COMPARISON OF PRACTICAL HYDROGEN-STORAGE VOLUMETRIC DENSITIES

Arnold R. Miller, Kris S. Hess, and David L. Barnes
Vehicle Projects LLC
Denver, Colorado, USA
www.vehicleprojects.com

6 April 2007

INTRODUCTION

An industry-government partnership is developing prototype fuelcell locomotives leading to commercial locomotives that will:

- Reduce air pollution in urban and interurban rail applications, including yard-switching associated with seaports
- Increase energy security of the rail transport system by using a fuel independent of imported oil
- Reduce atmospheric greenhouse-gas emissions
- Serve as a mobile backup power source ("power-to-grid") for critical infrastructure on military bases and for civilian disaster relief efforts

These objectives address issues affecting the rail industry and transportation sector as a whole. As vehicle traffic continues to rise, American cities and interurban traffic corridors are suffering increasing levels of air pollution due to engine emissions from automobiles, trucks, and trains. Energy security and its effect on cost and supply are critical contemporary issues for the transportation industry. About 97% of the energy for the transport sector is based on oil, and more than 60% is imported. World oil reserves are diminishing, demand is increasing, and political instability threatens supply disruptions. A consensus has been reached that the burning of fossil fuels and consequent atmospheric release of carbon dioxide is a significant factor in global climate change. The greenhouse-gas effect is the likely cause of the melting of the polar ice caps and the increased severity of storms.

Furthermore, a need exists for large vehicles that serve, in addition to conveyance, as mobile backup power sources for critical infrastructure. Power-to-grid applications include military bases and civilian disaster-relief operations. Indeed, following Hurricane Katrina, a makeshift jail in New Orleans was powered by an Amtrak diesel-electric locomotive.

In previous projects, Vehicle Projects LLC has developed both hybrid and non-hybrid large industrial fuelcell vehicles. We have developed a fuelcell-battery hybrid underground mine loader [Miller, et al, 2004], [Miller, et al, 2006] and the world's first fuelcell-powered locomotive [Miller, 2000], [Miller and Barnes, 2002], an underground mine haulage vehicle, that was not hybrid. We are currently developing a fuelcell-battery hybrid switcher locomotive for urban and military rail applications [Miller, et al. 2007].

As part of our fuelcell locomotive program, commencing in May 2003, this paper reports the results of feasibility studies of locomotive onboard fuel storage.

RESULTS AND DISCUSSION

Storage of hydrogen onboard the vehicle is a greater technical challenge than producing power from a fuelcell. Technically mature methods of storage for large, high-power vehicles such as locomotives include (1) direct storage of hydrogen as a compressed gas, (2) direct storage as a liquid, (3) direct storage as a reversible metal hydride [Miller, 2005], (4) onboard chemical transformation to hydrogen of a carbon-based feedstock such as a hydrocarbon or alcohol, and (5) physical dissociation of liquid ammonia to hydrogen.

For industrial vehicles in general, and especially for locomotives, minimum volume of the fuel storage system or powerplant is more important than minimum weight. That is, high hydrogen volumetric density is more important than high gravimetric density. Table 1 displays the limits of hydrogen volumetric density for the five fuels abovementioned. These limits are a theoretical construct – they provide a measure of the best possible volumetric density that a given fuel can attain. They omit the volume of the container, associated hardware, and chemical processor. For example, if one had a liter of hydrogen at a pressure of 350 bar, but stored it in a tank with piping, etc, of infinitesimal volume, the liter would store 25 g of hydrogen, corresponding to a volumetric density of 25 g/L. In the case of methanol, which requires reacting the alcohol with water at high temperature over a catalyst to produce hydrogen according to the equation,

$$CH_3OH + H_2O \rightarrow 3H_2 + CO_2$$

the limiting volumetric density also omits the volume of the reactant water (in principle, water can be obtained from the fuelcell). The results show that, in the limiting case, the reversible metal hydride is capable of the highest hydrogen volumetric density, namely, 125 g/L, and compressed hydrogen at 350 bar, the lowest.

TABLE 1: LIMITS OF HYDROGEN VOLUMETRIC DENSITIES

Fuel System	**Conditions of Storage**	**H_2 Density, g/L**
Compressed H_2	350 bar (5,100 psi)	25
Liquid H_2	ρ = .070 g/mL (P = 1 bar, T = bp)	70
Methanol	ρ = .79 g/mL, (T = 25 C)	99
Liquid Ammonia	ρ = 0.62 g/mL, (P = 7.2 bar, T = 15 C)	110
Reversible Metal Hydride	AB_5 alloy ($LaNi_5$), ρ = 8.3 g/mL, wt % = 1.5, 10 bar	125

Real systems require volume for their hardware, e.g., tank, piping, and valves, as well as chemical reactors for methanol and ammonia. Thus, the theoretical volumes in data-column one of Table 2, based on the limiting densities of Table 1, are smaller than the practical system volumes in data-column two, which are based on actual systems. The volume of systems using a chemical processor, a methanol reformer or ammonia dissociator, depends on power. That is, greater power of the vehicle, and thus greater hydrogen flow, requires a larger chemical reactor. Because our vehicles store hydrogen mass on the order of 100 kg and produce power on the order of 300 kW gross, we computed the volumes of Table 2 for a system storing 100 kg of hydrogen and sustaining a power of 300 kW.

Accordingly, the theoretical volumes in Table 2 are computed simply as 100 kg storage / Theoretical H_2 density; e.g., for compressed hydrogen, 100 kg / 25 kg/m^3 = 4.0 m^3. (Note that c kg/m^3 = c g/L.)

The practical volumes of Table 2 were computed from the known volumes of actual systems. Practical system volume (PSV), which is the volume of the smallest rectangular prism closely enveloping the system, of the compressed-hydrogen system is based on Dynetek^{TM} W205H350G8N carbon-fiber composite tanks, plus ancillaries[Miller, et al, 2006]. The PSV for liquid-hydrogen storage is based on scaling of the

BMW Hydrogen 7^{TM} automotive system [Brunner, 2006]. Volume of the methanol-reformer system is the sum of six Hestia^{TM} reformers developed by Intelligent Energy [Intelligent Energy, 2006]; each Hestia system is capable of providing hydrogen flow to support up to 50 kW. The volume of the practical methanol system includes the reactant water, as well as the reformer hardware. PSV of the ammonia dissociator system is based on the scaled volume of the Intelligent Energy MesoChannel^{TM} ammonia dissociator [Powell, et al, 2003]. PSV of the metal-hydride system is based on the measured volume of the mine-loader storage system of Vehicle Projects LLC [Miller, et al, 2006].

TABLE 2: VOLUMES OF 100 kg, 300 kW STORAGE SYSTEMS

Fuel System	Theoretical (Limit) Volume, m^3	Practical System Volume (PSV), m^3
Compressed hydrogen	4.0	10.
Liquid hydrogen	1.4	3.9
Methanol Reformer	1.0	4.3
Ammonia Dissociator	0.90	2.3
Reversible Metal Hydride	0.80	5.0

Practical hydrogen volumetric densities for the five systems are easily calculated as 100 kg / PSV from the data in Table 2 and are shown in Table 3. "Storage Efficiency" is defined as the Practical Density / Theoretical Density x 100%. For example, liquid H_2 has a storage efficiency of 26 g/L / 70 g/L x 100% = 37%. Storage Efficiency is a measure of how closely a storage system approaches its volumetric density limit or theoretical density; it is a measure of how well the system lives up to its potential, the limits of Table 1.

TABLE 3: PRACTICAL HYDROGEN VOLUMETRIC DENSITIES

Fuel System	Practical H_2 Density, g/L	Storage Efficiency, %
Compressed Hydrogen	10	40
Liquid Hydrogen	26	37
Methanol Reformer	23	23
Ammonia Dissociator	44	40
Reversible Metal Hydride	20	16

The results in Table 3 reflect today's technology, and improvements or breakthroughs in technology could change the results and rankings. Today, compressed hydrogen at 350 bar provides the lowest practical hydrogen volumetric density (10 g/L) and liquid ammonia provides the highest (44 g/L); compressed hydrogen at 700 bar would approximately double the value for compressed storage. At 40% each, compressed hydrogen and ammonia share the distinction for having the highest storage efficiency. The reasons are quite different: The high storage efficiency of compressed hydrogen results from the simplicity of the system infrastructure, whereas the high efficiency of ammonia results from the inherent high volumetric density of a liquid fuel and the fact that ammonia dissociators, unlike hydrocarbon or alcohol reformers, are compact. The low storage efficiency of the metal-hydride system reflects the intricate heat exchanger necessary to achieve a refueling time of 10-15 minutes [Miller, et al, 2006]. A tradeoff between refueling time and storage efficiency would appear to be inherent to metal-hydride storage technology.

In choosing a hydrogen storage system for a vehicle, factors other than volume may be important. Four examples are weight, safety, cost, and thermodynamic efficiency.

CONCLUSIONS

In conclusion, for actual systems using today’s technology, liquid ammonia, at 44 g/L, has the highest practical hydrogen volumetric density. Compressed hydrogen, at 10 g/L, has the lowest. Compressed hydrogen and liquid ammonia, at 40% each, have the highest storage efficiency, and reversible metal hydride storage, at 16%, has the lowest.

REFERENCES

[Brunner, 2006] T. Brunner, Liquid Hydrogen Storage – Roadmap to Mass Market. Proceedings of the Intertech-Pira Conference “The 2006 Hydrogen and Storage Forum,” Vancouver, Canada, 11-13 September 2006

[Intelligent Energy, 2006] Hestia hydrogen generator, scalable platform brochure, Intellignet Energy, October 2005

[Miller, 2000] A. R. Miller, Tunneling and Mining Applications of Fuelcell Vehicles. Fuel Cells Bulletin, May 2000

[Miller and Barnes, 2002] A. R. Miller and D. L. Barnes, Fuel Cell Locomotives. Proceedings of Fuel Cell World, Lucerne, Switzerland, 1-5 July 2002

[Miller, et al, 2004] A. R. Miller, D. L. Barnes, Brian D. Hoff, Omourtag Velev, Lindsay Sheppard, Prashant Chintawar, and Mark Golben, Fuelcell-Battery Hybrid Mine Loader. Proceedings of 2004 Fuel Cell Seminar, San Antonio, USA, 1-5 November 2004

[Miller, 2005] A. R. Miller, Fuelcell Locomotives. Proceedings of Locomotive Maintenance Officers Association conference, Chicago, 19 September 2005

[Miller, et al, 2006] A. R. Miller, D. H. DaCosta, and M. Golben, Reversible Metal-Hydride Storage for a Fuelcell Mine Loader. Proceedings of the Intertech-Pira Conference “The 2006 Hydrogen and Storage Forum,” Vancouver, Canada, 11-13 September 2006

[Miller, et al, 2007] A. R. Miller, D. L. Barnes, K. S. Hess, and T. L. Erickson, Fuelcell Hybrid Switcher Locomotive. Proceedings of Locomotive Maintenance Officers Association conference, Chicago, September 2007 (in preparation)

[Powell, et al, 2003] M. Powell, A. Chellappa, T. Vencill, and T. Foster, Ammonia-Based Hydrogen Production for the Proposed Fuel-Cell Locomotive. Final report from Intelligent Energy (MesoFuel), commissioned by Vehicle Projects LLC, December 2003

ACKNOWLEDGEMENTS

We thank the following funders for their generous support of the projects described in this paper: US Department of Energy (contracts DE-FC36-99GO10458, DE-FC26-01NT41052, DE-FC36-01GO11095, and DE-FC36-05GO85049); Natural Resources Canada (Emerging Technologies Program contracts 23440-991022-001 and EA9730-F01-01); Government of Canada (Action Plan 2000 on Climate Change contract 23440-0310202-001); US Department of Defense (contracts F42620-00-D0036 and F42620-00-D0028); BNSF Railway Company; subcontractors to Vehicle Projects LLC who contributed project cost-share; and the Fuelcell Propulsion Institute. *Disclaimer*: Funding support from the US Department of Energy, US Department of Defense, Natural Resources Canada, Government of Canada, or BNSF Railway Company does not constitute an endorsement by same of the views expressed in this paper.