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ENERGETIC AND ECONOMIC EVALUATIONS ON HYDROGEN STORAGE TECHNOLOGIES

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ABSTRACT

With a foreseeable 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, the former being chemical (metal hydrides, ammonia,) and physical (carbon nanotubes) adsorption of H₂. Also, a novel technology is in rapid progress, which is based on clathrate hydrates of hydrogen. The object of the present work is to evaluate the features and performances of those several 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, real and practical storage capacity, specific energy consumption (SEC). From our work, it is demonstrated that a technology based on clathrate hydrates of hydrogen, while being far from optimized, is strongly competitive with the classical approaches

Keywords: hydrogen hydrates, hydrogen storage, hydrogen, nanotubes, metal hydride, ammonia, specific energy consumption, compressed hydrogen, liquid hydrogen,

NOMENCLATURE

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

INTRODUCTION

Hydrogen storage is one main problem hindering the diffusion of the "Hydrogen Economy". The

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classical storage methods based on compression and liquefaction are an established and efficient approach, but involve huge problems of security clearance and the associated costs of compression work and cooling are high. 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 thermodynamic stable state, 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. Therefore, handling of hydrogen requires to bring it under different thermodynamic conditions, e.g., by compressing or liquefying it, or trapping the same 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 also a matter of energy. Indeed, energy required to move hydrogen from its natural conditions to storage conditions, and then the energy required to recover the same from the storage media is a critical issue. To compress hydrogen, energy as mechanical work is required; to liquefy the same, instead, 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 not to propose 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 hydrogen should have an interaction with its storage support of about ca. 20 Kcal/mol , namely 40000 KJ/Kg of hydrogen[1]. That value is intermediate between the interaction energy of a

covalent bond, typically about several tens of Kcal/mol , and the interaction energy of a weak bond, typically about of only a few Kcal/mol . Energy efficiency in hydrogen storage and transportation is a critical issue for various reasons. First, forecasting a next-future energy crisis [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 consuming conventional energy sources. Currently, hydrogen is mainly produced by fossil fuel gasification with an energy recovery efficiency 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 as concerns Greenhouse Gas (GHG) emissions, being fossil energy mainly based on carbon. Carbon dioxide emission 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 aluminium 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 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 storage system; this

because even though it is considered as a novel 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 they can be competitive as alternative hydrogen storage media[12]. In order to carry out this analysis, first the thermodynamic conditions have been identified, in which the various systems are once hydrogen has been stored, and thus the thermodynamic conditions under which the processes of storage and release take place. As a second step, all the required data have been collected, such as system gravity, theoretical storage capacity, specific heats, latent heats, etc. Then, the interaction energy between hydrogen and support has been gathered in order to evaluate how a system compares with the above mentioned "optimum" value of roughly 40000 KJ/Kg. Moreover, the processes required for practically carrying out hydrogen storage and release have been devised for any 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.

SEC calculation has been carried out not only by referring to a theoretical storage capacity, but also to the actual best storage capacity effectively obtained for the tested systems. It is worth noting that this capacity is, in certain cases, far below the theoretical value. Furthermore, also CO₂ emissions related to the particular process of storage and release, have been calculated, in order to evaluate also the environmental impact of each strategy.

The final object of the present work is the definition and quantification of 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 H₂) should be evaluated jointly with the costs of

transportation. 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 behavior. 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 processes considered in the calculations.

METHODS

In the calculation of the parameters considered, for each systems all the processes involved in the operations of storage and transport have been identified. 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 a wide bibliographic research.

The processes involved were gas compression, and system heating and cooling. To calculate the work of compression, all the compression stages were considered as single-stage adiabatic compressions without inter-cooling, with a compression efficiency of 35%. Calculations were carried out by means of iterative application of Langen's equation using proper coefficients for hydrogen. For all operations of heating or cooling, where the environment can be used as a heat source or sink, the efficiency of heat transfer was considered as of 80%. 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 efficiency of cooling was considered of ca. 30%. 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, it was necessary to take into account the typology of energy used. When heating up to a high temperature is required, the carbon dioxide emission was calculated according to CO₂ emissions for direct combustion of NG, while for mechanical work required to drive turbines, pumps, or cooling systems, the emission of CO₂ for a thermoelectric power station was considered, namely 0.65 Kg of CO₂ released for each KWh of electric power produced.

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 entire storing system has also been determined by taking into account the weight and volume of the container (cylinder). For the 200 bar standard, the classical steel cylinder of 50L size has been analyzed, that allows for a hydrogen storage of 1.3% by weight, with a system gravity of 742.98 g/l. 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 aluminium-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 single stage compression that is technologically unfeasible especially in large scale applications where turbine compressors are used, and also the energy cost for heat dissipation during compressions stages was not included. Thus the obtained data has to be considered as a minimum desirable for that technology. In conclusion, according with the SEC calculations, 14%, 17% and 21%, respectively, of system energy content required for the compression operations, have been obtained.

LIQUEFIED HYDROGEN

For liquid hydrogen we considered the net density of the liquid and the specific gravity of the final system taking into account containment systems in liquid form as those from Quantum technology for on-board applications, obtaining a storage capacity of 7.5% by weight 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. Whereas the energy cost for liquid hydrogen regasification has been calculated considering liquid hydrogen latent heat at 445.59 KJ/Kg and the non-negligible hydrogen heat capacity of 14.89 KJ/Kg/K (H₂ liquid has to be warmed from 20.4K up to RT). Obviously for small scale storage, regasification energy can be neglected, but for a large scale this is not true, because the hydrogen latent heat and heat capacity are remarkable and surely not negligible in certain cases. According with the present SEC analysis, energy required through the entire liquid hydrogen chain is assessable as 31% of its energy content. Recompression energy was not considered because we assumed hydrogen as used at 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 .

METAL HYDRIDES

We took three different molecular systems, i.e., 1) LaNi₅H₆ as representative of low temperature hydrides (LTHs), that shows a stoichiometric 1.4% by weight, 3.03 KJ/Kg/K as heat capacity, an interaction energy of 16400 KJ/Kg of hydrogen and a density of 8214.28 g/l. 2) MgH₂ as representative of high temperature hydrides (HTHs) that show a stoichiometric 8% by weight, 1.63 KJ/Kg/K as heat capacity, an interaction energy of 37500 KJ/Kg of hydrogen and a density of 1337.50 g/l, and 3) NaAlH₄ as alanates, which show a stoichiometric 8% by weight, 2.04 KJ/Kg/K as heat capacity, an interaction energy of 42000 KJ/Kg of hydrogen and a density of 1187.50 g/l.[7] The energy calculations were carried out considering heating energy to reach hydrogenation temperature, cooling work to dissipate hydrogenation heat, work for hydrogen compression up to hydrogenation pressure. For the release, heating energy necessary to reach the de-

hydrogenation temperature and providing for 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 problem 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 than 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 reportedly good performer $NaAlH_4$, 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 the 59% of its energy content is required during storage and release process, for the $LaNi_5H_6$ the value results to be 29% while for $NaAlH_4$ it is 64%. Obviously in the present calculation energy costs related to support fabrication and eventual regeneration are not taken into account.

CARBON NANOTUBES

Even if claimed to have a high storage capacity, single-walled carbon nanotubes (SWNT) have only attained a 3 wt% as a best performance, showing a system gravity of 1167 g/l. This result was obtained at 77K e and under a pressure of 20Bar. [13] Cooling down to 77K 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 presents the need of dispersing the relative high interaction heat of H_2 -nanotube, which may amount to ca. 18275 KJ/Kg H_2 . During regasification, in addition to supplying the heat subtracted during adsorption, it is also necessary to heat the hydrogen gas from 77K up to RT, which is not negligible as mentioned for liquid hydrogen (supra). 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 operation.

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.

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 vapor tension of 6 bar. Further, the ammonia production process in a very well established technology and plant facilities already exist for a large scale ammonia production, (around the billions tons per day). Moreover the hydrogen recovery by ammonia electrolysis is favored by the low dissociation potential of ammonia (ca. 0.5 V). Hence, an increasing number of researchers is proposing to use ammonia instead hydrogen as an energy carrier. This cycle should be as follows: store hydrogen in ammonia using atmosphere nitrogen, transport ammonia, reform ammonia using hydrogen and releasing 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. [14]

There exist three different processes: the Steam Reforming of Methane (SRM), the Auto Thermal Reforming (ATR) and the Partial Oxidation (POX). All these processes may use NG as a feedstock, and differ for the strategy used to achieve and maintain the high temperatures needed. Basically, in the 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 to the entire energy required for ammonia production the energy cost for the hydrogen production.

Unfortunately, things are not so simple, 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 synergic 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)[15] ammonia production plant analyzed as stand alone 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. Regarding direct hydrogen

production, based on data provided by a NREL Life Cycle Assessment (LCA) analysis for a stand alone SMR hydrogen production plant, designed according to the Best Available Technology (BAT)[3] 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 to produce ammonia an energy cost is required which is equivalent to 86% of its energy content.

Moreover, when considering the steam credit for the ammonia production, this value decreases considerably to 6.9 MJ/Kg that represents only 35% of the ammonia energy content.

For what concerns hydrogen recovery from ammonia, it 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 a 15200 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 29% of ammonia energy content is required to release hydrogen.[16]

Conversely, when ammonia is decomposed by electrolysis, the dissociation free energy must be supplied. Considering the current ammonia electrolyzer 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 FC 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 ammonia energy content.[17] 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 64%, while when steam

cannot be used efficiently, the SEC will increase up to 121%, 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 wide application scenario a practical and efficient usage of the huge amount of the steam produced has to be found.[18] Finally, ammonia is classified as a toxic compound, and its wide use as a fuel should face the problem of NOx emissions.

GAS HYDRATES

Hydrogen can be stored in hydrate form up to a theoretical 5 wt% [19] (compression ratio of 1/450), and a net content of 4 wt% has been realized in the laboratory, though with very slow kinetics [20] (several days or weeks). Several strategies have been proposed to speed up the hydrogen hydrate synthesis, but they suffer from the complexity of production facilities .

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, therefore opening the road to a hydrogen storage technology based on hydrogen hydrates [21]. In general terms, a theoretical 5% by weight 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 hydrate offers, according to this view, remarkable advantages, hydrogen can be actually stored, according to literature data, into hydrate up to 4% by weight by compressing the gas at 120Bar and cooling the system a few degrees below the water freezing point.

Thus to calculate energy required to store hydrogen into hydrate, we should calculate hydrogen compression work up to 120 bar, cooling work down to -8/-9°C, assessing heat capacity at 2.52 KJ/Kg/K, and dispersing the latent heat of formation assessed as 337.33 KJ/Kg. the interaction energy between hydrate lattice and hydrogen is assessable, by theoretical calculation at 1100 KJ/Kg of hydrogen stored in hydrate, that gives a value negligible when compared with 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, an heat typology that can be recovered from all system that use hydrogen. Thus, considering the energy required to store hydrogen into hydrate plus the energy required to recover the same, the entire process can work with a SEC of 13% according to theoretical 5% by weight of storage, and with a SEC of 29% based on actual performances of 4% by weight.

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 20.4K, keeping a system at 263K requires a remarkably lower amount of energy. Hydrogen hydrates are moreover distinguished from the other storing means for the following terms: 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 (marine); 3) efficiency: the very concept of refueling cycles loses of significance; 4) environmentally friendly: dramatic decrease of disposal costs. In summary, hydrogen hydrates may effectively represent a breakthrough in the field of hydrogen storage.

CARBON DIOXIDE EMISSIONS

To evaluate the carbon dioxide emissions by each storage system analyzed, it was necessary to take into account the typology of energy used. When heating up to a high temperature is required, the carbon dioxide emission was calculated according to CO₂ emissions for direct combustion of NG, while for mechanical work required to drive turbines, pumps, or cooling systems, the emission of CO₂ for a thermoelectric power station was considered, namely 0.65 Kg of CO₂ for each KWh of electric power produced

THE WORST SCENARIO

Being the novel technologies for hydrogen storage at an early stage, often safety aspects are not evaluated. So it was hypothesized a worst scenario where safety restrictions for material toxicity and high pressure systems are applied, then we compared hydrogen hydrate at half of its real storage capacity, i.e. 2% by weight, with the well

established technology of compressed hydrogen at 200 bar. CO₂ emission, in this case, are also estimated.

Figure 4: Best performer by weight and relative CO₂ emissions

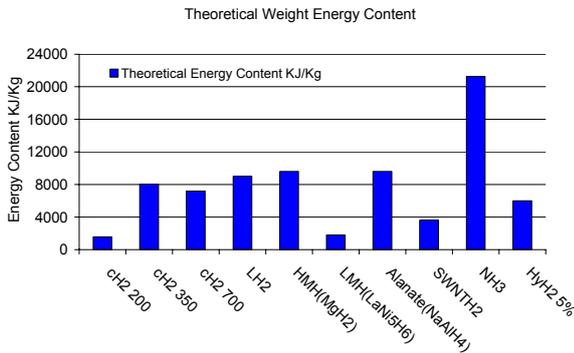


Figure 1: Theoretical storage capacity by weight

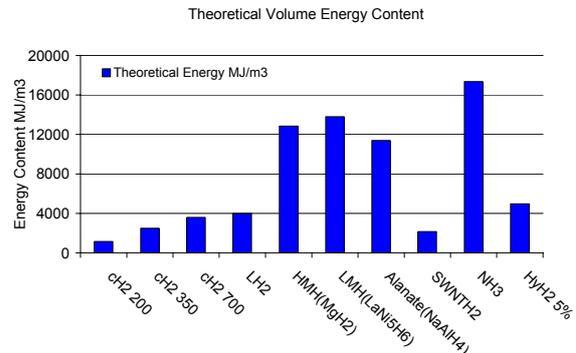


Figure 5: Theoretical storage capacity by volume

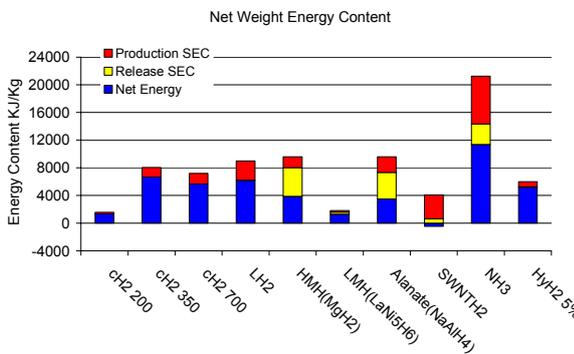


Figure 2: Theoretical storage capacity by weight considering Production and Release SEC

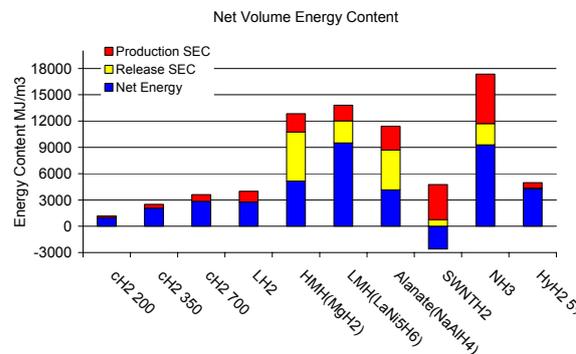


Figure 6: Theoretical storage capacity by volume considering Production and Release SEC

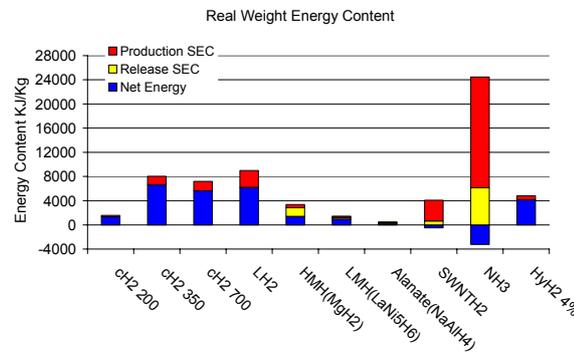


Figure 3: Real storage capacity by weight considering Production and Release SEC

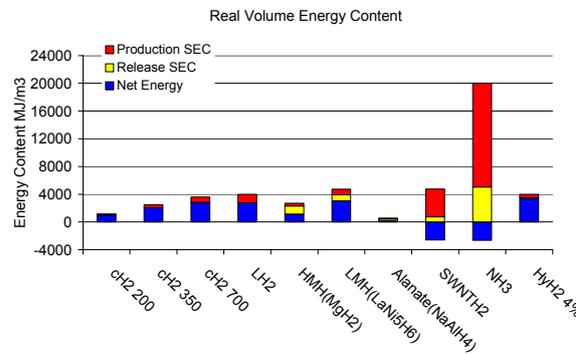


Figure 7: Real storage capacity by volume considering Production and Release SEC

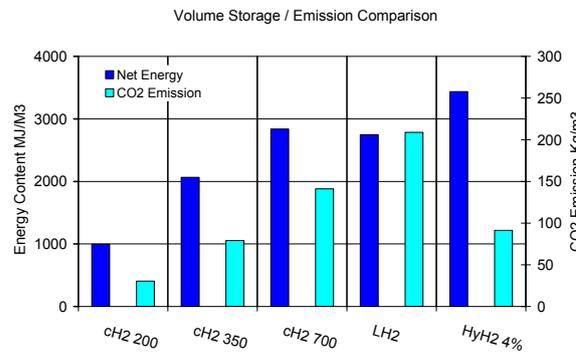
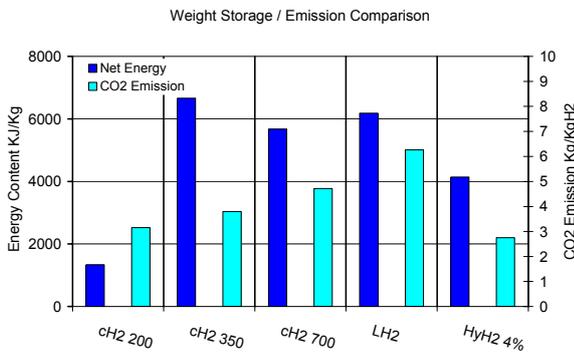


Figure 8: Best performer by volume and relative CO₂ emissions

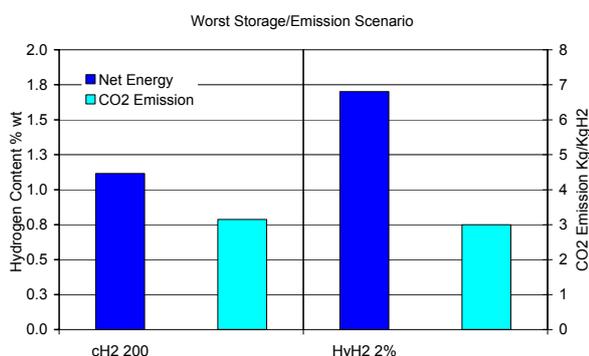


Figure 9: Worst scenario (safety restriction applies) of best performer, and hydrogen hydrate at only 2% wt of storage capacity

BRIEF DISCUSSION

Figures 1 and 5 show the comparison among the theoretical energy storage capacity, both by weight and volume, of the analyzed storage systems. Figures 2 and 6, show, instead, the net energy storage capacity, both by weight and volume, resulting after the SEC calculation for each storage system. Figures 3 and 7 show the real energy storage capacity, both by weight and volume, resulting when the SEC calculation is carried out on the effectively achieved storage capacity instead than the theoretical one. Figures 4 and 8, report the comparison among the systems that show the best performance for which also the CO₂ emission calculation has been carried out. In these two latter cases, it is important to note how hydrogen hydrates are still competitive when compared with a well established technology. Finally, Figure 9 shows an hypothetical scenario where high pressure and liquid storage do not meet a safety clearance, and hydrogen hydrate working only at half of its storage capacity. Also in this worst scenario, it is interesting to note how hydrogen hydrate is still competitive with a 200 bar compression standard both in terms of capacity and CO₂ emissions.

CONCLUSIONS

As proposed in the present work, the use of hydrogen as an *energy carrier* necessarily entails a mandatory consideration of the energy costs required for the processes involved in hydrogen storage and release. Systems that show a high storage capacity, such as certain hydrides or ammonia, cannot be proposed as hydrogen storage

media due to their 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%, their efficiency as hydrogen storage media may be demonstrated herein. 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.

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