

IV.G.4 Purdue Hydrogen Systems Laboratory*

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Contract Number: DE-FC36-06GO86050

Subcontractor:

National Renewable Energy Laboratory (NREL),
Golden, CO

Project Start Date: September 16, 2006

Project End Date: September 15, 2007

*Congressionally directed project

sections of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

On-Board Hydrogen Storage

- (A) System Weight and Volume
- (B) System Cost
- (J) Thermal Management
- (R) Regeneration Process
- (S) By-Product/Spent Material Removal

Biological Hydrogen Production

- (AR) H₂ Molar Yield
- (AT) Feedstock Processing Cost
- (AU) Systems Engineering

Technical Targets

| On-Board Storage | Units | 2007 | 2010 |
|-----------------------------|--------|------|------|
| System Gravimetric Capacity | kWh/kg | 1.5 | 2 |

| Biological H ₂ Production | Units | 2007 | 2010 |
|--------------------------------------|-------|------|------|
| Hydrogen Yield Percentage | % | 20 | 40 |

Objectives

- Understand catalytic and thermal mechanisms for hydrolysis of ammonia borane (AB) and to identify viable routes, including recycling, for practical applications.
- Develop a new method for hydrogen generation from water and AB using self-sustained combustion reactions.
- Develop a subscale recyclable AB-based hydrogen storage system and investigate thermal management issues.
- Investigate and evaluate initial processes for the production of hydrogen from various waste streams using microbial fermentation and investigate possible paths for implementation of the research in an energy source.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Storage and Production

Accomplishments

- Studied transition metal catalyzed AB hydrolysis to generate three equivalent of hydrogen and observed that ruthenium chloride gives the best results.
- Quantified ammonia liberated during AB hydrolysis at various high concentrations.
- Currently working on AB regeneration from ammonium borate salt, a by-product of the hydrolysis reaction.
- Studied properties of Ru catalyzed AB hydrolysis extensively, including reaction conversion and kinetics using aqueous solutions up to 25 wt% of AB, effect of long-term storage (up to 50 days) on conversion and kinetics, and byproduct solubility.
- Conducted first subscale AB hydrolysis test at a hydrogen flow rate of 2.9 SLPM.
- Developing a subscale 200 g/day AB regeneration system and evaluating overall regeneration efficiency.
- Demonstrated that the approach based on self-sustained combustion by highly exothermic metal-water reaction is feasible for hydrogen generation from AB; the AB/Mg/H₂O (4:4:3 mass ratio) mixture exhibits 9.1 wt% hydrogen yield.

- Isotopic tests showed that both thermolysis and hydrolysis play important roles in the process of hydrogen generation from high-temperature AB/water mixtures.
- Identified key operating parameters for the anaerobic production of hydrogen from food waste. Current tests indicate hydrogen concentrations in the 15-25% (molar) range.
- Statistical experimental tests have initially identified operating parameter ranges that optimize hydrogen production.
- Engineering and economic models for the modular local energy system have been updated to reflect recent test results.



Introduction

This project allows the creation of a Hydrogen Research Laboratory in a unique partnership between Purdue University's main campus in West Lafayette, Indiana and our Calumet, Indiana campus. This laboratory is focusing on basic research in hydrogen production and storage as well as research on systems level that is necessary for practical applications of the discoveries. The technologies developed will intrinsically advocate the concept of sustainability in addition to developing new theory and devices for the production and use of hydrogen.

The hydrogen storage work is focusing on the potentially low cost production of AB and an energy efficient way to recycle the byproducts from catalyzed AB hydrolysis. In addition, an innovative method utilizing combustible AB/metal/water mixtures is also being investigated. In this approach, AB is mixed with metal powder (Al or Mg) and gelled water, and heat of the metal-water reaction creates conditions for AB thermolysis. The proposed mixtures promise hydrogen yield of more than 10 wt% without water recycling from the fuel cell. In this method, however, AB hydrolysis is also possible that may decrease the hydrogen yield. It is necessary to understand reaction mechanisms in the proposed mixtures and determine conditions favoring thermolysis.

It is recognized that all hydrogen storage systems must critically rely on efficient thermal management. Thermal management for AB-based hydrogen storage is being studied. This research will demonstrate, for the first time, a recyclable chemical hydride-based storage system with a high gravimetric density. System-level studies of the dehydrogenation and recycling processes will be conducted with particular emphasis on thermal and chemical processes in the reaction chambers.

Bio-production of hydrogen is potentially an important renewable source of energy. Using organic wastes for bio-production of hydrogen not only has the potential to generate cost-effective and renewable energy but also can reduce pollution in the environment and provide a source of fertilizer for growing crops. The purpose of the current research effort is to investigate, obtain data, and evaluate initial processes for the production of hydrogen from various waste streams using microbial fermentation and investigate possible paths for implementation of the technology as a local electric and thermal energy source. This effort is targeted to assure that the developed technology will be applicable for integration into various current and future energy supply options including the Department of Energy Road Map.

Approach

We are developing methods for AB hydrogen release and regeneration reactions that will enable its use for chemical hydrogen storage. We screened transition metal catalysts for AB hydrolysis. We are studying characterization and regeneration reactivity of the hydrolysis by-product.

We are using combined combustion experiments and isotopic tests to investigate combustion stimulated AB dehydrogenation. The former type of experiments allows us to verify the validity of the proposed method and measure the main process parameters, while the isotopic tests help to understand reaction mechanisms (thermolysis *vs.* hydrolysis).

We are constructing and testing subscale AB hydrolysis and AB generation apparatus to address thermal management challenges. To facilitate the design and optimization of these subscale apparatus, we have investigated reaction kinetics and other thermo-chemical properties and also implemented computational fluid dynamics (CFD) simulations.

We are also considering methods to optimize hydrogen production and will form the foundation for the subsequent development of a modular device that will use various waste streams, including garbage and possibly animal or human waste, for the production of hydrogen. This hydrogen will be separated from the bio gas stream by use of nano catalyst or a membrane for use in a fuel cell or reciprocating engine to produce electricity locally. Methods to sequester carbon dioxide as part of the process are also being considered. Energy for the pre- and post- processing of feed streams will be obtained from a solar collector system or possibly from a supplemental methane bio-reactor. Current computer simulations of the process indicate that the system can be installed in a shipping container and used to provide local electric and thermal energy.

Results

AB hydrolysis was examined with various catalysts. The hydrolysis was catalyzed by mineral acids such as hydrochloric acid or sulfuric acid occurs instantly at ambient temperature. This protocol has the advantage of recycling the boric acid to AB. The hydrolysis of AB is also aided by transition-metal catalysts. It was observed that complete hydrolysis could be achieved within 3 minutes with the 0.2 mol% ruthenium chloride. The reaction rate can be controlled by the amount of the catalyst present. Ammonia, however, was liberated during the transition-metal catalyzed hydrolysis. This was quantified at different concentrations. It has been found that 10 to 25 wt% aqueous AB solutions liberate 2 to 10% of the total ammonia upon hydrolysis with transition-metal catalyst.

The regeneration of AB from ammonium borate that formed during the hydrolysis reaction was achieved by treating with hydrochloric acid to obtain boric acid followed by treatment with methanol to obtain trimethyl borate. Trimethyl borate was converted to sodium borohydride using lithium aluminum hydride. The yields are currently low and have to be optimized.

We also studied metal combustion stimulated dehydrogenation of AB. The mixtures included AB, aluminum or magnesium powder, and gelled water. The mixtures, placed in a quartz cylinder, were ignited by a high resistance wire in an argon atmosphere inside a stainless steel chamber. Digital video cameras were used for visualization of combustion while pressure was monitored by a pressure transducer. The product gas was analyzed by mass-spectrometry. The experiments have demonstrated that the approach based on self-sustained combustion by highly exothermic metal-water reaction is feasible for hydrogen generation from AB. The AB/Mg/H₂O (4:4:3 mass ratio) mixture exhibits 9.1 wt% hydrogen yield (theoretical yield 10.1 wt%). The propagation of combustion wave through the sample involves the following stages (Figure 1). For a sample ignited from the top, since pressure does not differ significantly from atmospheric, the process starts with water evaporation at temperature close to 100°C. In the evolving flow of water vapor, chemical transformation of AB occurs (either thermolysis or hydrolysis) while highly exothermic oxidation of metal (Al or Mg) by water vapor provides enough heat to support the self-sustained process.

To clarify the roles of thermolysis and hydrolysis in the process of hydrogen generation from high-temperature AB/water mixtures, we conducted isotopic tests, replacing water by D₂O. The isotopic tests allow us to discriminate between the sources of the released hydrogen: H₂ from AB thermolysis and HD from AB hydrolysis. The AB/D₂O mixtures, placed in a quartz cylinder, were heated under Ar pressure to 14.8 bar inside a reactor. Temperatures from 80 to 200°C were

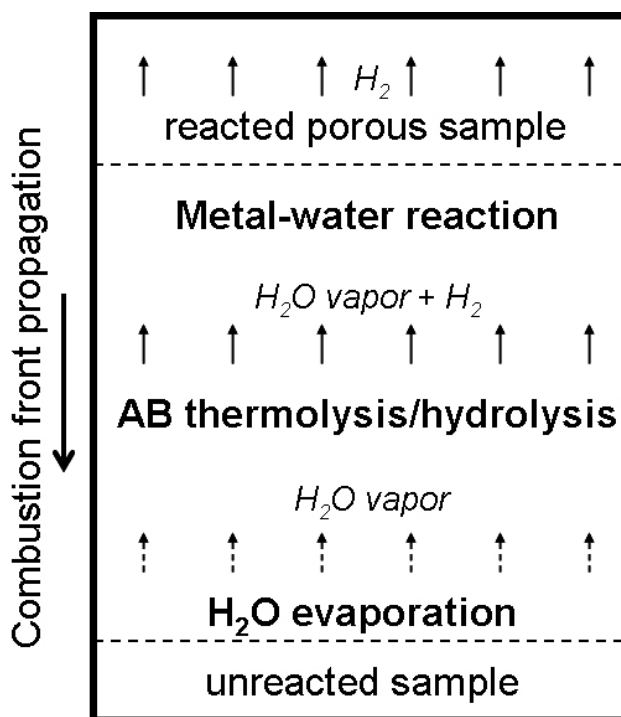


FIGURE 1. Schematic Representation of Combustion Wave Propagation in AB/Metal/Water Mixture

tested, thus covering the range where the first two steps of AB thermal decomposition occur (temperature did not exceed the boiling point of D₂O at the experimental pressure). The gas composition was analyzed by mass-spectrometry after cooling the reactor. The results show that the amounts of H₂ and HD are comparable. This indicates that both thermolysis and hydrolysis play important roles in overall hydrogen generation.

We studied a 3 wt% Ru-C catalyzed AB hydrolysis to facilitate reactor design. Up to 25 wt% (one mole AB and five mole water) aqueous AB solutions were tested. No stabilizer, such as NaOH, was used. Without a catalyst, no appreciable reaction was observed in a couple of hours. The density of AB solution decreases with AB concentration and may be expressed as, $\rho = 0.993 - 0.0037 * (\text{AB wt}\%)$, kg/L. Nearly 100% conversions were achieved in all tests. The hydrogen generation rate at 25°C was about **26.3 liter/min/g Ru**, almost independent of AB concentration. As illustrated by Figure 2, hydrolysis kinetics of 3 wt% Ru-C is faster than that of 10 wt% Co-Al₂O₃ reported [1]. An in-house CFD code [2] has been used to simulate AB hydrolysis reactors using these two catalysts. With the same inlet aqueous AB solution flow and same reactor cross section, a reactor three times longer is needed to achieve the same hydrogen output if the cheaper catalyst (cobalt) is adopted. In another words, approximately 12 times more (mass base) catalyst will be needed.

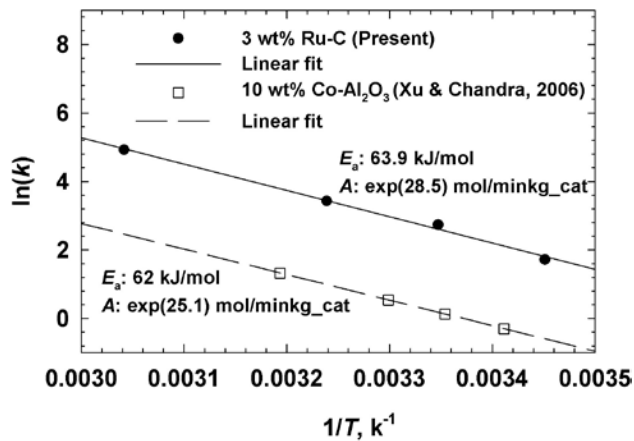


FIGURE 2. Arrhenius Plot for Catalyzed AB Hydrolysis

We also stored 10 wt% and 25 wt% aqueous AB solutions in expandable bottles for the study of long-term storage stability. After about 50 days, reaction conversions were reduced to 97% and 91% for 10 wt% and 25 wt% solutions, respectively. Reaction kinetics were slowed down by approximately 50%. In addition, we conducted the first subscale AB hydrolysis test at a hydrogen generation rate of 2.9 SLPM using a modified sodium borohydride (SBH) hydrolysis apparatus [3]. It was found that AB hydrolysis reactor can be 60% smaller than that of SBH (3 wt% NaOH) for the same hydrogen output.

Significant ammonia release and insoluble byproduct were observed when above 10 wt% aqueous AB solutions were tested. Ammonia was captured by 5 wt% aqueous CuSO₄ solution and quantified. To further increase gravimetric and volumetric hydrogen storage densities, a subscale system to implement nearly stoichiometric (one mole AB and two mole water) AB hydrolysis and to convert ammonia into hydrogen is highly desired.

Various inoculates have been tested and the concentration of hydrogen in the produced gas has been correlated with the experimental variables: pH, temperature, and substrate concentration. A micro gas chromatograph is used to determine the composition of the produced gas. The testing program is based upon a Central Composite Experimental Design. A preliminary numeric optimization of the hydrogen production level was conducted to identify combinations of variables that produce maximum amounts of hydrogen. Figure 3 depicts a case with an optimum point at 35°C, pH 5.9 and 0.5 g/20 ml concentration. Construction of a multiple testing device has started. This device will provide capability to conduct multiple simultaneous tests with automated data processing and monitoring. Continuous production testing capability is currently under development at Purdue Lafayette and NREL.

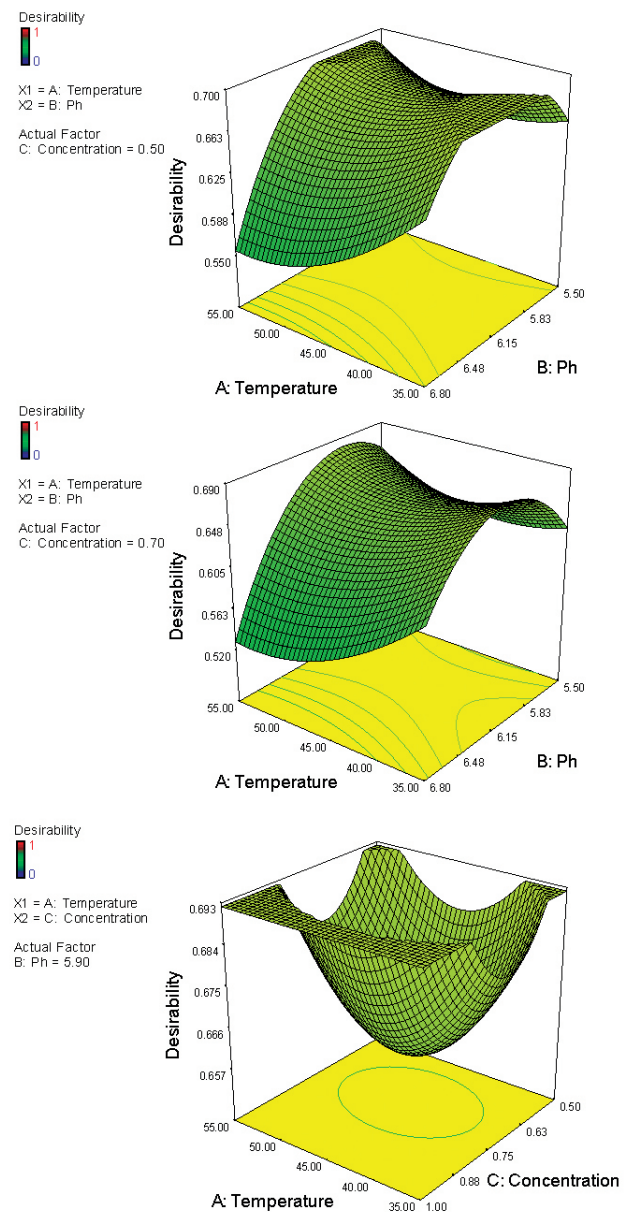


FIGURE 3. Preliminary Optimization Results for Initial Hydrogen Production Test

The system model for the modular energy system has been updated. New experimental values are being used for production and sizing calculations. The production of potable water from the modular system is also being considered as a future enhancement to the process. Initial efforts to consider a catalyst process for capture of carbon dioxide have started.

Conclusions and Future Directions

Aqueous AB solution without a stabilizer, such as NaOH, has reasonably good short-term and long-term storage stability. The Ru-catalyzed AB hydrolysis system

can provide good kinetics to meet the DOE 2010 target on hydrogen release rate. We are working to implement nearly stoichiometric AB hydrolysis and ammonia utilization so that an onboard AB hydrolysis system can meet DOE 2010 targets on gravimetric and volumetric hydrogen storage densities. The liberation of ammonia during the hydrolysis using a concentrated AB solution is a concern for the purity of the generated hydrogen. We will develop a procedure to avoid ammonia liberation during AB hydrolysis. We will develop a filter/trap to capture the liberated ammonia so as to provide pure hydrogen. We will accomplish ammonia borane regeneration in near quantitative yield and in a cost effective manner.

Self-sustained combustion was observed in mixtures of AB with water and Mg or Al powder; the maximum hydrogen yield observed was 9.1 wt%. **Isotopic tests** of AB using D₂O show that hydrolysis competes with thermolysis. Isotopic tests of AB/D₂O mixtures will be conducted at different pressures; purity of generated hydrogen and composition of resulting condensed products will be measured. Conditions favoring thermolysis and, on the other hand, minimizing the fraction of metal in AB/metal/water mixtures, will be established to obtain the highest hydrogen yield.

Hydrogen production concentrations of approximately 20% have been observed for various combinations of substrate and inocula with temperature, substrate concentration, pH, and time as experimental parameters. Statistical testing has allowed for preliminary optimization of parameters that maximize hydrogen production. These tests will be further refined the remainder of this year and should be expanded to include more detail and variability in subsequent efforts. An automated multiple testing device is under construction to refine, expand and automate testing efforts. Variability of substrate composition needs to be included in the experimental design. The energy system model should consider design issues for the biological reactor as part of the optimization of value. In subsequent efforts, a control system should be developed to maximize hydrogen production and system energy value based upon current and future testing results.

FY 2007 Publications/Presentations

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