# IV.B.4d Development of an Advanced Chemical Hydrogen Storage and Generation System

Ying Wu (Primary Contact), Xiaolei Sun, Jeffrey V. Ortega, Qinglin Zhang
Millennium Cell Inc.
1 Industrial Way West, Building E
Eatontown, NJ 07724
Phone: (732) 544-5718; Fax: (732) 542-2846
E-mail: wu@millenniumcell.com

DOE Technology Development Manager: Grace Ordaz
Phone: (202) 586-8350; Fax: (202) 586-9811
E-mail: Grace.Ordaz@ee.doe.gov

DOE Project Officer: Jim Alkire
Phone: (303) 275-4795; Fax: (303) 275-4753
E-mail: James.Alkire@go.doe.gov

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## Objectives

- Increase system storage capacity by improving hydrogen generation from concentrated sodium borohydride, with emphasis on reactor and system engineering.
- By the end of FY 2007, complete a conceptual system design based on sodium borohydride that will include key technology improvements to enable a hydrogen fuel system that will meet the system-based storage capacity of 1.2 kWh/L (36 g $H_2$/L) and 1.5 kWh/kg (45 g $H_2$/kg).
- Utilize engineering expertise to guide Center research in both off-board chemical hydride regeneration and on-board hydrogen generation systems.

## Technical Barriers

This project addresses the following technical barriers from the Hydrogen Storage section (3.4.4.2) of the Hydrogen, Fuel Cells, and Infrastructure Technologies Program Multi-Year RD&D Plan:

(A) System Weight and Volume
(B) System Cost
(C) Efficiency
(H) Balance of Plant (BOP) Components
(J) Thermal Management
(R) Regeneration Processes

## Technical Targets

| Criteria | 2007 Target | 2010 Target | Current Status |
|---|---|---|---|
| Specific Energy | 4.5 wt% 1.5 kWh/kg | 6 wt% 2.0 kWh/kg | 3.9 wt% 1.3 kWh/kg |
| Flow rate | 0.02 (g/s)/kW | 0.02 (g/s)/kW | 0.02 (g/s)/kW |
| Energy Density | 36 g/L (1.2 kWh/L) | 45 g/L (1.5 kWh/L) | 33 g/L (1.0 kWh/L) |
| Storage System Cost | \$6.00/kg $H_2$ stored | \$4.00/kg $H_2$ stored | \$6.70/kg $H_2$ stored |

## Accomplishments

- Completed sodium borohydride regeneration Data-Mining by providing two (2) reports to the Center: (1) "Summary of Analytical Techniques for Detecting Sodium Borohydride and Related Compounds" (2) "Summary of Synthetic Processes for the Production of Sodium Borohydride."
- A stereoscope and metallograph analysis of the catalyst was completed by using Millennium Cell's (MCEL's) catalyst sample and performance data combined with digitizing and catalyst packing software at PNNL to generate a "Virtual Catalyst Particle." Fundamental properties of the catalyst are incorporated in microscopic modeling based on Lattice-Boltzmann principles.
- Microscopic modeling has yielded transport and reaction parameters for use in the reactor macroscopic model. Dynamic reactivity characteristics such as the gas-shielding effect and varying activity have been examined.
- Developed customized macroscopic reactor model by PNNL using Fortran 90 and successfully transferred to MCEL. Validation of the model was completed at MCEL with experimentally measurable parameters.
- Simulated steady-state profiles of sodium metaborate concentration, water vapor flow, gas volume, and the hydrogen distribution in the reactor using the macroscopic reactor model.
- Initiated the optimization of the reactor performance by adjusting factors such as operating pressure, reactor geometry, fuel space velocity, and heat removal along the reactor wall.

## Introduction

The primary goal of this project is to develop a chemical hydrogen storage system to meet DOE's 2010 technical targets of 2.0 kWh/kg and 1.5 kWh/L by the end of five years. The first phase of the project, which spans two years, will use sodium borohydride as a model system to identify engineering problems and develop solutions that will advance the state of hydrogen storage technology. System engineering considerations will incorporate MCEL's state-of-the-art Hydrogen on Demand® technology to provide a practical on-board system. Knowledge and experience gained in this area will not only improve $NaBH_4$-based technology, but also provide valuable insight into the controlled hydrogen release from new and novel materials identified by the collective effort of the Center.

## Approach

To complete the conceptual system design based on sodium borohydride, reactor performance optimization is the crucial step. Reactor modeling has been carried out through two parallel strategies: development of a custom program (through collaboration with PNNL) and utilization of a commercially available software package (Star-CD computational fluid dynamics simulator). The custom reactor modeling program includes two parts: microscopic reactor modeling and macroscopic reactor modeling. Both are mainly developed by PNNL. The utilization of the custom program allows for increased control of computational details in executing the simulations.

### Custom Microscopic Modeling

In order to perform the microscopic modeling (particle level), stereoscope and metallograph analyses were performed to get the virtual catalyst geometry. Each catalyst particle was modeled as two parallel slabs with a gap in between. The particles were placed into the reactor and compressed, settled into place and were allowed to expand where possible. The compression factor employed was derived from liquid hold-up data and the particle density measurements. Each slab also has depressions and pores, which match the statistics of the real particle. The virtual particle also helped determine the void space (gap) used to space the two slabs apart in the compression calculation for each particle in the reactor.

Lattice-Boltzmann type calculations were then performed on this virtual catalyst particle in order to determine localized liquid flow patterns on and through the particles while evolving gas bubbles. A second order rate was utilized for the hydrogen evolution at the surface of the catalyst particles in the calculations, as determined by experimental reactor performance data. A combination of Laminar and turbulent-type flows was also incorporated into the calculations.

### Custom Macroscopic Modeling

Custom macroscopic modeling is a more complex 3-phase model to better characterize and study the reactor internal flow dynamics. This model required the fully characterized catalyst particles from the microscopic modeling and utilizing code written with Fortran 90. The program consists of 13 subroutines, and treats the reactor as a test bed. The reactor is divided into 10 rings axially, and 100 slices along the length of the reactor (Figure 1). By this means, the overall heterogeneous microscopic properties were converted into 1,000 individual homogeneous sections. Each section contains the pertinent data for that exact location in the reactor which was determined using the Lattice-Boltzmann microscopic calculations. The data includes values for: fluid and gas flow, temperature, mass and energy balances, heat and mass transfer, and the chemical kinetics of sodium borohydride consumption and hydrogen gas evolution. This method has the benefit of not requiring as much computing power as the Lattice-Boltzmann program, while also having the added benefit of being based on the original Lattice-Boltzmann calculations.

The input parameters of the program include: fuel concentration, fuel inlet temperature, fuel space velocity, reactor geometry (including reactor length, internal diameter, wall thickness, and material of construction), required system pressure, as well as catalyst packing porosity. The program elucidates the values for the following reactor dynamics: the axial distribution of sodium borohydride conversion, borates concentration, reactor inside temperature, pressure drop, hydrogen flow, liquid phase flow, water vapor flow as well as void fraction. The program has the capability to solve for both transient and steady-state solutions. The optimization of reactor performance can be achieved by

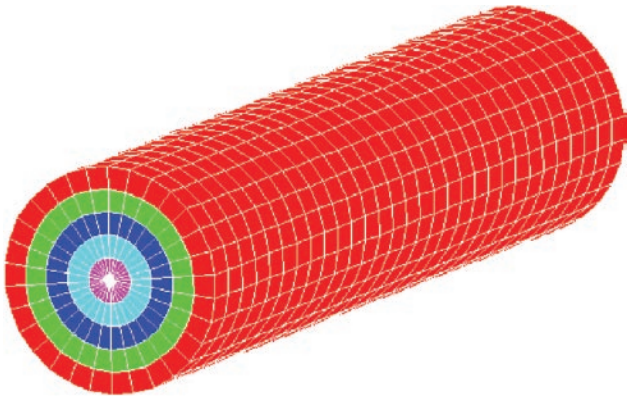

**FIGURE 1.** Visual Representation of the Fortran 90 Modeling Method

adjusting main design factors. Additional information can be obtained to improve overall heat integration and water management.

### Star-CD CFD Reactor Modeling

A Star-CD CFD simulator has been purchased and started running on-site at Millennium Cell. The Star-CD simulator has much more powerful post-processing function than the in-house custom program. The subroutines used for macroscopic custom program will be modified to adapt into Star-CD program after the custom program has been fully developed.

After the initial reactor modeling, the entire system will then be simulated and designed around the optimized reactor, followed by the unit building and testing. Due to Millennium Cell's extensive knowledge of $NaBH_4$ chemistry and previous successful system demonstrations, the new unit will be designed based on $NaBH_4$. However, adaptability to other chemical hydrogen storage materials, should one be found that is preferable to sodium borohydride, will also be taken into account and engineered for. Fundamentally, the goal is to reduce (or increase the efficiency of) the heat, cost, volume, and weight requirements of the system in order to develop a prototype utilizing any chemical hydride that will meet the 2010 DOE targets.

## Results

### Custom Microscopic Reactor Modeling

Figure 2 shows an example in which the image consists of a cross-sectional slice of the reactor simulated by microscopic modeling. In the figure, the solid catalyst particles are dark blue, liquid fuel is red, and generated hydrogen gas is light blue. During simulation, it was found that as soon as the liquid hit the solid face of the particles, there was a drop-off in the catalytic rate of the reaction due to the generation of hydrogen gas at the surface. It was also observed that the liquid occupied the larger gaps (open areas) between the particles while the smaller pores and immediate area covering the particle surfaces were occupied by gas. This is a visual representation of a shielding effect which severely reduces the efficiency of the catalytic rate of reaction. Any reactor design improvement will have to address this effect.

### Custom Macroscopic Reactor Modeling

**Modeling Method Validation.** The modeling program was validated by simulating the following reactor dynamics: overall pressure drop, sodium borohydride conversion at reactor outlet, reactor temperature rise along the reactor, as well as the hydrogen flow rate out of the reactor. These calculations were then verified with experimental data that had been measured previously.

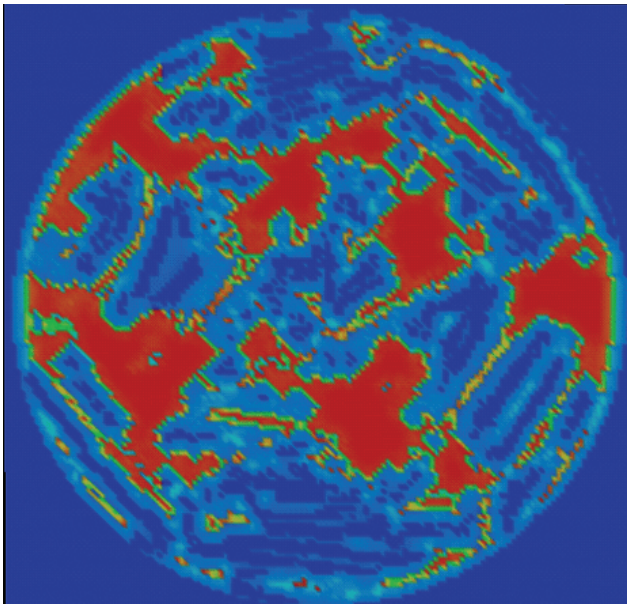

**FIGURE 2.** Modeled Cross-Section of the Reactor Showing the Catalyst Particles in Dark Blue, the Liquid Fuel as Red, and the Generated $H_2$ Gas as Light Blue

An example in Figure 3 shows the pressure drop profile within the reactor. The reactor pressure drop is mainly affected by catalyst porosity and packing density. With this example case, the program generated a pressure drop that agreed with the experimental observations. Once the validated program is developed, prediction over different catalyst substrate and packing density can be expected using this modeling program.

A second example in Figure 4 shows another verifiable parameter, the temperature profile within the reactor. The actual temperature profile is measured via thermocouples placed at regular intervals throughout the reactor, both internally and externally. Due to the exothermic nature of sodium borohydride hydrolysis, there is a sharp temperature rise at the inlet of the reactor. The heat removal through the reactor wall was calculated by accounting for both heat convection and radiation. The heat loss coefficient was taken by assuming a stagnant air environment externally around the reactor. Reactor temperature is an important factor that affects both the rates of reaction and water vaporization, which in turn affect the overall sodium borohydride conversion. There are several design factors that can be modified in order to optimize the temperature profile such as: system pressure, space velocity, fuel concentration, and heat loss through the wall.

**Parameter Optimization.** Once the modeling method was validated by experimental data, the internal dynamics of the reactor were then able to be simulated. The internal profiles that were elucidated from the program included: sodium borohydride consumption, borate formation, hydrogen flow, and water vapor flow. The simulations of these parameters gives us a better understanding of the reaction dynamics and therefore can instruct us to optimize the reactor performance which would then allow for the optimization of the overall hydrogen-generating system. The effects of the variation of some design factors such as system pressure, fuel space velocity and fuel concentrations were then explored, and the influence of these factors on the reactor performance was determined.

The example in Figure 5 gives the effect of system pressure on the sodium borohydride conversion. While the overall percent sodium borohydride conversion can be experimentally determined at the reactor output point, the internal characteristics cannot. Therefore this simulation exercise allows for the 'observation' of the activity within the reactor. It was determined from the simulations that the sodium borohydride conversion decreases as the system pressure decreases. An explanation for this is that the system pressure governs the peak temperature in the reactor. At lower pressure, the rate of water evaporation increases (which requires heat), therefore it limits the heat transfer within the liquid phase of the reactor and hinders the reaction rate. This indicates that system pressure is closely related to liquid water availability. Furthermore, high reactor pressure causes the water vapor pressure to be low, which results in a low void fraction within the reactor. The low void fraction in turn results in better contact between liquid fuel and catalyst, which increases the reaction rate.

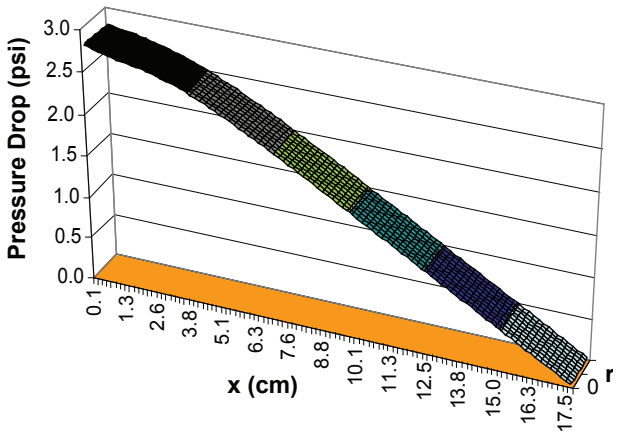


**FIGURE 3.** Simulated Pressure Drop across the Length and Radius of the Reactor Which Matches Experimental Data

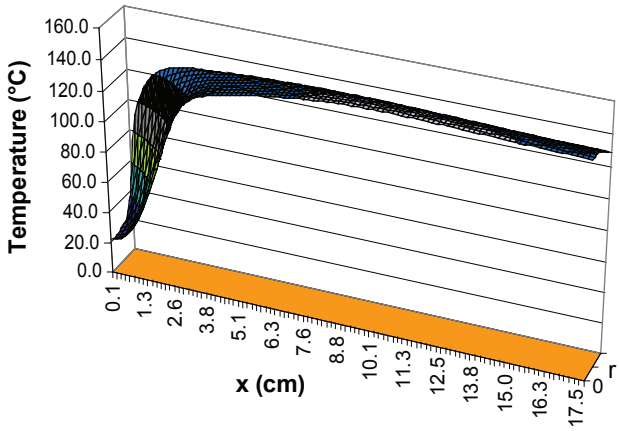


**FIGURE 4.** Simulated Temperature Profile across the Length and Radius of the Reactor Which Matches Experimental Data

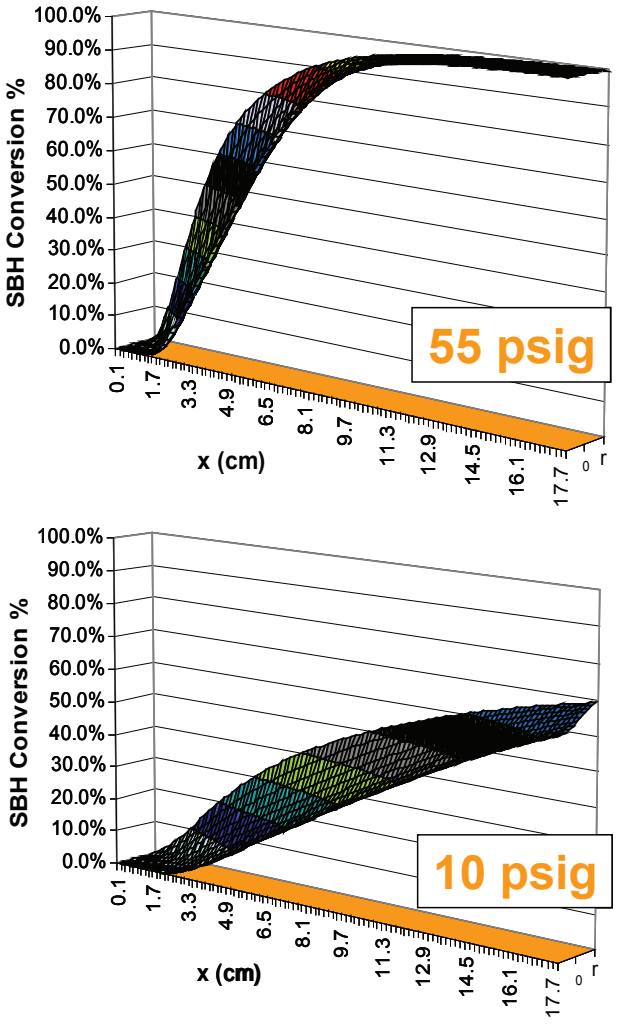


**FIGURE 5.** Sodium Borohydride Conversion Profiles at Two Different Applied System Pressures

Another example in Figure 6 shows the effect of fuel space velocity. An increase in fuel space velocity reduces the sodium borohydride conversion. However, the kinetics determines the extent. Since space velocity also is a design factor associated with hydrogen flow rate i.e. system power output, the reactor should be reasonably oversized to ensure its capability of proving temporarily required high peak power. This can be predicted by simulating reactor performance at higher space velocity.

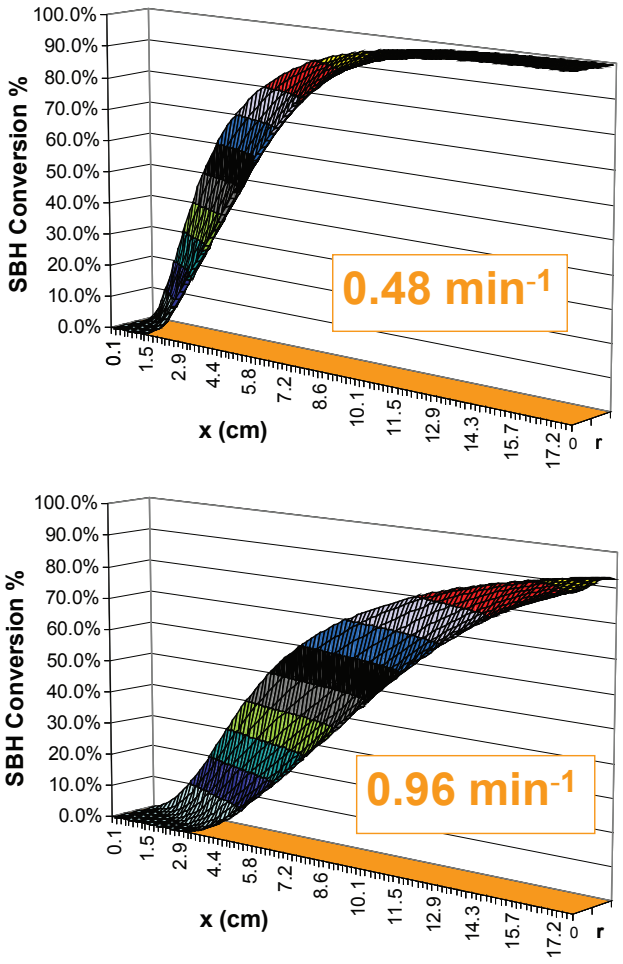


**FIGURE 6.** Sodium Borohydride Conversion Profiles at two Different Space Velocities

## Conclusions and Future Directions

- A reactor model was developed to generate an optimized and improved on-board hydrogen generator. The steady-state profiles of temperature, $NaBH_4$ concentration, pressure drop, and $H_2$ flow rate were simulated and used to validate the modeling by comparison with corresponding experimental data. The effects of fuel flow rate, fuel concentration, and system pressure were simulated and determined.
- To improve the accuracy of the model, reaction kinetics including both catalytic and thermal hydrolysis are necessary. The updated reaction kinetics should also account for the different levels of hydration of the resulting sodium borate material which will affect the water availability within the reactor.
- The model program has been built with a great flexibility for different reaction systems.
- The adaptation of the reactor to incorporate utilization of other chemical hydrides will be initiated when alternative hydrogen storage materials are identified.
- The next phase of the project will involve development of the conceptual design of the optimized on-board hydrogen generation system, including not only the reactor, but also the rest of the components.

## FY 2006 Publications/Presentations

**1.** "Development of an Advanced Chemical Hydrogen Storage and Generation System" Presentation by Ying Wu, Xiaolei Sun, Jeffrey V. Ortega, Dave Rector, and Qinglin Zhang at the DOE Annual Program Review, Washington, D.C., May 16, 2006.

**2.** "Catalyst and Reactor Development for Hydrogen Generation from Sodium Borohydride" Presented by Ying Wu, at the MRS Spring Conference, San Francisco, CA, April, 2006.