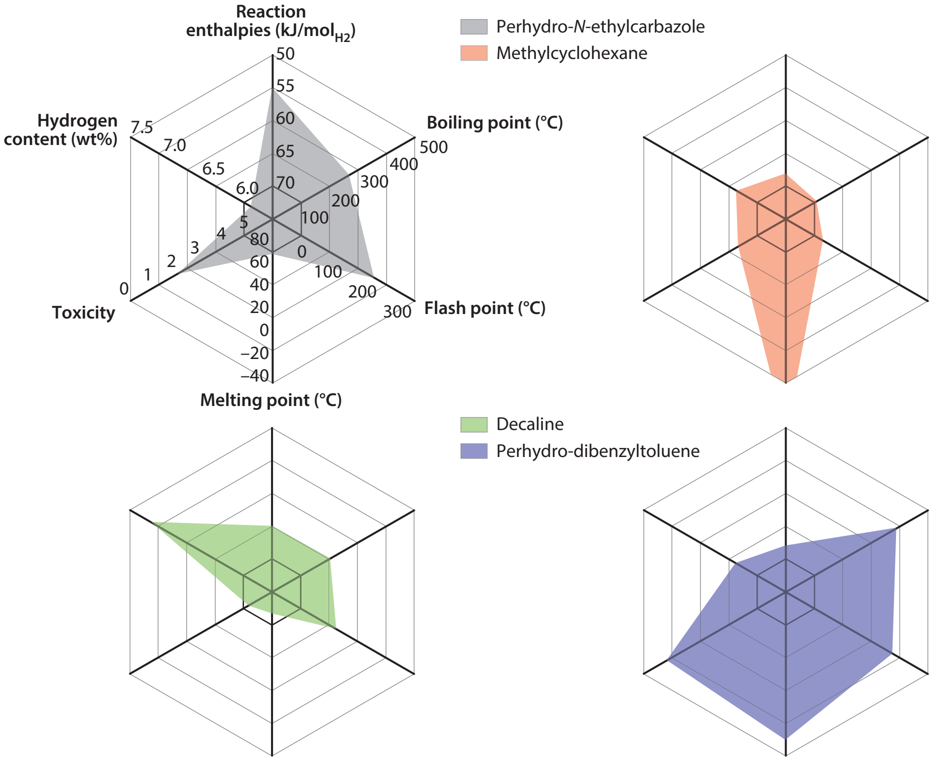

Figure 4

Compilation of important material properties for the hydrogen-lean forms of various liquid organic hydrogen carrier systems: perhydro-*N*-ethylcarbazole, methylcyclohexane, decaline, and perhydro-dibenzyltoluene.

point, flash point, melting point, toxicity, and hydrogen capacity. Toxicity was evaluated in a grading system ranging from 1 (very good, better than diesel fuel) to 6 (worse than petrol). A high boiling point is beneficial, whereas a low boiling point is not. This is due to the related effort required for producing high-purity hydrogen. For safety reasons, the flashpoint is included as an additional criterion in the assessment of the carrier molecules. A low flash point is a risk, considering the hot surfaces in the conversion units. The assessment is based on the available literature, which has been given in the respective sections above. **Figure 4** highlights the great variety of property profiles through the use of different LOHC structures. In addition, design strategies for the development of new LOHC materials can be derived from the given comparison.

From a current standpoint, dibenzyltoluene and benzyltoluene are particularly suitable for large- and medium-scale storage applications because they are cheap, robust, and available at a large scale. Even larger scales can be made available, as these compounds are easily accessible from toluene, which is a major component of Otto fuel. Should society decide to move away from mobility based on combustion engines, large quantities of toluene would be available. For highly dynamic applications, LOHC systems with lower dehydrogenation heat are in principle attractive but these systems should not compromise on aspects such as liquid range, stability, hydrogen capacity, and economics. Therefore, *N*-ethyl carbazole is more suitable for dynamic applications but probably not a suitable option for onboard hydrogen generation for cars. In contrast, dibenzyltoluene and benzyltoluene LOHC systems would be suitable for larger vehicles if proper heat or system integration between hydrogen release and fuel cell operation were successfully accomplished. The first attempts to realize direct LOHC fuel cell concepts are promising and attractive in this respect.

CONCLUSION

Our review is based on the assumption that hydrogen storage systems are the most attractive methods to store energy at the gigawatt-hour and terawatt-hour scales in a future energy scenario that is somewhat free of CO_2 emissions. Moreover, the stored hydrogen has to be distributed to the customer and its consumption should satisfy all means of energy need: mobility, heat, and even industrial production. We have compared the range of available hydrogen storage technologies and their potential relevance for future energy systems dealing with large shares of fluctuating, renewable input. We have described technologies of different readiness and highlighted their relevant and discriminating aspects.

Step-changing improvements and radical innovation are not expected to occur in state-of-the-art technologies for more than forty years, as in the case of physical hydrogen storage. Here, evolutionary technology development is remarkable but is often dominated by the conflict between higher efficiencies and higher specific investment.

In contrast, hydrogen storage in the form of organic liquids and power-to-X technologies is significantly less mature; therefore, a disruptive development may occur. Although some of the key steps (methane or methanol synthesis, aromatic hydrogenation) are well known in the chemical industry, the adaption of the relevant reaction sequences to hydrogen production, from fluctuating electrolysis to the special storage molecules of highest technical interest (CO_2, LOHC), still requires significant development work. Moreover, cost estimates for these technologies are difficult to predict because we are still dealing with prototypes and first-of-its-kind commercial demonstrations. So all cost estimates come with significant uncertainties. In this light, the summaries given for these technologies in **Supplemental Table 9** are based on technical potential rather than on the actual state of the art.

Supplemental Material

Industrialized societies aiming for an energy turnaround in the upcoming years will face significant challenges. Obvious concerns for such a radical change arise from the huge investment required, mostly in hardware such as compressor stations and cryogenic tank systems as well as in dedicated safety equipment and corresponding training. It may work well for industrial consumers, especially if technoeconomics are positive.

But physical hydrogen storage may create significant hurdles for private consumers. The general public is untrained and unfamiliar with handling gas at high pressures or low temperatures. Without additional investment in public training and some persuasion, it seems difficult to create a broad public readiness to use compressed hydrogen or cryogenic hydrogen in many areas of daily life.

The infrastructure for LOHC systems seems to be more convenient for unexperienced private persons. Therefore, the transition to a sustainable-hydrogen-based energy system may be a smooth one, especially because today's existing infrastructure for conventional fuel logistics (tank ships, road tankers, rail tankers, filling stations) is elaborate and accepted.

In conclusion, we stress two aspects for future work in hydrogen storage and logistics that should be emphasized in scientific and technological discussions. First, although comparisons of different options for hydrogen storage and logistics in a fully rolled-out hydrogen economy are appropriate and useful, exactly how we achieve such an economy is often neglected. Some technologies that are attractive for a fully hydrogen-based energy system may not be the best or most suitable for unveiling a reasonably cost-efficient technology. Thus, we will probably need some hydrogen technologies to catalyze transition and some others that may become relevant and even dominant in a largely transformed energy system.

Second, although CO_2 emission is to a large extent a problem caused by industrialized countries, it is important that technological solutions also be transferred to third-world countries to support sustainable development there. The only infrastructural prerequisite for the transport of hydrogen bound to organic liquids is suitable roads, whereas operating sophisticated compressor equipment, handling liquid hydrogen, or developing pipelines is likely impracticable for many less-developed countries. Because many third-world countries have a huge potential for renewable energy (lots of sunshine and favorable wind conditions), offering safe, efficient, and simple hydrogen storage technologies to these countries is a reasonable goal for future research and development in both academia and industry.

DISCLOSURE STATEMENT

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