SUSTAINABLE HYDROGEN FOR THE HYDROGEN ECONOMY

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INTRODUCTION

Hydrogen has immense potential as an efficient and environmentally-friendly energy carrier of the future. It can be used directly by fuel cells to produce electricity very efficiently (> 50%) and with zero emissions. Ultra-low emissions are also achievable when hydrogen is combusted with air to power an engine or to provide process heat, since the only pollutant produced, NO_X, is then more easily controlled. To realize this potential, however, cost-effective methods for producing, transporting, and storing hydrogen must be developed.

Thermo Power Corporation has developed a new approach for the production, transmission, and storage of hydrogen. In this approach, a chemical hydride slurry is used as the hydrogen carrier and storage media. The slurry protects the hydride from unanticipated contact with moisture in the air and makes the hydride pumpable. At the point of storage and use, a chemical hydride/water reaction is used to produce high-purity hydrogen. An essential feature of this approach is the recovery and recycle of the spent hydride at centralized processing plants, resulting in an overall low cost for hydrogen. This approach has two clear benefits: it greatly improves energy transmission and storage characteristics of hydrogen as a fuel, and it produces the hydrogen carrier efficiently and economically from a low-cost carbon source.

Our preliminary economic analysis of the process indicates that hydrogen can be produced for $3.85 per million Btu, based on a carbon cost of $1.42 per million Btu and a plant sized to serve a million cars per day. This compares to current costs of approximately $9.00 per million Btu to produce hydrogen from $3.00 per million Btu natural gas, and $25 per million Btu to produce hydrogen by electrolysis from $0.05 per Kwh electricity. The present standard for production of hydrogen from renewable energy is photovoltaic-electrolysis at $100 to $150 per million Btu.

The overall objective of the current project is to investigate the technical feasibility and economic viability of the chemical hydride (CaH_2 or LiH) organic slurry approach for transmission and storage of hydrogen with analysis and laboratory-scale experiments, and to demonstrate the critical steps in the process with bench-scale equipment. Specific questions which have been addressed in work to date include:

- What is the formulation and physical properties of slurries that meet the energy density criteria?
- What are the organics that can be used to form the slurry?
- What are the conditions required for hydrogen generation?
- What are the properties of the slurry after hydrogen generation?
- What is the projected efficiency and cost of hydrogen production?

DISCUSSION

The way in which the metal hydride/water reaction would be used in a closed loop system for the storage and transmission of hydrogen is illustrated in Figure 1. The process consists of the following major steps: (1) slurrying the metal hydride with a liquid carrier and transporting it to the point(s) of use, (2) generating hydrogen on demand from the metal hydride/liquid carrier slurry at the point of use by adding water and then transporting the resulting metal hydroxide/liquid slurry back to the hydride recycle plant, and (3) drying, separating, and recycling the metal hydroxide to the metal hydride at the centralized recycle plant and returning the liquid carrier for reuse.

A variety of metal hydrides react with water at ambient temperature to produce high purity hydrogen. Examples of reactions are:

$$CAH_2 + 2H_2O \rightarrow Ca(OH)_2 + 2H_2 \uparrow$$
$$LiH + H_2O \rightarrow LiOH + H_2 \uparrow$$
$$LiBH_4 + 4H_2O \rightarrow LiOH + H_3BO_3 + 4H_2 \uparrow$$
$$NaBH_4 + 4H_2O \rightarrow NaOH + H_3BO_3 + 4H_2 \uparrow$$

The hydrogen generation capability of these hydrides when reacted with water is outstanding. For example, the volume of H_2 (STP) produced by complete hydrolysis of 1 kg (2.2 lb) of lithium hydride is 2800 liters (99 ft^3), and by 1 kg (2.2 lb) of lithium borohydride is 4100 liters (145 ft^3).

In Table 1, the energy density of these hydrides when reacted with water is presented and compared to gasoline, as well as the storage of H_2 as a liquid, gas, and a reversible hydride. The energy densities of the reactive hydrides are given on the basis of the initial hydride mass. The energy densities of the hydride/water reaction are respectable when compared to gasoline or methanol, with $LiBH_4$ having the highest energy densities on both a mass and volume basis. The heat of reaction must be removed during the H_2 generation.

The comparison is based on the energy densities of the initial hydride as a 50% slurry and the mass and volume of the storage container assuming a 20% void fraction in the container when the hydride is completely spent. The LiH, $LiBH_4$, and $NaBH_4$ hydrides exceed the volumetric energy density goal by moderate factors (1.09 to 1.64). LiH and $LiBH_4$ exceed the gravimetric energy density goal by moderate factors (1.03 to 1.41), with CaH_2 slightly lower than the goal. It should be noted that energy density is not the only criterion that needs to be compared. Other factors such as cost and ease of handling must also be considered. In summary, several hydride/water reactions exceed the performance goals for both the volumetric and gravimetric energy densities. An additional feature is the ability to generate H_2 on demand and to control the rate of reaction by regulating the rate of water addition to the hydride bed. If desired, H_2 can also be generated at a high pressure for direct use in pressurized fuel cells without compression.

PRELIMINARY DESIGN OF HYDROXIDE REGENERATION SYSTEM

A preliminary design of the hydroxide to hydride regeneration system was conducted to identify process stream conditions and to allow the major equipment components to be sized such that a capital equipment cost could be developed. The system is shown in Figure 2. The analysis was conducted for both lithium hydroxide and calcium hydroxide regeneration.

The material and energy balances for the two metals were conducted for a plant supplying hydrogen to 250,000 cars. Such a plant would produce enough slurry to produce 13 tons of H_2/hr. It would be small relative to typical chemical engineering projects, however. The first Fluid Catalytic Cracking (FCC) plant was three times larger and today's FCC plants are 25 times larger.

Lithium hydroxide is combined with carbon for the reduction and fuel, streams 1, 2a and 2b, to form stream 3, and is fed to the top of an indirect vertical heat exchanger, which preheats the incoming reactants while cooling the stream containing the lithium hydroxide, streams 5 and 6. The possibility for removing heat from the indirect fired process heater is also provided, streams 7 and 8. The hot preheated and partially reacted reactants, stream 4, enter the reduction reactor in which they are heated indirectly to the reaction temperature by combustion of the recycled carbon monoxide, stream 10, and additional fuel, stream 12, with preheated air, stream 11. The possibility of adding direct heat to the reactor is accomplished by adding oxygen to the reduction reactor by stream 9. The products of reduction leave the reduction reactor through stream 5. Within the reactant preheater, the lithium hydride is formed through the non-equilibrium kinetics as the mixture of lithium, hydrogen, and carbon monoxide is cooled. Additional heat is taken out of the product stream for the generation of electrical energy, which is added back into the reduction reactor to reduce the additional fuel.

The product, lithium hydride, is separated from the carbon monoxide in the hot cyclone, stream 16. This is further cooled to produce additional power, which is also added to the reduction reactor. The hot carbon monoxide, stream 15, is passed through a self recuperator to get a cold stream of CO, which could have a barrier filter installed to remove all the lithium hydride and a blower to circulate the CO, stream 18. This stream is reheated with the incoming CO and fed into the indirect process heater as discussed above. The hot combustion products leaving the solids preheater, stream 8, are used to preheat the combustion air and produce power, which is fed back into the reduction reactor. The energy efficiency of the hydrogen storage is obtained by dividing the heat of combustion of the hydrogen in the metal hydride by the heat of combustion of the carbon used for the reduction and the additional fuel. The results are: lithium (52.1%) and calcium (22.9%).

ECONOMICS OF THE APPROACH

The preliminary economics for the process are obtained by first developing a capital cost for the process equipment and then estimating the operating cost to define the needed sales price of the metal hydride for the required after tax return on the investment.

The capital equipment costs for the process are shown in Table 2 for the lithium process. These estimates, as well as the operating cost estimates, were obtained using standard chemical engineering practice. The operating cost assumptions are shown in Table 3.

The sensitivity of the cost of the hydride and the rate of return as a function of plant size and carbon cost is shown in Figures 3 and 4 for lithium. In Figure 3, the cost of hydrogen is plotted versus the plant size for four values of the cost of carbon. For a 250,000 car-per-day plant, the cost of hydrogen is on the order of $3.61 per million Btu at a carbon cost of one-cent per pound and a fixed return on the investment of 15 percent. In Figure 4, the effect of plant size and carbon cost for a fixed hydrogen cost on the rate of return is shown. In this case, if the hydrogen can be sold for a value of $4.57 per million Btu, the return to the investors can range from 15 to 65 percent, depending on plant size and carbon price. The same trends are seen for calcium.

SUMMARY AND FOLLOW ON ACTIVITIES

The results of the work to date are:

- Best Organic - Light Mineral Oil
- Best Hydrides -LiH & CaH_2
- +95% Hydrogen Release/Recovery
- Reaction rate controllable
- pH/Pressure Control
- Stable slurry
- Polymeric dispersants sterically stabilize the suspension
- Cost of Hydrogen $2.75 to $6.00 per 10^6 Btu

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3. Breault, Ronald W., Rolfe, J., and McClaine, A., "Hydrogen For The Hydrogen Economy," 24th Coal Utilization and Fuel Systems Conference, Clearwater, FL, March 8-11, 1999.

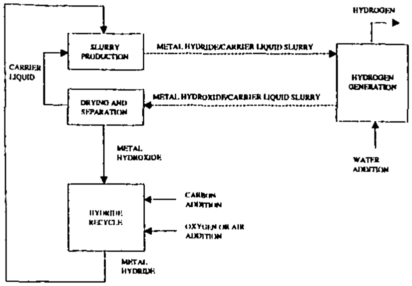

FIGURE 1. Simplified Process Diagram for Hydrogen Transmission/Storage With a Metal Hydride

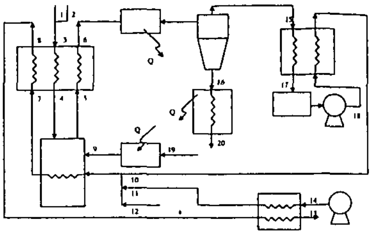

FIGURE 2. Hydroxide Regeneration System

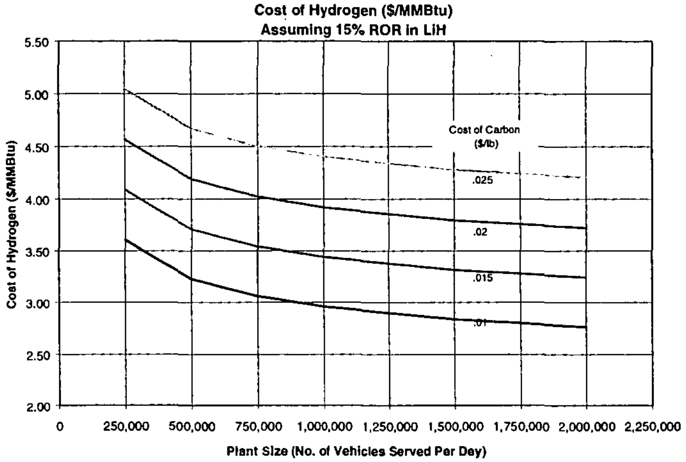

FIGURE 3. Sensitivity of Hydrogen Cost to Carbon Cost and Plant Size for Lithium Hydride

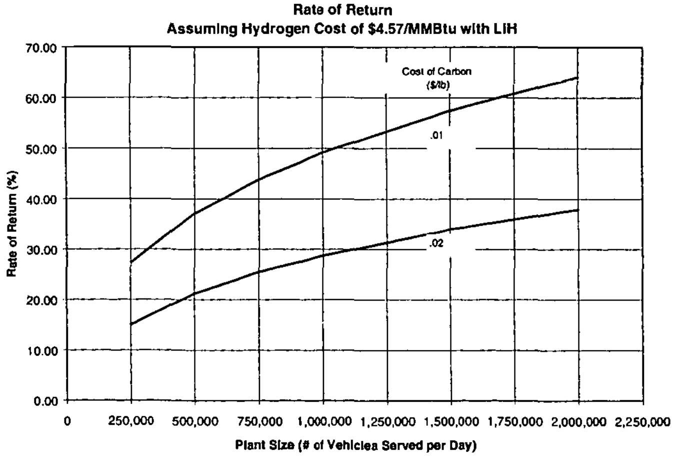

FIGURE 4. Sensitivity of Rate of Return to Carbon Cost and Plant Size for Lithium Hydride

TABLE 1. Comparison of Metal Hydrides to Other Hydrogen Storage Methods and Gasoline

Hydride	H_2 Volume Per Mass Hydride (STP ft^3/lb)	Energy Density		Water Reaction Enthalpy/HHV	Fraction Hydrolysis H_2 (lb H_2 per lb Hydride)	Hydride Density (gm/cm^3)
		HHV/Mass, Btu/lb	HHV/Bulk Volume (Btu/gallon)			
Ca H_2(1)	17.1	5,850	92,800	0.396	0.0958	1.90
Li H(1)	45.2	15,500	99,600	0.388	0.254	0.77
Li B H4(1)	65.9	22,600	124,500	0.212	0.370	0.66
Na B H4(1)	38.0	13,000	116,700	0.157	0.213	1.074
Fe Ti H(1.6)(2)	2.7	935	42,900	0.122(4)	0.0153	5.5
Liquid Hydrogen(3)	—	61,100	35,650	—	—	0.07
Gaseous Hydrogen (5000 psia, 300 K)	—	61,100	15,574	—	—	0.03058
Gasoline	—	20,600	130,000	—	—	—

(1) Reaction with Water
(2) Dissociation by Heating
(3) Liquid Fuel
(4) Based on Dissociation Energy

TABLE 2. Capital Cost - Lithium Hydride Regeneration

		Total cost
1	Furnace Cost, base 70m3	9,236,116
2	Solids preheater, 70 m3	9,236,116
3	Condensor, base 100MW	-
4	Hydride Reactor, Base 35m3	720,417
5	Blower, H2 from sep.base, 75m3/s	270,254
6	Steam Turbine Generator	25,693,663
7	Cent Slurry sep.	189,413
8	Hydride cooler, base 70 m3	9,236,116
9	Heat Exch/recuperator, base 20e9J/s	2,814,328
10	Hydrocarbon Decomp, base 100MW	-
	Sum, Total Cost	57,396,424

TABLE 3. Operating Cost Assumptions

Carbon	Variable, \$0.67 to 1.67/10^6 Btu
Fuel	\$2.5/10^6 Btu
Labor -Operators -Supervision & Clerical	 25 at \$35,000/yr 15% of Operators
Operators	
Supervision & Clerical	
Maintenance & Repairs	5% of Capital
Overhead	50% of Total Labor and Maintenance
Local Tax	2% of Capital
Insurance	1% of Capital
G&A	25% of Overhead
Federal and State Tax	38% of Net Profit