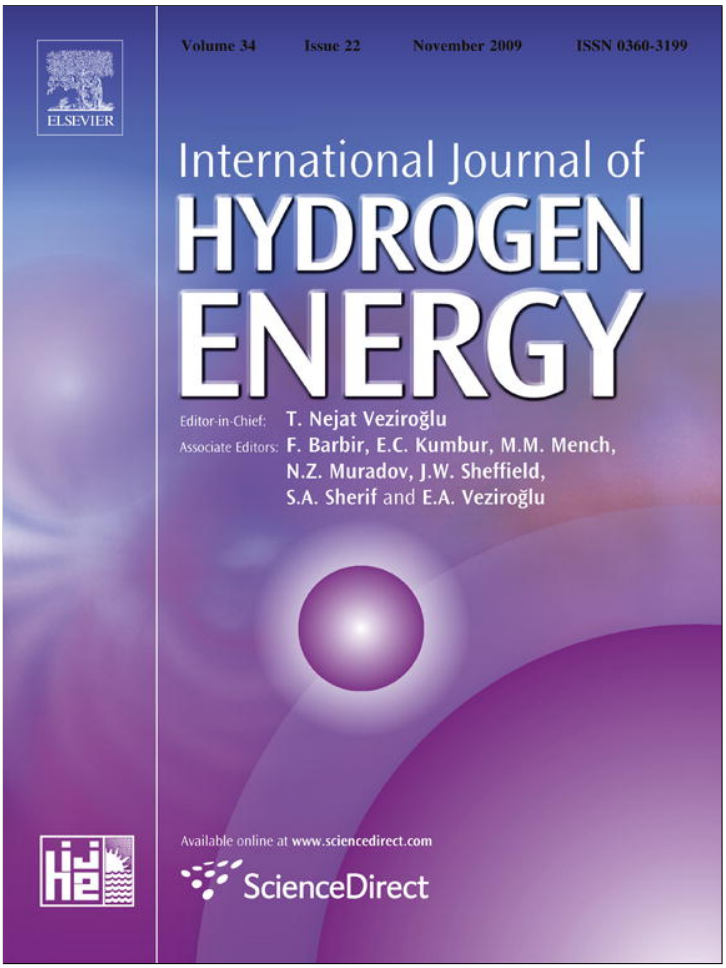

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Comparison of hydrogen hydrates with existing hydrogen storage technologies: Energetic and economic evaluations

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ABSTRACT

With the development of the hydrogen economy and FCV (fuel cell vehicles), the manner of storing and delivering large quantities of hydrogen arises as a major problem, and increasing research efforts are being targeted to solve this technological issue. Nowadays several hydrogen storage methodologies are available. Technologies are being developed and/or engineered other than the classical compression and liquefaction of hydrogen, which are based on the chemical (metal hydrides, ammonia) and physical (e.g., carbon nanotubes) adsorption of H_2. Also, a novel technology is in progress, which is based on clathrate hydrates of hydrogen. The object of the present work is to evaluate the features and performances of those storing systems with the aim to determine the best available technology throughout the "hydrogen chain". For each one of the storage solutions presented, we have compared key parameters such as: interaction energy between hydrogen and support, storage capacity, specific energy consumption (SEC). By this work, it is demonstrated that a technology based on clathrate hydrates of hydrogen, while far from being optimized, may be competitive with the other approaches.

1. Introduction

Hydrogen storage is a main problem hindering the diffusion of the "Hydrogen Economy". The classical storage methods based on compression and liquefaction are an established and efficient approach, but involve huge problems of safety and the associated costs of compression work and cooling are non negligible. On the other hand, several alternative approaches are currently under investigation. The aim of hydrogen storage technologies is to reduce the volume that hydrogen naturally occupies in its thermodynamically stable state under ambient conditions, i.e., as a gas. Hydrogen gas shows a very low density (0.089 kg/m^3), which means that only a little mass is contained within a large volume of gas. However, hydrogen shows a very high energy content by weight, thus being interesting as a fuel or energy carrier. Therefore, it is required to transform hydrogen into an easily handled form, e.g., by compression or liquefaction, or by trapping through interaction with other compounds, by means of strong or weak interactions, such as covalent bonds or van der Waals interactions.

The efficiency of a particular technology of hydrogen storage is not merely a matter of mass or volume capacity, but

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also of *net stored energy*. Indeed, energy required to transform hydrogen from the gaseous state to storage conditions, and then the energy required to recover the same from the storage media is a critical issue, which assumes practical implications in particular for metal hydrides. For compressing hydrogen, energy as mechanical work is required; for liquefying the same, on the other hand, cooling energy and compression work are required, plus a certain energy to keep hydrogen under proper thermodynamic conditions in order to maintain the liquid state. When hydrogen is, instead, stored onto (or into) a support, its stability will be higher the stronger its interaction with the support. In that case, a remarkable amount of energy will be required to recover H_2 from the support.

From these considerations, it is clear how the development of a novel hydrogen storage technology is not only a matter of storage capacity but also, and in some cases mainly, a problem of energy efficiency, because what we are storing *is substantially energy*, and one should be careful to avoid systems with an overall *negative energy* balance.

By considering a proper combination between stability of the storage system and easiness of hydrogen recovery, it is possible to estimate that an adequate interaction of hydrogen with its storage support should be of about ca. 20 kcal/mol, namely 40,000 kJ/kg of hydrogen. [1] That is an intermediate value between the interaction energy of a covalent bond, typically of about several tens of kcal/mol, and the interaction energy of a weak bond, typically about only a few kcal/mol. Energy efficiency in hydrogen storage and transportation is critical for various reasons. First, in the current demand for energy-efficient systems, [2] storage technologies that waste a remarkable amount of the energy they carry should be replaced with improved technologies, or at least confined to niche applications where other technologies cannot be applied. Secondly, wasting hydrogen is not merely wasting its energy content: hydrogen is not an energy source, i.e., it cannot be mined, but must be produced, e.g., by consuming conventional energy sources. Currently, hydrogen is mainly produced by fossil fuel gasification with an energy recovery efficiency of about 40–60%. This means that if 1 kJ of hydrogen is wasted, roughly 2 kJ of fossil fuel are wasted overall [3].

Third, wasting energy should also be avoided because of Greenhouse Gas (GHG) emissions, being fossil energy mainly based on carbon. Carbon dioxide emissions are an unavoidable and undesired end product, thus technologies that show a lower efficiency contribute to GHG emissions to a higher level than more efficient ones [4].

In the present work, various hydrogen storage systems for which a comprehensive physico-chemical database is available, have been compared in order to give a homogeneous comparison among the various approaches. As classical and well established systems, we chose compression standards at 200 bar into steel cylinders, and compression standards at 350 and 700 bar into the novel, carbon fiber-jacketed aluminum cylinders [5]. Moreover, hydrogen liquefaction has also been analyzed as an established technology [6]. For the class of storage systems based on a ''chemisorption'' principle, where a hydrogen molecule bond is broken to form new bonds with the storage support, metal hydrides have been analyzed using MgH_2 as representative of High Temperature Hydrides (HTH) [7] and $LaNi_5H_6$ as representative of Low Temperature Hydrides (LTH) [8]. $NaAlH_4$, exemplifying a relatively novel class of aluminum alloy-based hydrides (Alanates) [9] has also been analyzed. Single Walled Carbon Nanotubes (SWNTs) were also considered as representative of ''physisorption'' based systems, where hydrogen interacts with the support at the molecular level through weak interactions [10]. Particular attention has been paid to ammonia as a storage system; this because even though it is considered as a promising hydrogen storage system, it also offers the advantage of having a well established production technology [11].

All these systems have been compared with hydrogen clathrate hydrates, in order to evaluate whether the latter can be competitive as alternative hydrogen storage media. In order to carry out this analysis, first the thermodynamic conditions of the storage systems, with hydrogen stored therein, have been identified, and then the thermodynamic conditions under which the processes of storage and release take place have been evaluated. As a second step, the fundamental data have been collected, such as system gravity, theoretical storage capacity, specific heat, latent heat, etc. Then, the interaction energy between hydrogen and support has been obtained in order to evaluate how a system compares with the above mentioned ''optimum'' value of roughly 40,000 kJ/kg. Moreover, the processes required for practically carrying out hydrogen storage and release have been devised for each system tested, namely if the process requires warming, cooling, and/or compression. Finally, the actual calculation has been carried out, in order to define the Specific Energy Consumption (SEC), i.e., the portion of stored energy - under hydrogen form - which is required for the operations of storing and releasing hydrogen. By calculating a SEC, it is possible to define the *real energy storage capacity* for a certain system and thus evaluate its efficiency. Furthermore, also CO_2 emissions related to the particular process of storage and release, have been calculated, in order to evaluate the environmental impact of each strategy.

The final object of the present work is to define and quantify parameters describing the performances of the above storage systems with the aim to determine the best available technology *throughout the whole ''hydrogen chain''*, i.e., from its production to its delivery for final use. Obviously, the SEC is not the only parameter that defines the final efficiency of a storage system: as mentioned above, indeed, also the energy required to keep certain thermodynamic conditions (e.g., boil-off for liquid H_2) should be evaluated jointly with the costs of transportation, and, most importantly, the availability and cost of raw materials. However, to evaluate these latter parameters, further data are required such as storage time or shipping distance. These parameters may differ for different applications, hence they have not been included into the present calculations.

It should be noted also that real process data were available only for well established storage systems, and for all the other, novel experimental systems, storage and release processes have been hypothesized starting from their thermodynamic behaviour. Moreover, parameters such as inefficiency due to irreversibility of certain processes, or due to activation energies, have not been assessed and thus the SEC for those systems should be taken as only indicative and representing a *minimum energy cost* for a certain experimental system.

The following is a description of the several systems examined herein, and the relevant parameters and processed considered in the calculations.

2. Methods

In the calculation of the parameters considered, all the processes involved in the operations of storage and transport have been identified for each system. As mentioned above, this has been possible only for those systems for which technologies exist and are already in use; for the other systems, an operating process was hypothesized based on the data collected by bibliographic research.

The processes considered were gas compression, heating and cooling. To calculate the work of compression, all the compression stages were considered as multi-stage adiabatic compressions with inter-cooling, with a compression efficiency of 70%. For all operations of heating or cooling, where the environment can be used as a heat source or sink, the energy consumption was considered equal to zero. For systems that required heating up to elevated temperatures, the efficiency of heating was considered of ca. 80%. For systems that required cooling down to low temperatures, the coefficient of performance was considered of ca. 4. For electric motors that drive turbines, the efficiency conversion of electric energy to mechanical work is estimated at 90%. The efficiency of a thermoelectric power station is 35%.

Also, we considered no recovery of heat from compression operations and no enthalpic recovery from gas expansion. To calculate the molar volume of compressed hydrogen we used the Van der Waals equation of state using proper coefficients for hydrogen.

To evaluate the carbon dioxide emissions by each storage system analyzed, we took into account the type of energy used. When heating up to a high temperature is required, the carbon dioxide emission was calculated according to CO_2 emissions for direct combustion of natural gas (NG), while for mechanical work required to drive turbines, pumps, or cooling systems, the emission of CO_2 according to the standard carbon intensity of Europe's power sector was considered, namely 90 kg of CO_2 released per each GJ of electric power produced. The relevant parameters of energy storage for the hydrogen storage systems considered are reported in Table 1

2.1. Compressed hydrogen

With the aim of determining the true efficiency of hydrogen storage under compressed form, the compression standards of 200, 350 and 700 bar were compared. For all these systems, the net density of compressed gas was obtained by use of the Van der Waals equation for real gases; the true density of the whole storing system has also been determined by taking into account the weight and volume of the container (cylinder). For the 200 bar system, a standard 16-steel cylinder package (40L each) has been analyzed, that allows for a hydrogen storage of 0.8 wt.%. For the standards of 350 and 700 bar, the specific gravity related to the state-of the art systems from Quantum technology for carbon fiber-jacketed aluminum-alloy cylinders has been taken into account. For the latter two compression standards a storage capacity of 6.7% and 6.0% by weight, respectively, were obtained, with a system gravity of 310 and 500 g/l [5]. It should be emphasized that the work calculations were made by considering a multi-stage compression as mentioned above, and also the energy cost for heat dissipation during compression stages was not included. Thus the obtained data has to be considered as a minimum level desirable for that technology. In conclusion, according with the SEC calculations, 9%, 10% and 12%, respectively, of energy content required for the compression operations, have been obtained.

2.2. Liquefied hydrogen

For liquid hydrogen we considered the net density of the liquid and the specific gravity of the final system taking into account such containment systems in liquid form as those from Quantum technology for on-board applications, obtaining a storage capacity of 14 wt.% and a system gravity of 444.44 g/l [5]. For liquid hydrogen production, energy calculations were based on data obtained from existing plants based on conventional liquefaction process. According to the present SEC analysis, energy required through the entire liquid hydrogen chain is estimated at ca. 36 wt.% of its energy content.

Recompression energy was not considered because we assumed hydrogen as used under ambient conditions. For current liquid hydrogen storage systems, a boil-off of 1–2% per day has to be considered, however in this calculation this was not introduced because it concerns the transportation energy cost, which is not considered in the present work.

2.3. Metal hydrides

We took three different molecular systems, i.e., 1) $LaNi_5H_6$ as representative of low temperature hydrides (LTHs), that shows a stoichiometric 1.4% by weight, 3.03 kJ/kg/K as heat capacity, P_{abs} of 20 bar, T_{abs} of 20 °C and T_{des} of 25 °C. 2) MgH_2 as representative of high temperature hydrides (HTHs) that show a stoichiometric 8% by weight, 1.63 kJ/kg/K as heat capacity, P_{abs} of 7 bar, T_{abs} of 300 °C and T_{des} of 350 °C, and 3) $NaAlH_4$ as alanates, which show a stoichiometric 8% by weight, 2.04 kJ/kg/K as heat capacity, P_{abs} of 84 bar, T_{abs} of 80 °C and T_{des} of 180 °C [7]. The energy calculations were carried out considering heating energy to reach hydrogenation temperature, and work for hydrogen compression up to hydrogenation pressure. For the release, heating energy necessary to reach the de-hydrogenation temperature and providing the de-hydrogenation energy was calculated.

These data give a non-trivial idea of the real performances of these systems, which are further lowered (even dramatically) when one takes into account the storage performances effectively measured. First of all, a remarkable amount of energy is transferred during the hydrogenation/de-hydrogenation process, thus in an hypothetical on-board storage during refueling, a remarkable amount of energy must be dissipated in a few minutes. This means very high powers to deal with. Also, during a vehicle's run, the same amount of energy has to be provided, withdrawing it from the same hydrogen stored. These problems are dramatic mainly for HTHs such as MgH_2. However, also the best performing LTHs such as $LaNi_5H_6$ still have problems in the release percentage

attainable in practical temperature ranges, that can be variable from 80% to 60%; moreover, their volume storage capacity suffers from the packing limit of these powder materials, and the difference in specific volume between the hydrogenated and de-hydrogenated forms amounts to ca. 40% [9].

Perhaps, however, the most important thing is the availability of the raw materials: the case of $LaNi_5H_6$ applied on a large scale poses the problem of the availability of a large amount of pure lanthanum, which could be an unsolvable problem. Thus packing problems and complexity of storage tanks suited for a proper thermal management in hydrogen storage as MgH_2 lower its storage capacity from the theoretical 8% to a actual 2.8% by weight. In the same way we could assess $LaNi_5H_6$ that suffer more from packing problems than from thermal management, and however switches from a theoretical 1.4% to an effective 1.1% by weight. Also $NaAlH_4$ presents a critical management of heat flows, which depend on its heat capacity. Finally, the last one, with a theoretical weight storage capacity of 8 wt.%, was effectively measured at a low 0.4 wt.% in a demonstration unit of the US-DOE. In conclusion, according with the described SEC analysis for MgH_2, 59% of its energy content is lost during storage and release processes, for the $LaNi_5H_6$ the value being 29% while being 64% for $NaAlH_4$. Obviously in the present calculation energy costs related to support manufacture and regeneration are not taken into account.

2.4. *Carbon nanotubes*

Even if claimed to have a high storage capacity, single walled carbon nanotubes (SWNT) have only attained a 2.3 wt.% as a best performance. This result was obtained at 80 K and under a pressure of 70 bar [12]. Cooling down to 80 K and the successive regasification are the critical points in this process, as we may estimate a heat capacity of 0.71 kJ/kg/K which entails the need of dispersing the relatively high interaction heat of H_2-nanotube. Finally, as reported for metal hydrides, nanotubes suffer from the same packing problems of hydrides. According to the SEC calculation up to 98% of their energy content may be wasted during storage and release operations.

As mentioned for hydrides, also for SWNT energy costs related to their production, regeneration and boil-off during transport have not been evaluated. It is also very important to highlight that SWNT are reportedly toxic.

2.5. *Ammonia*

Ammonia shows a very high stoichiometric content of H_2 (ca. 17.7%), is a compound with a relative stability, is liquid at 15 °C and shows a vapour tension of 6 bar. Further, the ammonia production process is a very well established technology and plant facilities already exist for a large scale ammonia production, (around the billion tons per day). Moreover, hydrogen recovery by ammonia electrolysis is favoured by the low dissociation potential of ammonia (ca. 0.5 V). Hence, an increasing number of researchers is proposing to use ammonia instead of hydrogen as an energy carrier. This cycle should be as follows: store hydrogen in ammonia using atmosphere nitrogen, transport ammonia, reform ammonia, and finally use hydrogen and release nitrogen; a cycle that seems virtually carbon- and pollution-free. For all those reasons, ammonia as carrier deserves a deeper analysis in order to comprehend if it features a positive energy balance.

First, energy required for production has to be evaluated. Currently ammonia is not produced directly from hydrogen, so operating reports on existing plants are not available and a direct energy cost for hydrogen stored as ammonia cannot be easily obtained. Ammonia is instead produced starting with natural gas, substantially by combining methane with water at high temperature that is an endothermic reaction. Analyzing the whole process, it is possible to verify that it encloses the entire hydrogen production process from natural gas, with the same costs of hydrogen purification due to the modern ammonia production catalysts (KAAP) that require hydrogen purity comparable with that for PEM fuel cells [13].

There exist three different processes: the Steam Reforming of Methane (SRM), the Auto Thermal Reforming (ATR) and the Partial Oxidation (POX). All these processes can use NG as a feedstock, and they differ for the strategy used to achieve and maintain the high temperatures needed. Basically, in SRM, energy is provided by means of direct external fuel combustion that supplies heat to the process, whereas, in the ATR and POX processes, the energy is supplied by an additional exothermic stage embedded directly into the main process and using a portion of the feedstock. These three processes are just the same currently used for hydrogen production, thus the energetic cost of ammonia can be obtained by subtracting from the whole energy required for ammonia production the energy cost for hydrogen production.

Actually, things are more complicated, because in the ammonia process as a whole, an energy credit is available, due to the exothermic ammonia step, that can be used in the first stage where hydrogen is produced, which is endothermic. Hence the coupling of these two processes, one exothermic and the other exothermic, offers a synergistic benefit compared with the two processes separately. However the ammonia production step that requires high compression of gases and further re-condensation cannot be carried out for free.

Based on data provided by Kellogg Brown & Root, Inc. (KBR) regarding a 2200 Mega Ton Per Day (MTPD) [14] ammonia production plant analyzed as a standalone plant with no energy import and export, and assuming a steam credit sufficient to generate *in situ* the electric power required by the plant, ammonia can be synthesized at a practical energy cost of 30.7 MJ/kg. Thus, in terms of hydrogen, to produce 1 kg of hydrogen stored as ammonia, an actual energy cost of 173.9 MJ/kg (based on NG Lower Heating Value (LHV)) is required. As relates to direct hydrogen production, based on data provided by a NREL Life Cycle Assessment (LCA) analysis for a standalone SMR hydrogen production plant, designed according to the Best Available Technology (BAT) and where, in the same way, the steam credit is sufficient for the self-generation of the required electric power, hydrogen can be produced at 155.6 MJ/kg (on NG LHV). Hence the net energy required to store hydrogen as ammonia can be assessed as a minimum of 18.3 MJ/kg. This value is significant considering that the ammonia energy content is equivalent to 21.2 MJ/kg. Therefore, an energy cost which is equivalent to 86% of its energy content is required. Moreover, when considering the steam credit for ammonia production, this value decreases considerably to 6.9 MJ/kg, which represents only 35% of the ammonia energy content.

Hydrogen recovery from ammonia differs remarkably according to the strategy chosen to decompose ammonia into hydrogen and nitrogen. Ammonia shows very different values of dissociation enthalpy (−45.7 kJ/mol) and dissociation free energy (−16.7 kJ/mol). These values can be considered to stem from the interaction energy between hydrogen and support, respectively at 15,200 kJ/kg and 5550 kJ/kg of hydrogen stored as ammonia. When ammonia is decomposed by thermal cracking, dissociation enthalpy must be supplied. Considering that current thermal cracking technologies work at 86% efficiency, an additional 83% of ammonia energy content is required to release hydrogen [15].

Conversely, when ammonia is decomposed by electrolysis, the dissociation free energy must be supplied. Considering the current ammonia electrolyser technology, which works with an efficiency of only 12%, this means that an additional 38% of its energy content is required to recover hydrogen from ammonia by electrolysis. In this latter case, it should be noted that this 38% has to be provided as *electric power*; if this energy is withdrawn from the system that uses hydrogen released from ammonia, such as a fuel cell station, this fraction of energy is produced from hydrogen at an efficiency of 40%, thus this 38% actually sums up to 96% of the entire hydrogen energy content [16].

In conclusion, for what concerns hydrogen storage as ammonia, in the best case where the production is carried out with an efficient steam credit use, the SEC can be estimated as 118%, namely a strongly *negative energy transport* system.

It is important to note that the present global ammonia production is equivalent to a merely 17% of the US gasoline demand, thus, even if the inclusion of a steam credit gives a benefit to the ammonia energy balance, in a large scale application scenario a practical and efficient use of the huge amount of the steam produced has to be found [17]. Finally, ammonia is classified as a toxic compound, and its wide use as a fuel should face the problem of NOx emissions.

2.6. *Gas hydrates*

Hydrogen could be ideally stored in hydrate form up to a theoretical 5.6 wt.% [18] (compression ratio of ca. 1/450), and a net content of 4 wt.% has been reported, though with very slow kinetics [19] (several days or weeks). Some strategies have been proposed to speed up the hydrogen hydrate synthesis, but they suffer from the complexity of production facilities [20]. For a general review on clathrate hydrates, see the fundamental text by Sloan and Koh [21].

In our research group at the CEMIN, we have developed a novel nanotechnology and chemical promoters for improving such a slow kinetics to a level of a few minutes, and without adding surface-enhancing solid supports which remarkably increase the overall weight of the system [22,23]. Our production process for hydrogen hydrate follows a ''nanotechnologic'' approach, i.e., we are able to form hydrate nanoparticles from ''bottom-up'', starting with water-in-oil nanoemulsions (water pools or droplets a few nanometers across) which are stabilized by a monolayer of amphiphile molecules into a bulk organic solvent. The system thus obtained (a nanoemulsion) is macroscopically homogeneous, and the water droplets can then be induced to form hydrate nanoparticles when the system is put under the appropriate P and T conditions. The extremely small size of those nanodroplets allows for an enhanced gas flux to be captured under hydrate form, with a resulting hydrogen hydrate formed within tens of minutes.

A ''nanoemulsion'' method is also advantageous in that:

i) the presence of an organic solvent allows for a much broader choice of co-formers: the presence of a bulk, dispersing phase formed by e.g. an organic solvent allows to employ also water-insoluble co-formers, and the bulk organic phase serves as a reservoir of the co-former which is kept ready for hydrate formation when the latter begins;
ii) the bulk dispersing phase acts also as a ''partition buffer'' to limit the concentration of very water-soluble molecules (e.g., THF) into the water droplets, thus ideally enhancing the concentration of the hydrate former (e.g., H_2) in water;
iii) the reaction system can be kept under homogeneous conditions avoiding clogging of the reactor, due to agglomeration of hydrate fine particles. Indeed, hydrate nanocrystals which form from the water pools precipitate to the bottom of the reactor in form of a slurry which is free-flowing and does not tend to clog, e.g., a discharge pipeline;
iv) the present process can be made continuous by simply adding water and co-former; addition of fresh water/co-former mixture substantially replenishes the shrinking, surfactant-coated water pools, leading to a continuous production of hydrogen hydrate.

Table 1 – Relevant parameters of energy storage for the hydrogen storage systems considered.

	Storing Energy (kJ/kg)	Releasing Energy (kJ/kg)	Spent Energy/Stored Energy	Energy Content (MJ/kg)	Energy Content (MJ/m^3)	CO_{2eq} Emission (kg)
$CH_{2\ 200}$	10300	0	0.09	1.05	714	0.93
$CH_{2\ 350}$	12264	0	0.10	8.04	2492	1.10
$CH_{2\ 700}$	14883	0	0.12	7.20	3599	1.34
LH_2	42600	0	0.36	16.81	3999	3.83
LMH	6226	1071	0.06	1.08	13798	0.66
HMH	10865	6724	0.15	3.47	12838	1.58
Alanate	10589	4080	0.12	3.47	11398	1.32
SWNT	15998	0	0.13	3.60	2159	1.44
Ammonia	6900	17670	1.16	21.23	17351	2.21
HyH_2	11215	0	0.09	6.00	4979	1.01

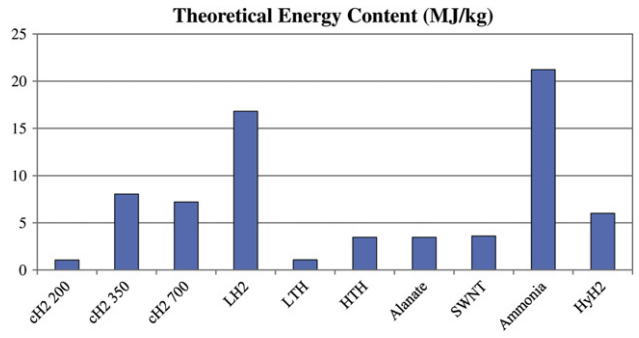

Fig. 1 – Theoretical storage capacity by weight.

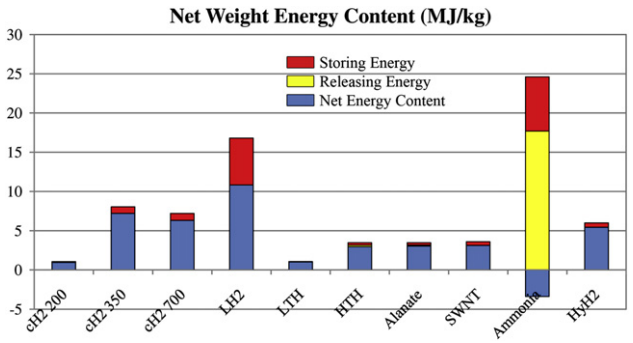

Fig. 3 – Theoretical storage capacity by weight considering Production and Release SEC.

v) the presence of a bulk organic phase enhances the concentration of hydrate former in the liquid phase.

We used hydrate-forming nanoemulsions made from the known emulsion stabilizers (AOT from Sigma-Aldrich, NEODOLs by Shell, and others synthesized in our laboratory), by using iso-octane (Sigma-Aldrich, anhydrous 99.8%) as a bulk organic phase. In a typical nanoemulsion preparation to be subjected to hydrogen hydrate formation, 200 ml of iso-octane as a dispersing medium is used, and a proper amount of AOT is dissolved in the solvent, so to obtain a concentration of 0.1 M AOT in iso-octane. Then water is added in such an amount to keep the system in the stability region of the nanoemulsion and avoid phase separation. Finally, a co-former (e.g., THF) is added in an amount depending of its partition equilibrium between water and the organic solvent, and also depending on the target amount of co-former in the final hydrate structure.

As relates to the present example of THF-H_2 hydrate formation by a water-AOT-iso-octane nanoemulsion, it is possible to synthesize THF-H_2 hydrates in a simpler way as compared to the known approaches. In particular, due to the existence of the partition equilibrium of co-former between water and organic solvent, the kinetics of pure co-former hydrate formation, that is in competition with the binary co-former-H2 hydrate, is suppressed in a predictable way through the total amount of THF added to the system. The use of a hydrocarbon (e.g., iso-octane) as a dispersing medium enhances the hydrogen mass transfer to the hydrate, because of a much higher solubility of hydrogen in iso-octane as compared to bulk water, thus upgrading hydrate formation and reducing the induction time.

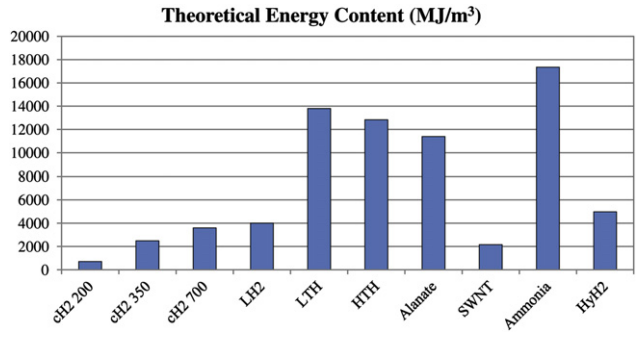

Fig. 2 – Theoretical storage capacity by volume.

The presence of a surfactant that gives water nano-droplets dispersed into hydrocarbon (reverse micelles), maximizes the surface contact between water and hydrogen gas, and provides for the formation of the first hydrate crystals which are orders of magnitude smaller than those with the existing processes. At present, we have reached about 1 wt.% of hydrogen storage with this process [22].

In general terms, a theoretical 5.6 wt.% is not a remarkable performance, but it has to be taken into account that the storage and release processes from hydrates require a very low energy. Thus hydrogen hydrates offer, according to this view, remarkable advantages, e.g., hydrogen can be stored into hydrate by compressing the gas at around 60–120 Bar and cooling the system a few degrees below the water freezing point, or even above that value. Thus, to calculate the energy required to store hydrogen into hydrates, we should calculate hydrogen compression work up to 120 bar, cooling work down to −8/−9 °C, heat capacity at 2.52 kJ/kg/K, and disperse the latent heat of formation assessed as 337.33 kJ/kg. The interaction energy between hydrate lattice and hydrogen can be estimated, by theoretical calculations, at ca. 1100 kJ/kg of hydrogen stored in hydrate, that gives a negligible value when compared to the hydrate heat of fusion. Hence it is possible to consider - as the hydrogen releasing energy - the energy required to decompose a hydrate lattice. Hydrogen hydrate dissociation can be obtained by simply providing the latent heat of fusion; in this case, being the system at quite low temperatures, even a highly ''entropic'' heat can be used, namely waste heat at low temperature, which can be

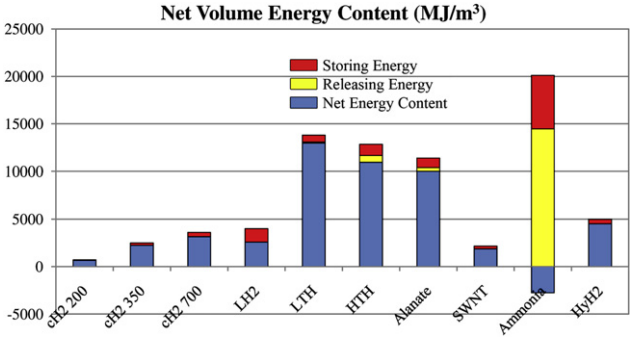

Fig. 4 – Theoretical storage capacity by volume considering Production and Release SEC.

recovered from any hydrogen-using systems. Thus, considering only the energy required to store hydrogen into hydrate, the entire process can work with a SEC of 9% based on a theoretical 5.6% by weight of storage.

Obviously, also in this case further energy is required to keep the system under stable conditions, namely cooling energy. As for liquid hydrogen, this aspect is not assessed here, but it is possible to hypothesize that, as compared to liquid hydrogen, that has to be kept at 20.4 K, keeping a system at 263 K requires a remarkably lower amount of energy. Hydrogen hydrates are moreover distinguished from the other storing means by the following features: 1) safety: they do not explode and may be rendered self-extinguishing; 2) low cost: the main component is water, which may be both pure and salt-water (sea water); 3) efficiency: the very concept of refueling cycles loses of significance; 4) environmental considerations: a dramatic decrease of disposal costs. In summary, hydrogen hydrates may effectively represent a breakthrough in the field of hydrogen storage.

3. Carbon dioxide emissions

To evaluate carbon dioxide emissions by each storage system analyzed, it was necessary to take into account the type of energy used. As mentioned above, when heating up to a high temperature is required, the carbon dioxide emission was calculated according to CO_2 emissions of the European Mix standard, which amounts to 90 kg of CO_2 for each GJ of electric power produced.

4. Results and discussion

Table 1 and Figs. 1 to 6 report the results of comparison among the various hydrogen storage systems, which was carried out according to the methods described above. In the graphs, energy consumed for storing hydrogen is depicted in red, while energy consumed for releasing hydrogen is in yellow.

Figs. 1 and 2 show the comparison among the theoretical energy storage capacity, both by weight and volume, of the storage systems considered. On the other hand, Figs. 3 and 4 show the net energy storage capacity, both by weight and volume, resulting after the SEC calculation for each storage system. Figs. 5 and 6 report the comparison among some of the systems investigated, for which also the CO_2 emission calculations have been carried out. In these two latter cases, it is important to note how hydrogen hydrates could be competitive (should the theoretical limit be approached) when compared to well established technologies, in particular when considering the energy stored per unit volume. In our opinion, a hydrate-based technology would be particularly suitable for large scale hydrogen storage. A possible scenario could be the following: Hydrogen will be produced by (sea-) water electrolysis with electric power from windmill fields during low-demand hours, and stored in hydrate form. This can be accomplished at low cost because the temperature, pressure and raw materials (i.e., water) needed for hydrate production are present with no restriction on the seafloor. Then hydrogen will be released from the hydrate on demand, and converted

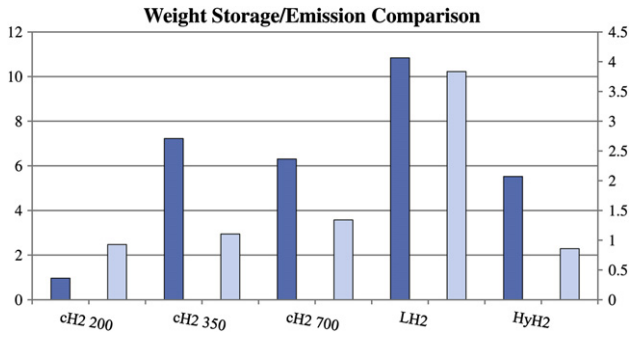

Fig. 5 – Energy storage by weight and relative CO_2 emissions for some of the investigated systems.

to energy by on site fuel cell stacks. Alternatively, produced hydrogen hydrate may be transported in a safe and economic manner (as already demonstrated for methane hydrates) to utilization sites on the mainland.

Ammonia is not reported as a ''best performer'', but this is also because it is the only system from which the energetic cost of hydrogen production from fossil fuels has to be subtracted, as clearly discussed in the relevant section in the METHODS. It should be added that, for systems such as ammonia which require an electrolysis step to retrieve hydrogen for consumption, another matter of concern relates to the metal catalysts used for such a process. In other words, metals such as platinum and palladium, which work quite well in that process, are relatively scarce on our planet, at such a level that the mass-scale use of hydrogen as a fuel, based on noble-metal catalysed electrolysis, cannot be considered as a feasible future scenario.

Metal hydrides are the best performers when the net energy stored per unit volume is taken into account. However, these systems all suffer from two common problems. First, large amounts of heat are released during refueling, and even if such a feature has not been considered into the calculations based on the consideration that heat dissipation can be done (very slowly) by the environment ''for free'', automotive applications of hydrides as hydrogen storage media will certainly be hindered by such a factor, unless an effective dissipation device and process is envisaged. Secondly, the recovery percentage of stored hydrogen is remarkably lower than the amount originally stored, due to a sort of ''passivation'' that characterizes hydrogen adsorption onto metal

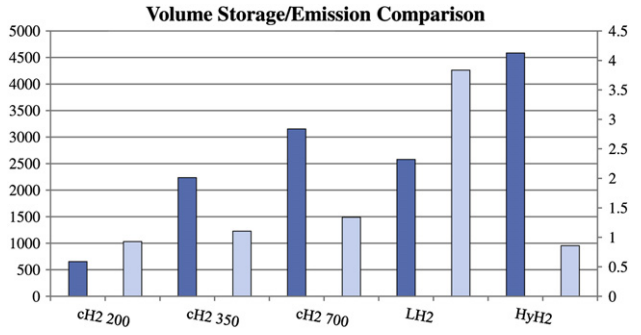

Fig. 6 – Energy storage by volume and relative CO_2 emissions for some of the investigated systems.

alloys. In other words, a fraction of the adsorbed hydrogen tends to remain into the alloy unless (unfeasibly) high temperatures are used. Neither of the above two problems have been considered into the calculations.

5. Conclusions

As proposed in the present work, the use of hydrogen as an *energy carrier* necessarily entails a mandatory consideration of the energy cost required for the processes involved in hydrogen storage and release. Systems that show a high storage capacity, such as certain hydrides or ammonia, show a high SEC that can be even greater than their energy storage capacity. For what concerns hydrogen hydrates, instead, their SEC results to be quite low and comparable with the well established technologies. Thus, even being their storage capacity limited to a theoretical 5.6 wt.%, their efficiency as hydrogen storage media may be considered very good - provided their storage percent is remarkably increased. Also, additional aspects are shown by hydrogen hydrates regarding their intrinsic safety, low cost, and environmental aspects. In conclusion, according to the present work, energy efficiency, jointly with storage capacity, should be seriously evaluated when technological targets are fixed.

Glossary

ATR	Auto Thermal Reforming
BAT	Best Available Technology
FC	Fuel Cell
FCV	Fuel Cell Vehicles
GHG	Greenhouse Gas
HTHs	High Temperature Hydrides
KAAP	KBR Advanced Ammonia Process
KBR	Kellogg Brown & Root
LCA	Life Cycle Assessment
LHV	Lower Heating Value
LTHs	Low Temperature Hydrides
MTPD	Mega Ton Per Day
NOx	Nitrogen Oxides
NREL	National Renewable Energy Laboratory
P_{abs}	Hydrogen absorption pressure
POX	Partial Oxidation
RT	Room Temperature
SEC	Specific Energy Consumption
SRM	Steam Reforming of Methane
T_{abs}	Hydrogen absorption temperature
T_{des}	Hydrogen desorption temperature
US-DOE	United States-Department Of Energy

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