COMPARISON OF HYDROGEN STORAGE TECHNOLOGIES: A FOCUS ON ENERGY REQUIRED FOR HYDROGEN INPUT

Monterey R. Gardiner and Andrew Burke

Institute of Transportation Studies
One Shields Ave.
University of California, Davis, CA 94539

Introduction

Why focus on hydrogen as a fuel? Fuel cell vehicles (FCVs) are rapidly approaching commercialization. Honda will be the first to market here in the US, with plans to offer a small number of passenger FCVs for fleet applications next year (2003). DaimlerChrysler and Ford will follow shortly with plans to offer a limited number of vehicles in 2004. With the rapid approach of FCVs, more detail is needed with respect to near term options for hydrogen storage. Hydrogen for a direct hydrogen fuel cell vehicle (DHFCV) is seen as both the near term and long term fuel choice for auto manufacturers and society as a whole. Due to challenges of storing hydrogen onboard vehicles, two midterm fuel solutions have been suggested. They are methanol or a specially designed hydrocarbon. However, in the near term compressed hydrogen gas (CHG) and liquid hydrogen (LH_2) are the most mature methods of onboard storage. However, other options exist such as metal hydrides and sodium borohydride.

The purpose of this paper is to add to and consolidate information about the range of onboard hydrogen storage options. There are journals and papers with informative graphs of wt% or vol% hydrogen stored or their respective pairs specific energy storage density by weight and volume, however updated information is required for the comparison. A base line of 5 kgs of hydrogen is chosen as the amount of hydrogen to be stored to facilitate the comparison. This is the amount of hydrogen required to attain a FCV range comparable to an ICE vehicle. The value was calculated with the UC Davis fuel cell vehicle model using a combined FUDs and HIWY driving cycle.[1]

In order to expand upon and update available information regarding hydrogen storage options, energy required to store the hydrogen needs to be taken into consideration. A detailed look at the required energy to store the hydrogen will allow one to put into perspective the energy cost between 10 kpsi CHG and a possible metal hydride for example. With the option of home refueling as a partial solution to the "infrastructure problem", the most cost effective and convenient storage method still needs to be determined. This paper will assist in that process. The following calculations are a first approximation at determining the energy required to store hydrogen for four different onboard storage technologies: LH_2, CHG, metal hydrides, and sodium borohydride.

Calculations

Liquid Hydrogen. The energy cost for this storage method is one of the most difficult to approximate due to the multiple steps required to liquefy hydrogen, therefore I will outline the method for determining the ideal work for the liquefaction of hydrogen which, is relatively straight forward. However, I will also provide the liquefaction energy based on the nitrogen pre-cooled Linde process, which uses liquid nitrogen to first cool the hydrogen. Liquid hydrogen requires a temperature of 20 K. At this temperature almost all the hydrogen has a para-hydrogen electron configuration. At room temperature 25% of the hydrogen is para-hydrogen and 75% is ortho-hydrogen. The conversion is an exothermic reaction and releases a significant amount of heat (527 kJ/kg).[2] The conversion is very slow, but can be done much faster using a catalyst. The theoretical process for ideal liquefaction uses a reversible expansion to reduce the energy required for liquefaction. It consists of an isothermal compressor, followed by an isentropic expansion to cool the gas and produce a liquid.[3] The following values of entropy, enthalpy, pressure and temperature are used to calculate the ideal work per kilogram to liquefy hydrogen.[4]

$$S_1 = 15.472\frac{cal}{gm \bullet K} \quad h_1 = 1003\frac{cal}{gm} \quad P_1 = 1\ atm \quad T_1 = 300K$$

$$S_2 = 4.35\frac{cal}{gm \bullet K} \qquad T_2 = 300K$$

$$S_3 = 4.35\frac{cal}{gm \bullet K} \quad h_3 = 70\frac{cal}{gm} \quad P_3 = 1\ atm \quad T_3 = 20K$$

$$w = T_1(S_1 - S_2) - (h_1 - h_2) \qquad w = 2.795\frac{kW \bullet hr}{kg}$$

The ideal work required to liquefy hydrogen is 2.795kWh/kg, while the work calculated for the nitrogen pre-cooled liquefaction of hydrogen is 19.839kWh/kg.[5] At 5kg this is 99.195kWh.

Compressed Hydrogen Gas: 3500 psi, 5000 psi, 10000 psi. The energy to compress the hydrogen can be found in a similar manner. The example shown is for 3500 psi.

$$S_1 = 15.472\frac{cal}{gm \bullet K} \quad h_1 = 1003\frac{cal}{gm} \quad P_1 = 1\ atm \quad T_1 = 300K$$

$$S_2 = 4.35\frac{cal}{gm \bullet K} \quad h_2 = 1033\frac{cal}{gm} \quad P_2 = 238\ atm \quad T_1 = 300K$$

$$w = T_1(S_1 - S_2) - (h_1 - h_2) \qquad w = 1.931\frac{kW \bullet hr}{kg}$$

Table 1. Compression Energy

	3500 PSI	5000 PSI	10000 PSI
kWhr/kg	1.93	2.08	2.39
KWhr at 5kg	9.66	10.38	11.95

Table one clearly shows, the energy required to compress hydrogen gas, starting at an initial pressure of 1 atm and the energy for 5 kilograms.

Metal Hydrides. The work required to store hydrogen in a metal hydride depends on the type of hydride and how quickly it needs to be done. Typically hydrogen is supplied a little over atmospheric pressure to the metal alloy. The process is slightly exothermic. For large systems, cooling may be needed. When all the metal has reacted the pressure will begin to rise. The hydrogen is stored at a relatively low pressure, ~30 psi. To discharge the gas, slight heat needs to be added, however sufficient waste heat is available from the fuel cell. Little to no energy is required for hydrogen gas input to metal hydrides.

Sodium Borohydride. $NaBH_4$ in aqueous solution produces 4 moles of hydrogen when passed over a catalyst.

$$(2)\ NaBH_4 + 2H_2O \rightarrow 4H_2 + NaBO_2 + \text{Heat } 300\text{kJ}$$ [6]

Two moles of hydrogen come from the sodium borohydride and two moles of hydrogen come from the water. Therefore, the energy calculation only needs to be done for 2.5kgs of hydrogen. The process for making sodium borohydride involves reacting boric acid with methanol to produce tri-methyl borate, which is then reacted with sodium hydride at elevated temperatures. The product of equation (2) is essentially sodium tetraborate, more commonly known as Borax. We can use the exothermic heat as a very rough estimate for the absolute minimum energy required to change the sodium meta-borate back into sodium borohydride. The energy required, is 300 kJ per eight grams of hydrogen. This is equivalent to 10.48kWhr/kg of hydrogen. 5kgs of hydrogen requires 52.08 kWhrs, assuming an ideally reversible reaction.

Results

The energy calculated for the liquefaction of 5 kgs of hydrogen is 99.195kWh, which is a little bit high. A rule of thumb is that the energy it takes to liquefy the hydrogen is equal to the energy in 30% of the total amount of hydrogen liquefied. Using the upper heating value of hydrogen, 142MJ/kg, the energy for liquefaction should be about 65 kWhr for 5kgs of hydrogen. However, the energy to liquefy the hydrogen is much higher than the energy required to compress the hydrogen, which is ~12kWhr at 10000 psi for 5kgs of hydrogen. The energy for the sodium borohydride is similar to the energy for LH_2 at 52.08kWhr for 5 kgs. This number still needs to be verified, with data from the actual process. Metal hydrides have no energy requirements and look like the best option, when only considering the "energy input" metric. Two more common metrics of hydrogen storage technologies are specific storage density by weight (wt%) and specific storage density by volume (vol%). It is important to clarify if these numbers are for the material or the entire storage system. The following numbers are for storage systems.

Table 2. Weight and Volume % for Storage Systems

Technology	Wt%	Vol %
Liquid Hydrogen	7.50	0.03
CHG 5000 PSI	6.67	0.02
CHG 10000 PSI	6.00	0.03
Low Temp MH	5.45	0.06
Sodium Borohydride	4.50	0.02

Table two shows the comparison of total system weight and total system volume for the different storage technologies.

Discussion

The energy to store hydrogen is just one variable among many for deciding which storage option is best. There are many advantages and disadvantages for each option that need to be considered. The main advantage/disadvantage that people tend to take into account is cost of the storage material or technology and secondly, the relative safety of a particular technology. Sodium borohydride is very inert and no hydrogen is released without the addition of a catalyst. In addition, the raw material is relatively inexpensive. Another advantage, which may be minor, is the fact that the gas from the sodium borohydride is already humidified to a certain extent, because of the exothermic reaction and half the hydrogen is coming from the water. The largest challenge facing this technology is finding an economical way to recycle and charge the sodium borohydride. Right now, metal hydrides are still quite expensive for the material itself, and they need a certain amount of thermal management, which makes the storage system relatively complex. However, the material does not have any serious safety issues. Liquid hydrogen, is one of the more mature technologies, however, a tank can not be kept full longer than 30 days due to boil off issues. Compressed hydrogen offers the simplest delivery system of the hydrogen gas to the fuel cell, though it does need to be humidified. The high pressure tanks are also relatively expensive. Auto manufactures are concerned about the public's receptiveness to high pressure tanks. In reality, the different options will be chosen depending on the particular niche they are most suited for.

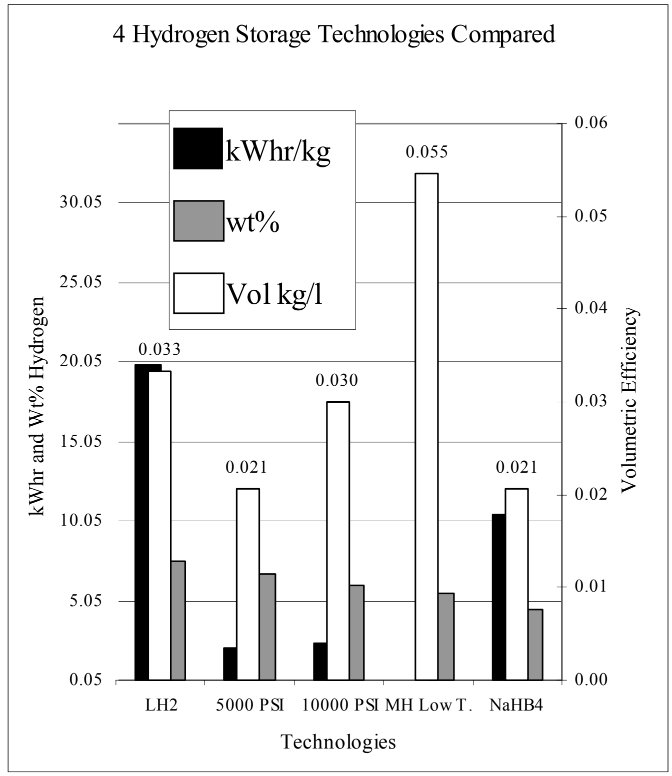

Figure 1. Comparison of kWhr/kg of hydrogen, total system weight and total system volume for four different storage technologies.

Conclusion

Figure one shows how difficult the decision is, to choose between the four technologies. By system weight % LH_2 is best. When looking at volumetric efficiency, metal hydrides are the best option. As far as energy to store the hydrides, metal hydrides are also the best option. However, two main factors are missing from this chart, cost of the system and the relative safety of the systems or public perception of the that safety. These two unknown factors will have a large impact on the best choice and will likely depend on the particular application the storage will be used in.

References

(1) Gardiner, M., Cunningham, J., Moore R.M., *Society of Automotive Engineers, Future Transportation Technology Conference*, **2001**, 2001-01-2531, p. 4.

(2) Noganow, L.S. "Hydrogen." *McGraw-Hill Encyclopedia of Science & Technology*. 7th edition. Vol. 8. New York: McGraw-Hill; **1992;** pp. 581-588.

(3) Timmerhaus, C.; Flynn, T.M. *Cryogenic Engineering*. Plenum Press: New York: **1989**.

(4) McCarty, D.R, "Hydrogen Technological Survey-Thermophysical Properties", Cryogentics Div, Inst. for Basic Stds. Nat. Bureau of Stds, Boulder CO. Sci. and Tech. Info. Office, Washington, DC **1975**

(5) Amos, W.A., *Costs of Storing and Transporting Hydrogen*, NREL/TP-570-25106 **1998**; p. C-5

(6) S. Amendola etal, "*A safe, portable, hydrogen gas generator using aqueous borohydride solution and Ru catalyst*", Int. J. Hydrogen Energy 25 **2000**; p.969-975