IV.B.4 Chemical Hydride Rate Modeling, Validation, and System Demonstration

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Project Start Date: February 2009
Project End Date: February 2015

Overall Objectives

- Develop an automotive chemical hydrogen storage system capable of meeting all of the 2017 DOE targets simultaneously
- Develop and validate chemical hydrogen storage system models
- Quantify viable chemical hydrogen storage material properties that will meet DOE 2017 technical targets with our current system
- Develop and demonstrate “advanced” (non-prototypical) engineering concepts

Fiscal Year (FY) 2013 Objectives

- Quantify reaction characteristics of liquid exothermic media (methoxy propylamineborane), slurry endothermic media (alane), and slurry exothermic media (ammonia borane)
- Design, build, and demonstrate advanced dehydrogenation reactors
- Develop an onboard fluid-phase chemical hydrogen storage system; system designer

Technical Barriers

This project addresses the following technical barriers from the Technical Plan - Storage section of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan:

(A) System Weight and Volume

(B) System Cost

(C) Efficiency

(D) Durability/Operability

(E) Charging/Discharging Rate

(F) Codes and Standards

(G) Materials of Construction

(H) Balance-of-Plant (BOP) Components

(J) Thermal Management

(K) System Life-Cycle Assessment

(R) By-product/Spent Material Removal

Technical Targets

The summary of our progress in relation to the DOE 2017 technical targets for both ammonia borane and alane can be seen in Figure 1. The cost target was assumed to be $7/kg of hydrogen. The estimated values are based on the Hydrogen Storage Engineering Center of Excellence’s chemical hydrogen storage system design. Both systems assume 50 wt% slurry loadings for ammonia borane and alane.

Accomplishments

- Designed, built and tested novel auger reactor
- LANL was the first to demonstrate and characterize flow through reactor studies on 20 wt% alane slurry and 20 wt% ammonia borane slurry
- Identified reactor operating limits for various fluid-phase chemical hydrogen storage media
- Quantified impurities generated from ammonia borane slurries, alane slurries, and methoxy propylamine borane
- LANL developed the first empirical rate expression describing slurry alane dehydrogenation from flow reactor data

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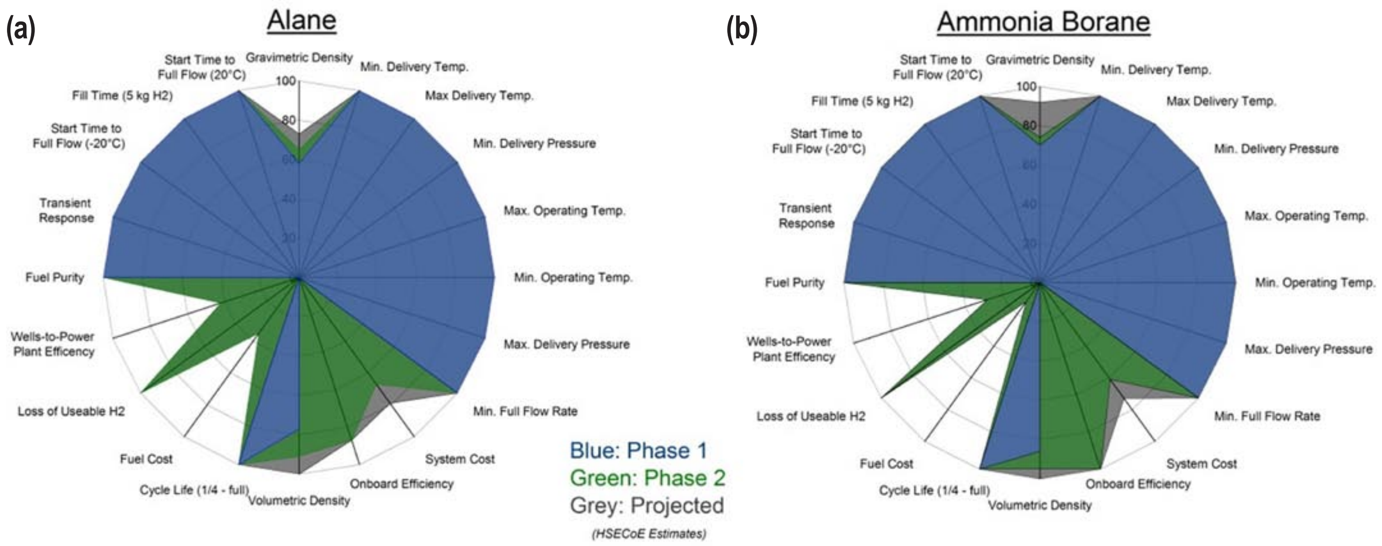

FIGURE 1. Spider chart summarizing our progress in meeting the DOE 2017 technical targets for (a) 50 wt% alane slurry and (b) 50 wt% ammonia borane slurry.

INTRODUCTION

Hydrogen storage systems based on chemical hydrogen storage materials require a chemical reactor to release the hydrogen from the storage media, which is a fundamental difference from the other modes of hydrogen storage, adsorbents and metal hydrides. This hydrogen-release reactor is crucial to the performance of the overall storage system, especially in meeting the DOE targets for hydrogen generation rate, transient operation, and startup times. The reactor must be designed to achieve these targets while meeting the constraints of the overall system volume and weight targets.

LANL will also address the unique requirements of onboard automotive hydrogen storage systems. For example, these systems require fast startup, operation over a wide dynamic range (10:1 turndown or greater), and fast transient response to meet the demands of a drive cycle. The LANL team will develop novel reactor designs and operation strategies to meet these transient demands. In addition, the shelf life and stability of the hydrogen storage media is crucial for an automotive system, especially pertaining to safety and cost. Starting with the kinetics models, the LANL team will develop mathematical models for the aging characteristics of candidate hydrogen storage media (for example, complex metal hydrides or chemical hydrogen storage materials) subjected to a range of environmental factors. These models can be incorporated into system-level models of performance and cost and also used for the development of accelerated aging protocols necessary for later testing.

RESULTS

Reaction Characteristics of Slurry Alane and Slurry Ammonia Borane with Auger Reactor

Experiments were performed using our novel in-house built auger reactor to determine the reaction characteristics of 20 wt% “uncatalyzed” alane slurry, and 20 wt% ammonia borane slurry. The reaction characteristics of interest are reaction selectivity (i.e., impurities), conversion, and hydrogen production. Reactor durability and operability are also important performance characteristics. Typical operating conditions for ammonia borane slurries consisted of feed flow rates ranging from 0.5–3.12 mL/min and reactor temperatures ranging from 150–225°C. All reaction runs used 20 wt% ammonia borane slurry. Although this is not the highest ammonia loading achievable, it is however the loading that was used to screen potential reactor designs without exhausted our ammonia borane supply. The products observed from ammonia borane dehydrogenation as a function of temperature are shown in Figure 2. The identified fuel cell impurities include ammonia, borazine and diborane. Low-temperature dehydrogenation favors ammonia formation while high temperature operation favors borazine and diborane. The most favorable reactor temperatures for producing the least amount of fuel cell impurities are around 150°C. Lower reactor temperatures, however, demonstrate slower kinetics. Slower reaction kinetics result in larger reactors in order to generate the necessary hydrogen flow rates. The auger reactor demonstrated significant improvements in durability and operability as compared to the typical flow through reactor, evidenced by continued reactor operation without fouling during reactor testing.

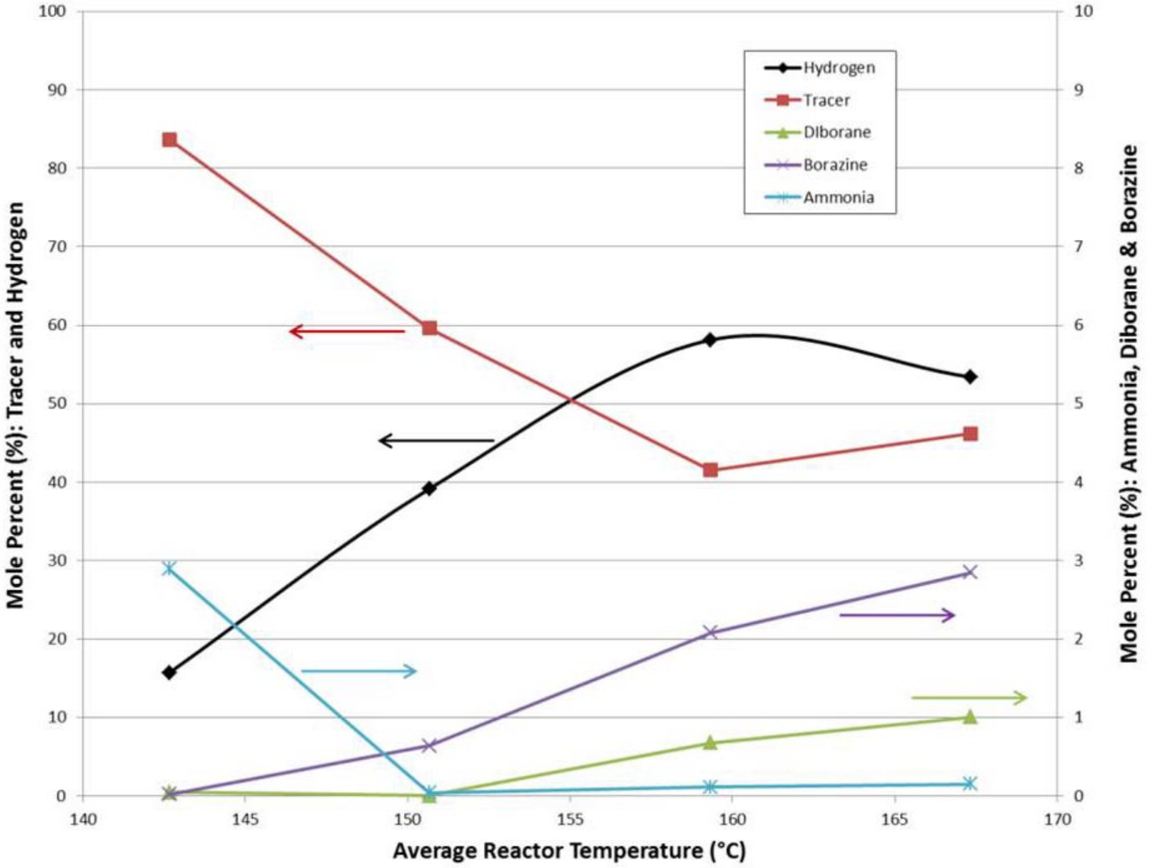

FIGURE 2. Effluent mole percentages observed during dehydrogenation of 20 wt% ammonia borane slurry as a function of temperature (auger reactor operating at 40 rpm).

Dehydrogenation of alane slurry was also investigated using our novel in-house built auger reactor. The alane slurries consisted of as-received, "uncatalyzed" alane from ATK. Typical operating conditions for alane slurries consisted of feed flow rates ranging from 0.5–2.0 mL/min and reactor temperatures ranging from 150–275°C. The auger speed was maintained at 40 rpm for all runs. Alane conversions of one were observed for reaction temperatures around 260°C and a space-time of 6.8 min. The elevated reactor temperatures required for complete alane conversion is directly attributed to the fact that alane was not "catalyzed" or "pre-activated." Lower dehydrogenation temperatures can be achieved by doping and/or "pre-activating" alane. These approaches will likely be required for on-board automotive applications because of the increased energy efficiency, decreased start-up time, and decreased system mass and volume (e.g., radiator, reactor, etc,). Alane is attractive not only because of its relatively high hydrogen content (10.1 wt% H_2), but also due to its high hydrogen selectivity. No impurities were observed during the dehydrogenation of alane for temperatures lower than 210°C. Reaction temperatures greater than 210°C resulted in undesired side reactions of alane with silicon oil. Consequently, trace amounts of gas phase impurities were observed for reactor temperatures greater than 210°C. Reactor fouling was not observed during 10 hours of continuous reactor operation with alane slurries. Data collected was regressed using a power rate law. The fitted rate expression for alane dehydrogenation with our novel in-house built auger reactor is

$$-r_{Alane}\big|_{apparent} = kC_{alane}^{0.5}$$

$$k(T) = Ae^{\left(\frac{-E_a}{RT}\right)}, \quad A = 3.7x10^6, \quad E_a = 90.75\frac{kJ}{mol}$$

The fitted rate expression can be seen in the alane conversion parity plot shown in Figure 3. The parity plot shows good agreement in comparing the model predicted alane conversion to the experimentally observed alane conversion.

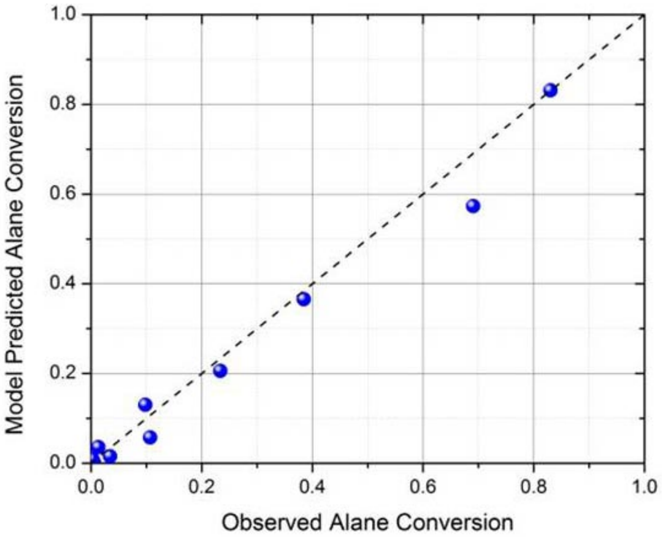

FIGURE 3. Parity plot comparing model predicted alane conversions to experimentally observed alane conversions collected with LANL in-house built auger reactor.

SUMMARY

- Successfully designed and built novel fluid-phase reactors
- Performed flow reactor studies with methoxy propylamineborane, alane slurries, and ammonia borane slurries without reactor fouling or reactor slugging
- Quantified gas phase impurities produced alane and ammonia borane slurries

FUTURE DIRECTIONS

Material Properties

- Develop viable material property guidelines for chemical hydrogen storage media that will meet the DOE 2013 technical targets.

Reactor Testing

- Perform reaction studies with 30 and 50 wt% alane slurry loadings and 30 and 50 wt% ammonia borane slurry loadings.

Borazine Scrubber

- Perform additional borazine scrubbing experiments to determine pressure effects on borazine adsorption capacities with activated carbon.

FY 2013 PUBLICATIONS AND PRESENTATIONS

1. "Overview of LANL's Engineering Research Efforts for Chemical Hydrogen Storage" WHEC 2012, Toronto, CA, *Invited Speaker.*

2. "Chemical Hydride Rate Modeling, Validation, and System Demonstration" 2013 Annual Merit Review, Washington, D.C., May 2013.