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Hydrogen For A PEM Fuel Cell Vehicle Using A Chemical-Hydride Slurry

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Abstract

Over the last ten years, there have been extensive efforts to identify candidates for the onboard storage of pure hydrogen for fuel cell vehicles (FCVs). These candidate technologies include: 1) compressed hydrogen, 2) liquefied hydrogen, 3) rechargeable metal hydride, 4) carbon adsorption and hybrid systems, and 5) liquid hydrides and other chemical hydrides. However, the volume and/or weight energy densities of these onboard hydrogen storage technologies are significantly lower than those of internal combustion engines or the DOE hydrogen program goals. Therefore, development of a high energy density subsystem to supply hydrogen for a fuel cell operation remains a critical technology for the successful development of FCVs.

To supply high-purity hydrogen for FCV operation, Thermo Power Corporation has developed an advanced hydrogen storage technology. In this approach, a chemical (light metal) hydride/organic slurry is used as the hydrogen carrier and storage media. At the point of use, high purity hydrogen will be produced by reacting the hydride/organic slurry with water. The fluid-like nature of the hydride/organic slurry will provide us a unique opportunity for pumping, transporting, and storing these materials. The final product of the program is a user-friendly and relatively high energy storage density hydrogen supply system for fuel cell operation. In addition, the spent hydride can relatively easily be collected at the pumping station and regenerated utilizing renewable sources, such as biomass, natural gas, or coal at the central processing plants. Therefore, the entire process will be economically favorable and environmentally friendly. This paper presents test data from development tests and the design of an on-board system.

Introduction

Because of the inherent advantages of high efficiency, environmental acceptability, and high modularity, fuel cells are potentially attractive power suppliers. Worldwide concerns over clean environments have revitalized research efforts on developing fuel cell vehicles (FCVs). As a result of intensive research efforts, most of the subsystem technologies for FCVs are currently well established. These include: high power density PEM fuel cells, control systems, thermal management technology, and secondary power sources for hybrid operation. For mobile applications, however, supply of hydrogen or fuel for fuel cell operation poses a significant logistic problem.

Currently, various technologies have been considered to provide hydrogen for FCVs. These technologies can be conveniently classified into two categories: 1) onboard fuel processing, wherein liquid fuel stored on the vehicle undergoes reformation and subsequent processing to produce hydrogen; and 2) onboard storage of pure hydrogen provided by stationary fuel processing facilities. Onboard liquid hydrocarbon reforming provides an attractive way to supply hydrogen at a high system power density. In high-temperature fuel cells, such as solid oxide fuel cells, low molecular weight hydrocarbons may be used directly via direct internal reforming. However, these types of fuel cells are not suitable for FCVs, since they may require frequent on/off cycling. Although there has been limited success in direct methanol-powered PEM fuel cell technology, fuel crossover and CO poisoning still pose significant problems, and long-term performance is yet to be demonstrated.

Over the last ten years, there have been extensive efforts to develop a reforming process to produce hydrogen from liquid fuels. As a result, numerous hydrocarbon reforming processes have been established. However, the product gas streams usually contain high levels of contaminants, such as CO. The presence of CO in the fuel gas stream is harmful to many fuel cells, especially PEM fuel cells, since the performance of the PEM fuel cell is substantially degraded over a short period of time via the catalyst poisoning. Despite costly efforts, limited success has been achieved in controlling the CO content in the fuel gas stream. We believe that the conventional approach to reform liquid hydrocarbons to produce hydrogen cannot meet the stringent requirements in fuel quality for the PEM fuel cells.

A great many technologies have also been investigated as candidates for the onboard storage of pure hydrogen for FCVs. These technologies include: 1) compressed hydrogen, 2) liquefied hydrogen, 3) rechargeable metal hydride, 4) carbon adsorption and hybrid systems, and 5) liquid hydrides and other chemical hydrides. However, the volume and/or weight energy densities of these onboard hydrogen storage technologies are significantly lower than those of internal combustion engines or the DOE hydrogen plan. Therefore, development of a high energy density subsystem to supply hydrogen for fuel cell operation is an urgently needed technology for the successful development of FCVs.

To supply high purity hydrogen for FCV operation, Thermo Power Corporation's Advanced Technologies Group will use an advanced hydrogen storage technology. In the approach, a metal hydride/organic slurry is used as the hydrogen carrier and storage media. At the point of use, high-purity hydrogen will be produced by reacting the metal hydride/organic slurry with water. In addition, Thermo Power has conceived the paths for recovery and regeneration of the spent hydride (practically metal hydroxide). The fluid-like nature of the spent hydride/organic slurry will provide us a unique opportunity for pumping, transporting, and storing these materials. The final product of the program will be a user-friendly and relatively high energy storage density hydrogen supply system for fuel cell operation. In addition, the spent hydride can relatively easily be collected at the pumping station and regenerated utilizing renewable sources, such as biomass, natural gas, or coal, at the central processing plants. Therefore, the entire process will be economically favorable and environmentally friendly.

Background And Technical Approach

Hydrogen (H_2) has been suggested as the energy carrier of the future. Like electricity, it is not a primary energy form, but rather serves as an energy carrier through which a primary energy source can be transmitted and utilized. Hydrogen has a number of advantages as an energy carrier, but several problems restricting widespread use of H_2 exist. These problems include: 1) poor energy storage characteristics, and 2) relatively high production cost compared to fossil fuels. For example, specific weight and specific volume of most hydrogen storage technologies, both currently available and advanced future technologies, are not suitable for transportation applications. Some advanced technologies may satisfy the requirements of the DOE hydrogen plan, however, operational energy loss and infrastructure requirements may not be appropriate for transportation applications in the near future. Pros and cons of the currently available and advanced hydrogen storage technologies, along with expected performance of the proposed technology, are summarized in Table 1. A plot showing how chemically-reacting hydrides compare with other fuels is shown in Figure 1.

Table 1. Hydrogen Storage Technology Status.

Storage Technology	Specific Weight (HHV)		Specific Volume (HHV)		Remarks
	Wh/kg	%H_2	Wh/L	kg H_2/m^3	
DOE Goal • Liquid/Gas	3963/5323	9.9/13.4	1100/828	28/21	-DE-RA02-97EE50443
Liquid H_2 • Cryogenic	6350	16.1	1250	32	-Not including boil-off loss
Gaseous H_2 • 5000 psia	2630	6.7	780	20	-Could be better with new high-pressure tanks
Carbon Adsorption • 794 psi at 78°K	2858	7.2	1535	39	-New materials with better capacities
Liquid Hydride • Methylcyclohexane	2070	5.9	1618	46	-Need more fundamental research
Proposed Chemical Hydride Slurry • CaH_2	2670	6.8	2430	62	-Includes weight and volume of the container, and ancillary components -Does not include reactant water, which is assumed to be provided partially from exhaust gas
• LiH	5050	12.8	2430	62	
• $NaBH_4$	4760	12.1	2570	65	
• $LiBH_4$	6350	16.1	2640	67	

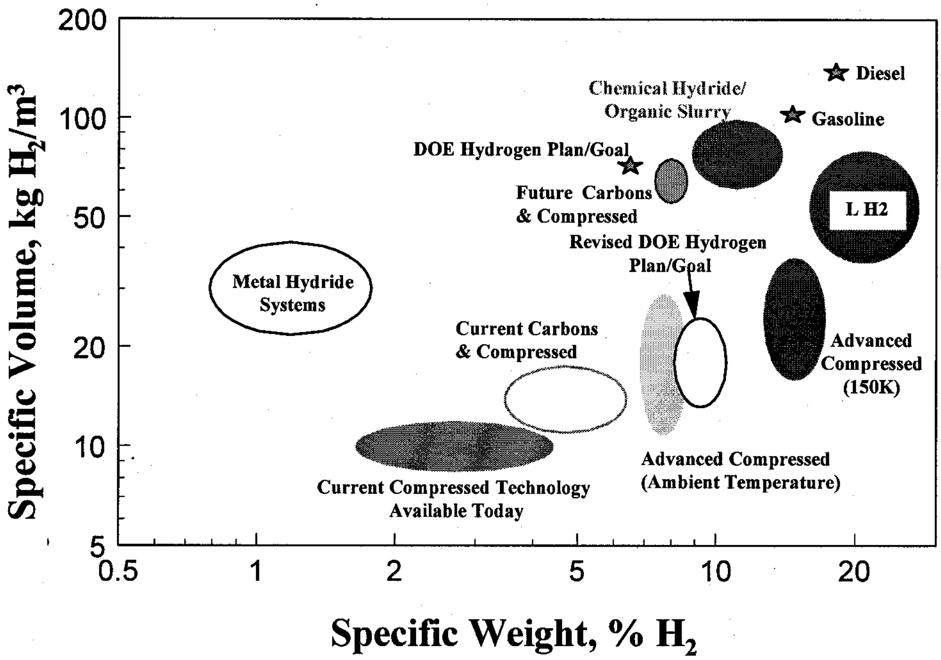

Figure 1. Summary of Current and Future Hydrogen Storage Systems

This paper addresses a new approach, which greatly improves the energy transmission and storage characteristics of H_2 as a fuel for transportation and industrial applications. An essential feature of the approach is to develop a relatively high energy storage density hydrogen supply system based on exothermic chemical reactions between metal hydrides and water. Hydrogen production via metal hydride and water reactions is a well-established industrial process. In fact, several groups of researchers have investigated the metal hydride/water reaction process to supply hydrogen for fuel cells for mobile power generations. In this research, it has been identified that reaction rate control, frequent on/off operation, and safety of the operation could be significant problems for high energy density operations.

One of the key technical challenges in the program is, therefore, to precisely control the metal hydride and water reaction. In the program, the continuous organic slurry media will act as a path for dissipating heat that is generated from the hydride/water reaction. Furthermore, by controlling surface chemistry of the organic media, the water/metal hydride reaction rate can easily be controlled. This concept is shown in Figure 2. In Figure 2a, a sketch is shown of two hydride particles, one surrounded by oil and one not. The oil layer inhibits the water access to the hydride and thereby controls the rate of reaction, which would otherwise be explosive. In Figure 2b, the hydride suspension is shown to exemplify how the dispersant acts to hold the particle in suspension within the oil and further inhibit the reaction with water.

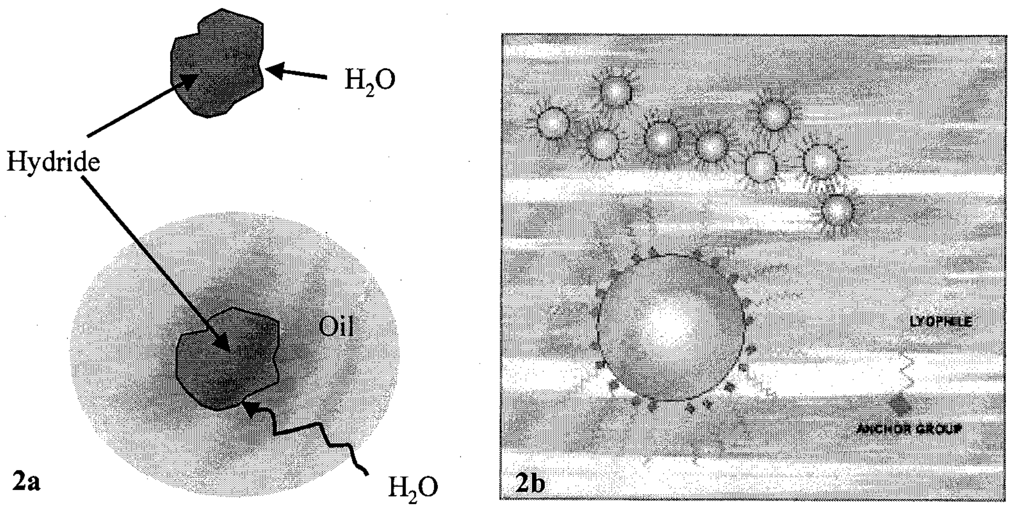

Figure 2. Hydride-Water Reaction Concept

There are several factors needing consideration in hydride selection and storage system design. As an example, calcium hydride (CaH_2) has been selected to illustrate some of the technical aspects and advantages of the concept, even though it does not have the highest volumetric or gravimetric energy density of the hydrides (Table 1). These advantages include low raw stock (calcium hydroxide) material cost and readily available technical information on material properties and process reactions. Regarding safety, CaH_2 is highly ionic and insoluble in all common inert solvents. It can be handled in dry air at room temperature without difficulty. Only when heated to about 900°F will it react with air to form both calcium oxide and calcium nitride. CaH_2 is substantially inert to organic compounds that do not contain acidic hydrogen. CaH_2 reacts vigorously with water to form calcium hydroxide and hydrogen gas. $Ca(OH)_2$ is slaked lime and non-hazardous. It is a component of mortar, plaster, cement, and other building materials, and is widely used without difficulty.

Because of the reaction rate control afforded by the organic media, the hydrogen reactor can be a simple device. Water and hydride slurry are metered into the reactor, where they are thoroughly mixed to ensure complete reaction. This reaction goes to completion quickly, leaving a powdery waste. Hydrogen production rate is controlled by the injection rate of water and hydride. Heat released by the reaction can be absorbed by the evaporation of water. No complicated control systems are needed to ensure proper and safe operation of the hydrogen reactor.

The water required for thermal control and hydrogen reaction is provided by condensed vapor from the hydrogen fuel cell. Only a small reservoir of water is required for startup, makeup, and surge demand. Thus, the required water does not significantly affect the volumetric and gravimetric energy storage densities.

The slurry form of hydride has other benefits beyond reaction control. The hydride fuel can be handled as a liquid, simplifying transportation, storage, and delivery. Use of a slurry permits refueling similar to current gasoline filling stations, allowing the tank to be easily topped-off at any time. The hydroxide waste products produced by the hydrogen system can be washed from the onboard storage tank during the slurry filling operation. Both the hydride fuel and hydroxide waste product can be easily transported between the distribution centers and a central recycling plant.

The used reactant slurry containing LiOH is returned to a central processing plant where the LiOH is recycled to LiH in a large-scale chemical process. The LiH is remixed with the slurry fluid and transported back to refueling stations scattered over a large area as needed. The basic energy input to the system is provided at the central plant and can be from a variety of energy sources, including fuels like coal, biomass, natural gas, and petroleum oil. All environmental emissions occur at the central processing plant. The vehicle is zero emission, with no hydrocarbon, CO, or CO_2 emissions. The central plant can include more sophisticated emission cleanup processes than would be possible for an onboard processing system.

An important concept feature that needs to be pointed out is the recovery and recycle of the spent hydride at centralized processing plants using a low cost fuel, such as coal or biomass. Regeneration process analysis has indicated that recycling can be performed utilizing a carbothermal process with minimum energy input and at a low cost. Compared to current hydrogen costs of about \$9.00 to \$25.00 per million Btu, this concept should enable hydrogen costs as low as \$3.00 per million Btu to be realized for a LiH system[1&2]. Also, because the hydride reaction will liberate only pure hydrogen, fuel cell catalyst life should be maximized, resulting in high system performance and reliability.

The Bench-top Prototype System

At the completion of the program, we will have a prototype system, which can supply 3.0 kg/hr of pure hydrogen for fuel cell operation (50 kW electric power equivalent, assuming 50% fuel cell efficiency). This system concept, shown in Figure 3, includes: 1) a hydride/hydroxide tank, pumps for hydride/organic slurry charge/discharge, a water addition device, a water/hydride reactor, a pressure/temperature measurement and control unit, and a connecting port to the fuel cell stack. A race for the development of zero emission vehicles has already begun across the globe. Developing a reliable hydrogen source for fuel cell operation is the most serious technical challenge in developing fuel cell vehicle technology. Thermo Power's advanced metal hydride-based hydrogen supply system will fully satisfy all the requirements for FCV development.

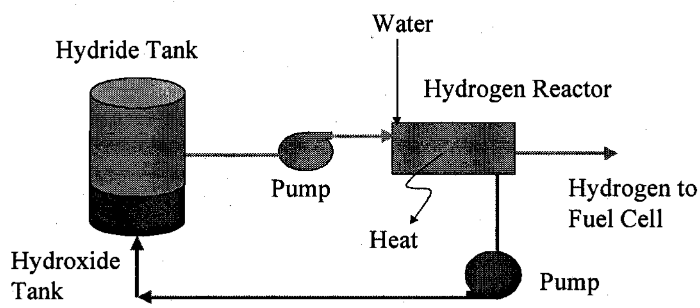

Figure 3. Hydrogen – Hydride Concept

Thermo Power is developing a prototype, 50 kW electric power equivalent hydrogen supply system utilizing an innovative chemical hydride/organic slurry technology. The development effort is comprised of two stages. During the first stage, we optimized the hydrogen generation efficiency of the proposed process utilizing a laboratory-scale reactor unit (1 kW equivalent). In the second phase, we are fabricating and will evaluate the performance of a prototype hydrogen supply system for 50 kW fuel cell systems. The specific technical objectives are to:

- Investigate and select metal hydride and organic slurry materials to achieve maximum specific energy.
- Optimize the hydride/organic selection for minimum weight and high stability.
- Develop a system for quick, complete activation of the hydride with minimum weight.
- Establish thermal management design for a prototype system including heat dissipation and use.
- Design and fabricate a 50 kW-equivalent prototype system.
- Evaluate and optimize performance of the prototype system.
- Complete hydrogen supply system integration into simulated power sources and performance evaluation.

Developmental Prototype

The major objectives of this hydrogen generation development effort are twofold. The first is to use a laboratory-scale system to determine optimum materials and hydrogen generation process conditions to achieve high specific energy for hydrogen supply. The second objective is the design and fabrication of a prototype hydrogen generation system capable of supplying 3.0 kg/hr of high purity hydrogen for fuel cells.

Although there are numerous metal hydrides and organic carrier candidate materials, only a limited number of metal hydrides and organic carrier materials can be used to satisfy DOE's goals of specific weight and volume. One of the essential considerations for the metal hydride is its hydrogen generation efficiency, which includes reaction chemistry between metal hydride and water to complete hydrolysis reactions in a safe and controlled manner. The organic carriers should be chemically inert toward metal hydrides and spent hydrides for storing and transporting, and during hydrolysis reaction. These materials also should be easily separated from spent hydrides, either thermally or mechanically, and be recycled for reuse. Although regeneration of the spent hydrides is not part of the technical effort of this program, it is an important issue for economical and commercial development of the technology.

In the initial effort, we thoroughly analyzed, both theoretically and experimentally, the reaction chemistry of a variety of metal hydrides and water, and the chemical stability of the organic carriers in contact with metal hydrides and spent hydrides. Since detailed hydrolysis reaction kinetics of the metal hydride/organic carrier slurry were not known, we conducted experiments using a high-pressure (2000 psi) and high-temperature (232°C) vessel with temperature, pressure, and magnetic stirrer control capabilities (500 cm^3 internal volume). For this investigation, we selected the candidate materials based on the guidelines listed in Table 2.

Table 2. Considerations for Selecting Metal Hydrides and Organic Carriers

Metal Hydrides	Organic Carriers
• High specific energy density • High hydrogen generation efficiency • Relatively inert during storage before and after reaction with water • Ease of regeneration • Low costs	• Non-reactive with metal hydrides and spent hydrides • Low molecular weight • Easy to recycle (easy to separate from spent hydride and water, and to collect for reuse)

In the development of a hydride/water activation system, several ideas were considered. These are:

- Single Tank Reactor
- Slurry Atomization Reactor
- Water Bathed Reactor
- Auger-aided Water Vaporizing Reactor

The single tank reactor, shown in Figure 4, is the simplest system. However, several problems exist for this system. The heat exchanger allows hot spots, increasing hydrocarbon contamination. It will also have a slow response to H_2 demand. Furthermore, it is likely that not all hydride will react, leaving a hazardous waste product, and a large volume containing pressurized hydrogen exists.

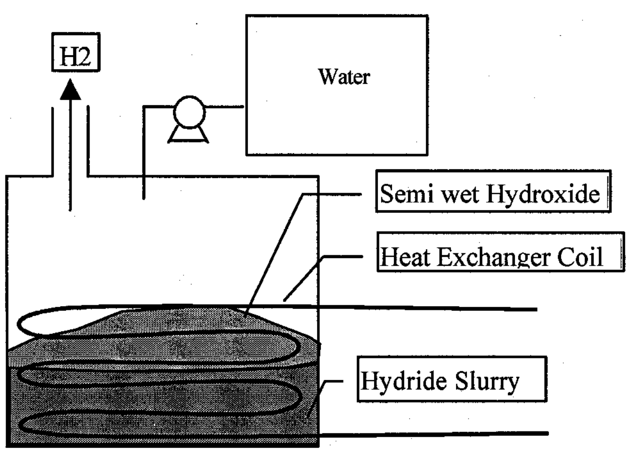

Figure 4. Simple One Tank Concept

The atomized slurry reactor, shown in Figure 5, was conceptualized to remove heat from 15µm droplets by direct hydrogen heat transfer. This system is complicated and has a wear-prone slurry atomization system. The ½ m^3/sec H_2 flow rates needed for cooling are quite high. In addition, the heat exchanger may be fouled by dust. There is also the likelihood of poor hydride/water mixing reducing generation efficiency, and a large pressurized hydrogen volume is required.

In the water-bathed reactor configuration, shown in Figure 6, heat is removed by the recirculated flow of water. Excess water assures low reaction temperature and complete reaction in a relatively small water to air heat exchanger. Problems, such as the water soaked LiOH waste product and the weight of wasted water, push this concept outside the system goals. The water could be separated by a filter or a filter press, but neither a filter or filter press system allows the concept to reach the weight goals. Also, unfiltered particles will wear the recirculation pump.

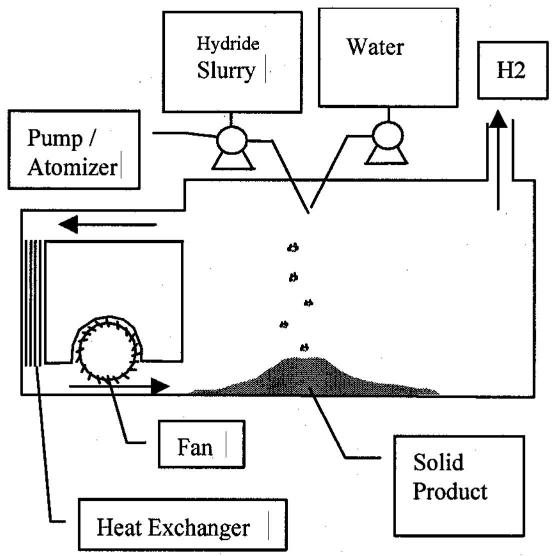

Figure 5. Atomized Slurry Reactor Concept

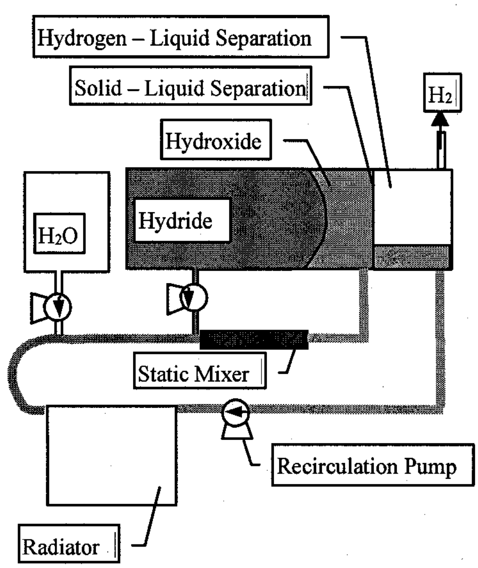

Figure 6. Water Bathed Reactor Concept

In the auger-aided reactor, shown in Figure 7, reactants are pumped to a mixing auger. At 300 rpm, the auger mixes, crushes particles, and eliminates foaming within the hydrogen generation reactor. The waste product contains 10% by mass of water and is a dry, free-flowing powder. About three times the stoichiometric water is added and vaporized by the heat of reaction to control the temperature.

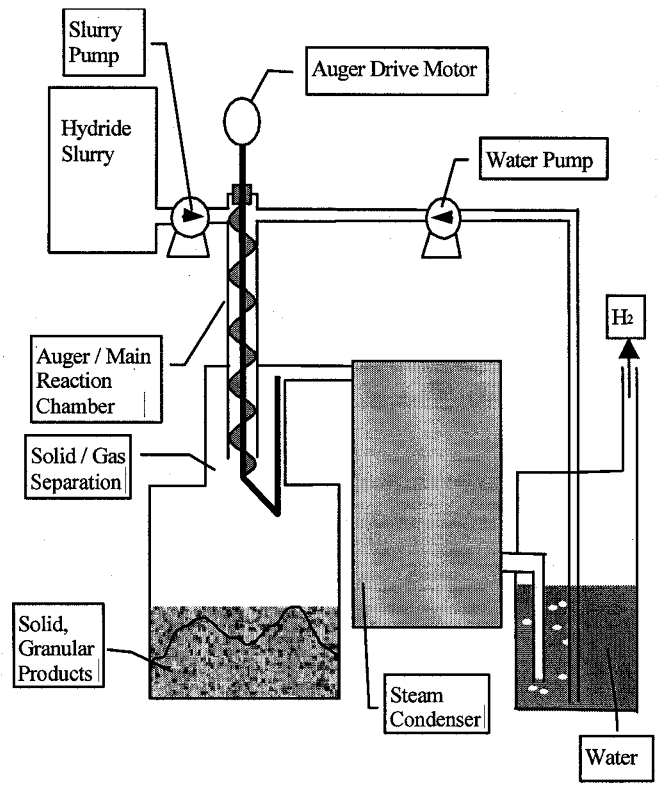

Figure 7. Auger-Aided Reactor Concept

The hydrogen water vapor content in the auger-aided reactor depends on the heat exchanger outlet temperature. Vapor condensation is slowed by the presence of hydrogen, increasing the size of the heat exchanger. The water vapor content could also be reduced by using hydride as a desiccant. This hydrogen production system device achieves the weight and volume goals.

Based on the preliminary analysis and testing of the various concepts discussed above, a prototype system to produce up to 3 kg/hr of hydrogen was designed. This system is shown in Figure 8. To produce the hydrogen, 0.5 l/min 60% LiH slurry flows into the auger reactor, along with 1.4 l/min water for reaction and vapor cooling. The system produces up to .75 kg hydrogen per run. A 1.6 gallon SS reservoir of 60% LiH slurry, a 5.5 gallon SS water reservoir, and a 12 gallon SS hydroxide container make up the reactant and product volumes. A computer controls the hydride and water pumps. Data acquisition of pertinent pressures, temperatures, hydrogen flow, hydrocarbon, and water vapor content are recorded. The system is self-contained on a rolling cart.

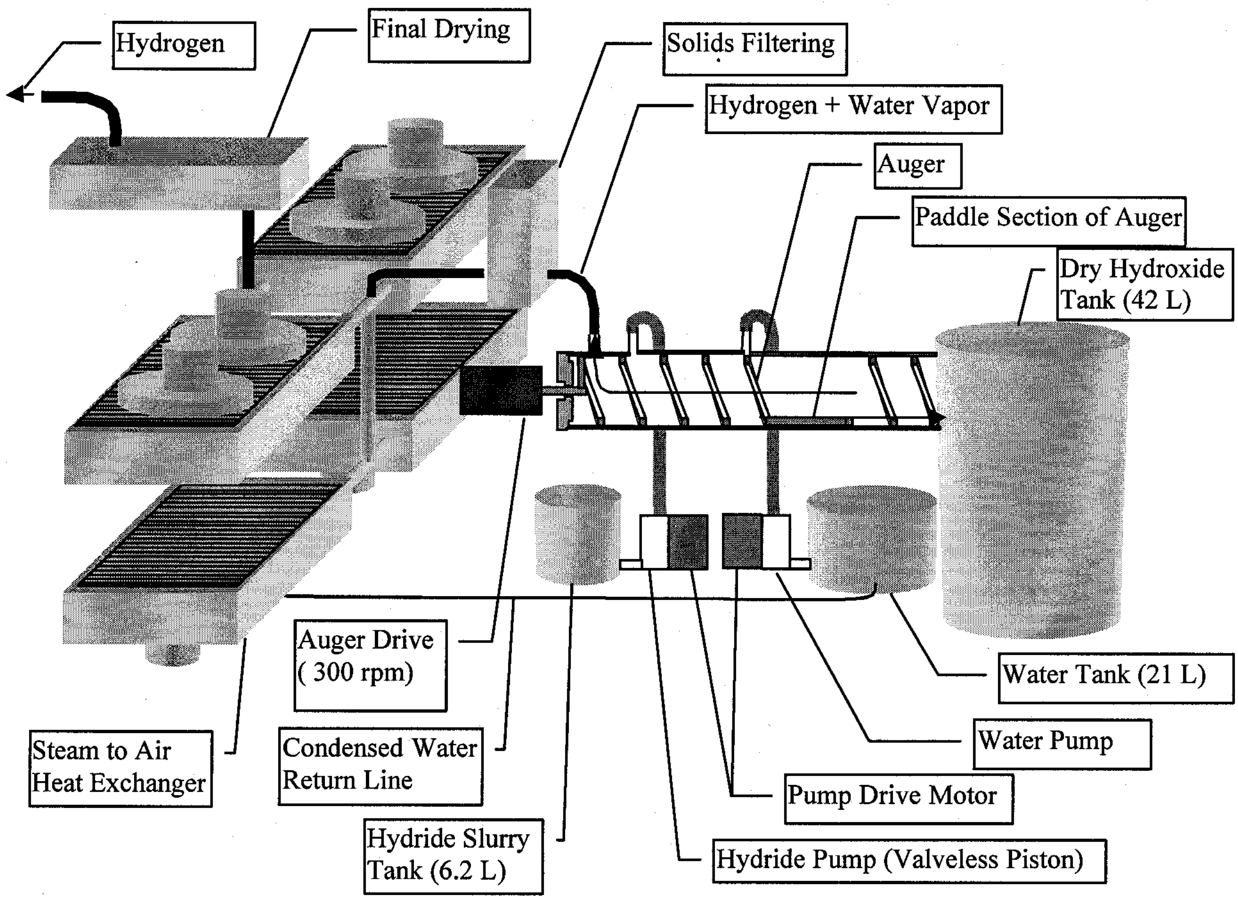

Figure 8. Auger-Aided Reactor System Being Built

A valveless ceramic piston pump is used for the LiH slurry and a gear pump is used for water flow. Four heat exchanger cores with 8-10" fans are used to condense the water from the hydrogen. Table 3 summarizes the energy mass and volumetric densities for the system. The system is capable of achieving the 3355 Whr/kg and 929 Whr/l goals.

Table 3. System Mass and Volumetric Design Summary

Run Time (hr)			5			
Hydrogen Energy (Watt*hr)			603500			
Mass Of Hydrogen (kg)			15			
Goals (watt-hr/kg, watt-hr/liter)			3355	929		
System Goals (kg, l)			179.9	649.6		
					Projected System	
		#	Wt (kg)	Vol (L)	Wt (kg)	Vol (L)
65 % Lithium Hydride Slurry		1	95.5	111.5	95.5	
Hydroxide		1	178.17	310		
Heat Exchanger	Direct Gas to Air HX Copper Tube, Aluminum Fin	3	10.46	27.5	31.38	82.5
Hydride Tank	Stainless	1	20	120	20	120
Hydroxide Tank	Plastic	1	12	310	12	310
Hydride Metering Pump	Valveless Piston	1	6.8	4	6.8	4
Water Metering Pump	Gear Pump	1	3	2.5	3	2.5
Auger Drive Motor	1/8 Hp, 5.5:1 DC Gear Motor	1	4	2.3	4	2.3
Auger Construction	SS Materials	1	5	10	5	10
Total					177.7	531.3
System Goals (kg, l)					179.9	649.6
Total -System Goals					-2.2	-118.3
System Values (watt-hr/kg, watt-hr/liter)					3397	1136
Goals (watt-hr/kg, watt-hr/liter)					3355	929
System Values - Goals					42	207

Summary

In summary, the following can be stated:

- A hydride/water activation process (the hydrogen generation reactor) has been developed.
- Thermal management design for prototype system has been established.
- A chemical hydride slurry can be used to generate hydrogen for transportation vehicle applications.
- The system has the potential to be safe and easy to use.
- Chemical hydride-based systems can achieve DOE's energy density goals.

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