Production of hydrogen from chemical hydrides via hydrolysis with steam

Michael, A. Matthews, Thomas A. Davis, Jason Crews, and Eyma Y. Marrero-Alfonso
University of South Carolina
Department of Chemical Engineering

This is an investigation of a gas/solid chemical reaction between steam and chemical hydrides that liberates pure hydrogen gas. The aim is to obtain fundamental kinetic, chemical, and thermodynamic data on the reaction so that sufficient information is known to evaluate this technology rigorously for its potential as a means of delivering hydrogen for fuel cells and internal combustion engines. In this paper we report on the rates and yields of the reaction under different conditions and the characterization of the hydrated solid by-products.

It is known that simple chemical hydrides (e.g. LiH, CaH_2) as well as complex hydrides ($NaBH_4$, $LiBH_4$, and others) react with liquid water to produce H_2. For example, $NaBH_4$ has been extensively studied:

$$NaBH_4 + (2+x)\ H_2O \rightarrow 4H2 + NaBO_2 \cdot xH_2O + \text{heat} \quad (1)$$

In equation 1, x is the “excess hydration factor”, representing the fact that the solid byproduct can exist in varying degrees of hydration. The liquid-phase reaction has some disadvantages. For example, in aqueous hydrolysis of $NaBH_4$, an acid catalyst is required [2] to liberate 100% of the hydrogen, because dissolved $NaBH_4$ is stable in basic solution, and the byproducts (sodium borate and similar compounds) are basic in solution. In reaction (1), the ideal case is where $x = 0$, in which case the mass yield is 10.3 kg H_2 per 100 kg of reactants. In practice, excess water is required so that the $NaBH_4$ and byproducts remain completely dissolved. Excess water reduces the mass efficiency of the system.

A recent discovery [1] shows that by vaporizing water prior to contact with the hydride, hydrogen yields in excess of 90% may be obtained without the need for a catalyst. Thermodynamic considerations show that, in principle, the heat liberated by the reaction is more than sufficient to vaporize the stoichiometric water required for the steam. Thus, there is the possibility of developing a hydrogen reactor/delivery system that is autothermal at steady state, that produces pure hydrogen in 100% yield, that requires no catalyst, that does not involve strongly caustic solutions, and that uses a minimum of water. Furthermore, the solid reaction products should be nearly free of water, which in the long term will facilitate recycling and regeneration to the hydride.

The steam hydrolysis system used in this work consists of a quartz tube reactor inside a furnace that keeps the temperature constant. All experiments are conducted with one gram of $NaBH_4$, which is mixed with glass beads and then loaded into the reactor between glass-wool plugs. After loading, the reactor is purged with nitrogen until the hydrolysis begins. Water is pumped at the desired constant flow rate (0.1mL/min, 0.006mol/min) to a steam generator. Steam flows through the reactor, and both hydrogen as well as unreacted water exit the reactor. Condensable water is removed in a cold trap, and the humid hydrogen is dried with a gas drier. The volumetric flow rate and cumulative volume of hydrogen are measured as the volume of water is displaced from an Erlenmeyer flask to a graduated cylinder.

Figure 1 shows the volume of hydrogen collected over the course of the experiments. The horizontal line labeled “Theoretical Yield” shows that 2,550 mL (0.106 mol) of H_2 can be produced from 1 g of $NaBH_4$ at 100% conversion. The three lines labeled “Theoretical rates” were calculated based on the Equation (1), assuming that water is the limiting reactant and that the reaction is instantaneous. For example, if no excess water is added (x=0) and the water flow rate is 0.1

Report Documentation Page	*Form Approved* *OMB No. 0704-0188*

1. REPORT DATE **01 NOV 2004**	2. REPORT TYPE **N/A**	3. DATES COVERED **-**

4. TITLE AND SUBTITLE **Production of hydrogen from chemical hydrides via hydrolysis with steam**	5a. CONTRACT NUMBER
	5b. GRANT NUMBER
	5c. PROGRAM ELEMENT NUMBER
6. AUTHOR(S)	5d. PROJECT NUMBER
	5e. TASK NUMBER
	5f. WORK UNIT NUMBER
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) **Department of Electrical Engineering, University of South Carolina, Columbia, SC 29208, USA**	8. PERFORMING ORGANIZATION REPORT NUMBER
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)	10. SPONSOR/MONITOR’S ACRONYM(S)
	11. SPONSOR/MONITOR’S REPORT NUMBER(S)

12. DISTRIBUTION/AVAILABILITY STATEMENT

Approved for public release, distribution unlimited

13. SUPPLEMENTARY NOTES

See also ADM001789, Fuel Cell Technology Hybrid Advanced Fuel Cell Power Sources.

14. ABSTRACT

15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT **unclassified**	b. ABSTRACT **unclassified**	c. THIS PAGE **unclassified**	**UU**	**4**	

mL/min (0.0055 mol/min), the theoretical rate of hydrogen production is 0.011 mol/min, which is the slope of the line shown in the graph.

Figure 1. Experimental H_2 yield for 1 gram of $NaBH_4$ at 110^{o}C & 140^{o}C

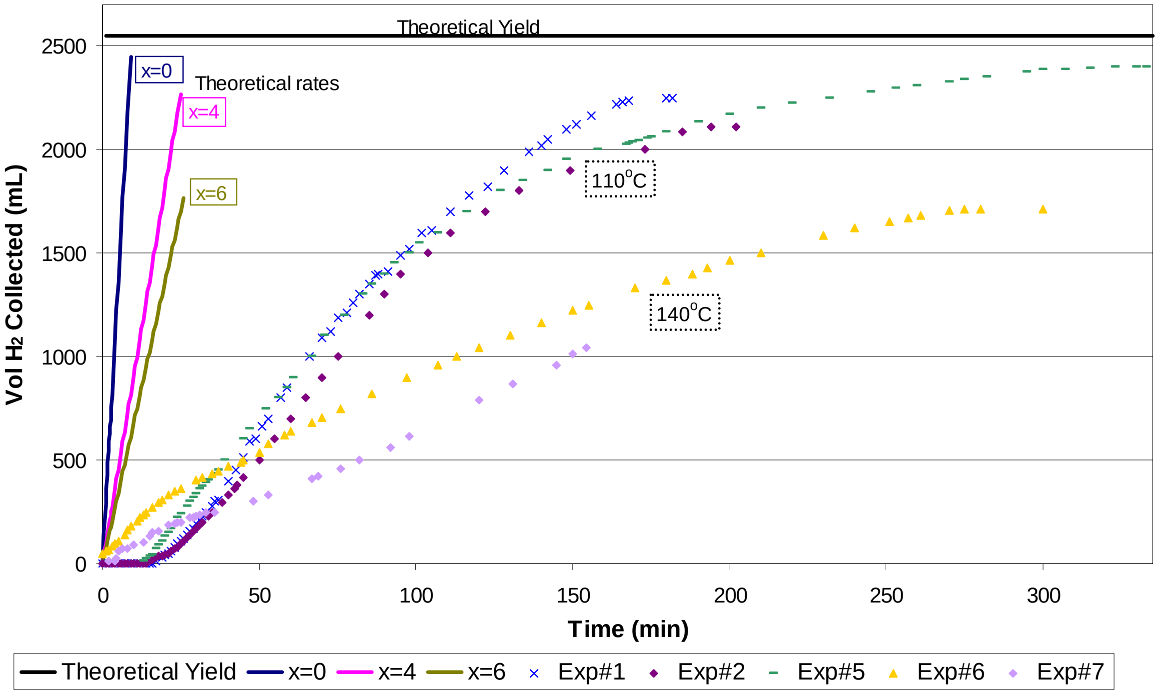


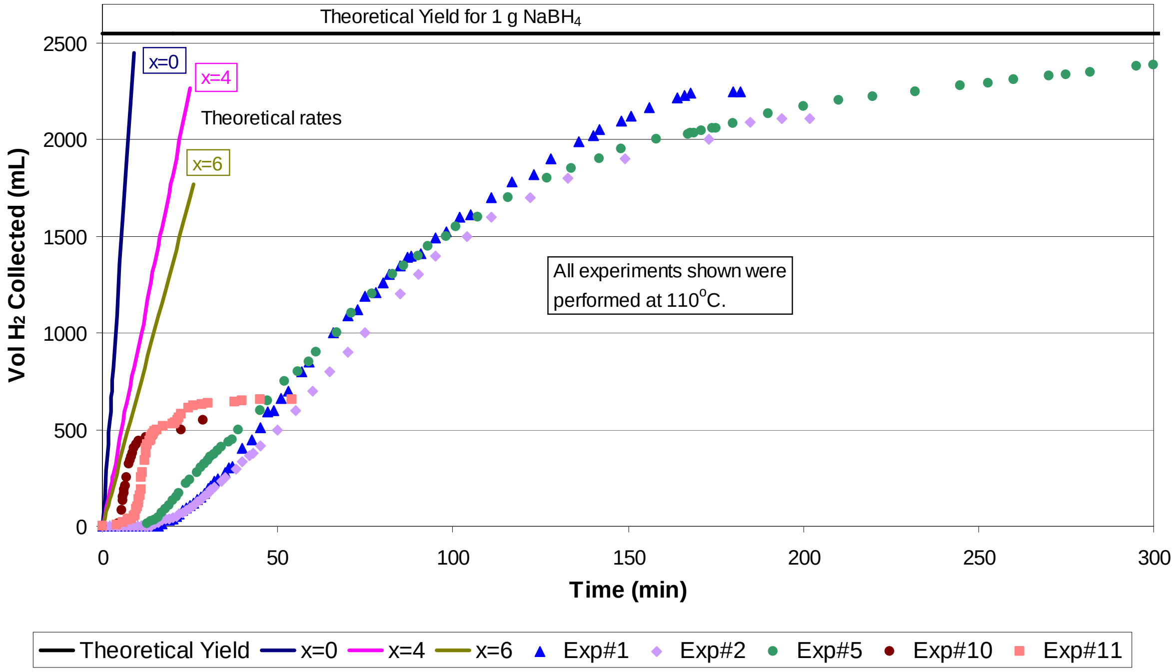
Figure 1 shows the experiments done with pure steam at 110^{o}C and 140^{o}C. The data show good reproducibility and are in agreement with work done in the past [1]. Hydrogen yields from 82% to 94% of the maximum were obtained without the need of a catalyst. All the experimental rates are lower than the theoretical rates, because the excess water required moves the slope to the right. The 15-min. induction period seen in some of the curves was an artifact of the apparatus used at that time, and it disappeared when the design was modified.

The lower rates and yields at higher temperature are counterintuitive, but they might be attributable to mass transfer limitations in the particle. Examination of the reactor contents after the experiments revealed that the solid particles were agglomerated. The agglomerated material was soft and wet after the 110ºC experiment and hard and dry after the 140ºC experiment. Presumably the $NaBH_4$ on the surface of the particle reacts first and forms a layer of sodium borate ($NaBO_2$), which grows in thickness as the reaction proceeds. That layer retards steam diffusion through the $NaBH_4$ particle, decreasing the production of hydrogen. The lower reaction rates at higher temperatures would be explained if the drier form of $NaBO_2$ is less permeable to water vapor. This theory remains to be proven.

An approach to reducing mass transfer limitations is to increase the surface area of NaBH4 available for contact with water vapor. The approach used was to dissolve the $NaBH_4$ in a non-reactive solvent and then allow the hydride to deposit on the surface of 4mm glass beads, creating a thin film around the bead, approximately 27 µm of $NaBH_4$ coating thickness was calculated.

Experiments conducted with coated beads (Figure 2) show that the reaction rate improved and is approximately the theoretical rate when the excess hydration factor is equal to 3 (x=3). Some delay due to the reactor configuration is also observed here, but the faster rate of reaction is noticeable after the beginning of the reaction. The hydrogen yield decreased with the use of coated beads, approximately 20% yield was obtained. This small yield may be related to channeling around the glass beads due to slow linear velocity of steam and an aspect ratio of 6.

Figure 2. Comparison of results from $NaBH_4$ coated beads and powder form



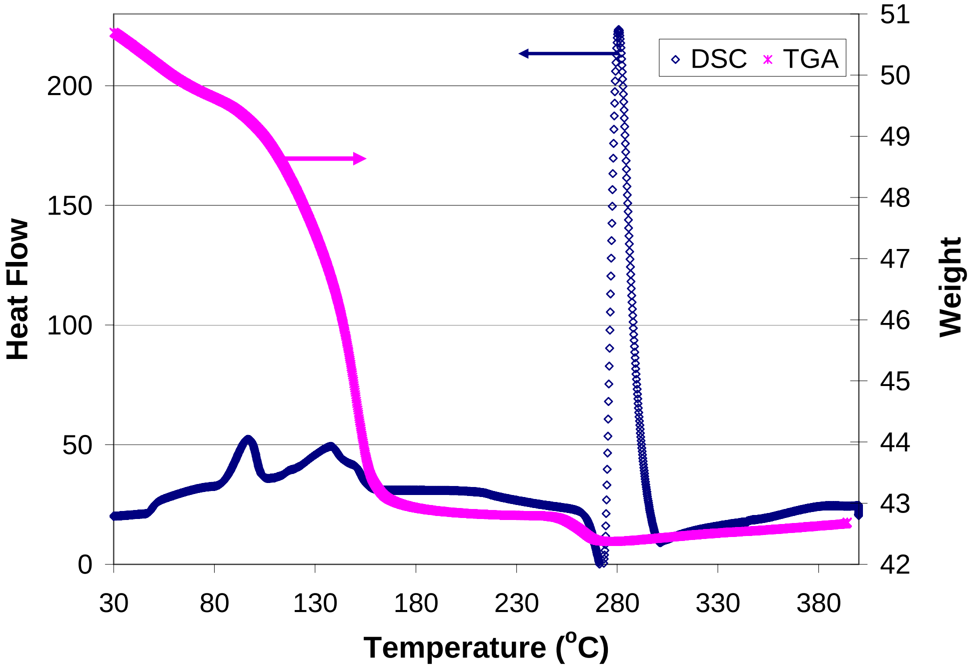
Excess water affects the degree of hydration of the byproduct and therefore the rate of the reaction and the mass and volumetric efficiency of a hydrogen system. We seek to understand the crystal structure and degree of hydration of the products of the steam hydrolysis reaction and whether this can be controlled. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were used. The temperature program from both the TGA and DSC scans from 25°C to 400°C at a rate of 10°C per minute.

Approximately 15 mg of solid byproduct from the reactor is placed in the sample pan for both TGA and DSC. Each graph shown in Figure 3 comes from a different sample, and it is should be noted that the solid samples from different runs are not homogeneous.

The TGA scan of the reaction product is shown in Figure 3. The sample lost 20% of its weight (free water and water of hydration) during the heating in the TGA. There are four inflection points that shows difference in the rate of water released, apparently due to changes in the hydration of $NaBO_2$. No weight loss occurred above approximately 275°C.

The DSC scan in Figure 3 show two peaks around 100°C and 150°C, which tentatively are ascribed to structural transformations from changes in the degree of hydration of the borate. In this range of temperatures the TGA indicates that the sample is still losing water. A peak around 280°C may show a change in the crystal structure of $Na_2B_4O_7 \cdot 4H_2O$ without any loses of water. This agrees with literature that indicates that $Na_2B_4O_7 \cdot 4H_2O$ has a glassy transformation at 300°C.

Figure 3. TGA and DSC of powder product



The experimental data show that more than 80% yield of H_2 can be obtained when $NaBH_4$ reacts with pure water vapor. Sodium borohydride powder gave high yields with slow rates and excessive use of water. Higher rates were obtained with thin films of $NaBH_4$ on glass beads, but yields were low, apparently due to channeling in the reactor. The rates and yields are sensitive to operating temperature and amount of water. The intrinsic reaction kinetics may be obscured because of impermeable byproducts. Further refinement will help to increase the rate and yield of the reaction and reduce the amount of excess water; this will also improve the mass efficiency of the system.

Acknowledgement.

This work was carried out under Agreement No. DAAB07-03-3-K416 with the US Army Communications-Electronics Command (CECOM) for Hybrid Advanced Power Sources with guidance from the RDECOM / CERDEC Fuel Cell Technology Team at Fort Belvoir, VA.

References

(1) Aiello R.; Sharp J.; Matthews M. *International Journal of Hydrogen Energy;* **1999**, 1123-1130.
(2) Amendola et al., J. Hydrogen Energy, 25, 969, 2000; U.S. Patent 6,534,033