IV.B.5a Development of an Advanced Chemical Hydrogen Storage and Generation System

Oscar A. Moreno (Primary Contact),
Jeffrey V. Ortega, Qinglin Zhang

Millennium Cell Inc. (MCEL)
1 Industrial Way West, Building E
Eatontown, NJ 07724
Phone: (732) 544-5759; Fax: (732) 542-2846
E-mail: moreno@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.
- Complete, by the end of FY 2007, a conceptual system design based on sodium borohydride that will include key technology improvements to enable a hydrogen fuel system meeting 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 MCEL's engineering expertise to guide Chemical Hydrogen Storage Center of Excellence (CHSCoE) research in both on-board hydrogen generation systems and off-board chemical hydride regeneration.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Storage section 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	MCEL Current Status
Specific Energy	4.5 wt% 1.5 kWh/kg	6 wt% 2.0 kWh/kg	4.5 wt% 1.5 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)	36 g/L (1.2 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 preliminary design of an on-board fuel system that meets DOE 2007 targets.
- Completed sodium borohydride regeneration data-mining by providing two reports to the CHSCoE: (1) "Summary of Analytical Techniques for Detecting Sodium Borohydride and Related Compounds;" and (2) "Summary of Synthetic Processes for the Production of Sodium Borohydride."
- Completed a stereoscope and metallograph analysis of catalyst using MCEL's catalyst sample and performance data combined with digitizing and catalyst packing software at Pacific Northwest National Laboratory (PNNL) to generate a "virtual catalyst particle." Fundamental properties of the catalyst are incorporated in microscopic modeling based on Lattice-Boltzmann principles.
- Completed microscopic modeling that has yielded transport and reaction parameters for use in the reactor macroscopic model. Examined dynamic reactivity characteristics such as gas-shielding effect and varying activity.
- 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 hydrogen distribution in the reactor using 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 the 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 the 5-year program. 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 chemical hydrogen storage technology. System engineering considerations will incorporate Millennium Cell'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 of Excellence for Chemical Hydrogen Storage.

Approach

To complete the conceptual system design based on sodium borohydride, reactor performance optimization is the crucial step. The reactor modeling is being carried out through two parallel strategies: development of the custom program – cooperation with PNNL and utilization of the commercial package, Star–CD (CD-Adapco) computational fluid dynamics (CFD) simulator. The custom reactor modeling program includes two parts: microscopic reactor modeling and macroscopic reactor modeling. Both are mainly developed by PNNL. The use of the custom program assists the CHSCoE to fully understand the model program, thereby leading to much more flexibility in the modeling exercise. Incorporation of the commercial simulator was performed at MCEL to take advantage of the customized program.

Custom Microscopic Modeling for Reactor

In order to perform the microscopic modeling (particle level), stereoscope and metallograph analyses were performed to determine 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, compressed, settled into place, and 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, which was determined by experimental reactor performance data. A combination of laminar and turbulent-type flows was also incorporated into the calculations.

Custom Macroscopic Modeling for Reactor

Custom macroscopic modeling uses a more complex 3-phase model. This model required the fully characterized catalyst particles from the microscopic modeling. The model was implemented by utilizing code written in Fortran 90. The program consists of several subroutines, and treats the reactor as a test bed. The reactor is divided into 10 rings axially, and 100 slice sections 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 an exact location in the reactor, 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 does, while also having the added benefit of being based on the original Lattice-Boltzmann calculations.
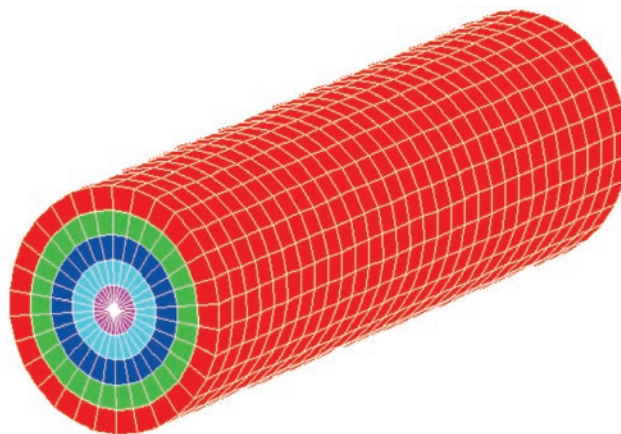
FIGURE 1. Visual Representation of the Reactor Domain for Modeling Using Finite Volumes

The input parameters of the program include: fuel concentration, fuel inlet temperature, fuel space velocity, reactor geometry (including reactor length, internal diameter, reactor wall thickness), 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, and void fraction. The program has the capability to solve for both transient and steady state situations. The optimization of reactor performance can be achieved by adjusting main design factors. Additional information can be obtained to improve overall heat integration and water management.

Star-CD CFD Reactor Modeling

The Star-CD (from CD-Adapco) simulator has much more powerful processing function than the in-house custom program. It can calculate parameters in 3D domains. The subroutines used for the macroscopic custom program will be modified to adapt them 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, and followed by the unit building and testing. For this task the process simulator from Honeywell, UniSim has been selected. In addition, to simulate the thermodynamics, the OLI Electrolytes simulator is paired with UniSim to achieve this objective. Due to MCEL, 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 has been enabled for the contingency of any being found to be preferable to sodium borohydride. Fundamentally, the goal is to improve the efficiency of heat management, 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.

On-Board Fueling System – Preliminary Design

The Honeywell UniSim simulation software is used in the process simulation of a 50 kWh system. The thermodynamic properties are implemented by using OLI Systems Aqueous Electrolyte package. The basic components are: fuel tank, reactor, and ancillary equipment to manage gas purity, pressure and flow rate.

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. The simulation result 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, and hydrogen flow rate out of the reactor. These calculations were then verified with experimental data that had been measured previously. The example in Figure 3 shows the conversion profile within the reactor at various flow rates and pressures. The conversion is mainly affected
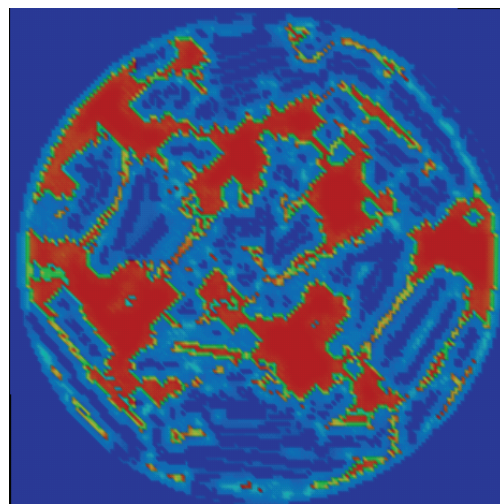
FIGURE 2. Modeled Cross-Section of the Reactor Showing the Catalyst Particles in Dark Blue, the Liquid Fuel as Red, and the Generated H_2 Gas as Light Blue
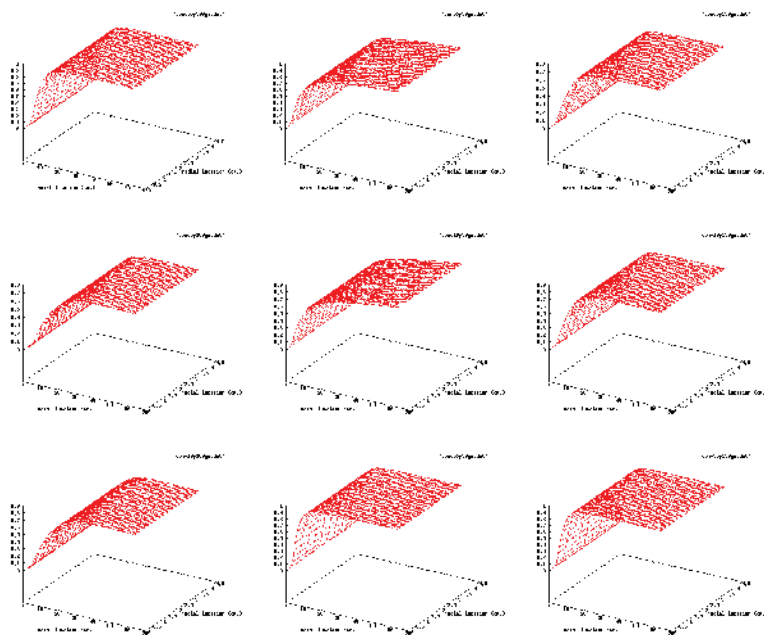
FIGURE 3. Simulated Reaction Conversion at Various Pressures and Fuel Flow Rates in the Axial and Radial Directions for a Large Reactor

by catalyst activity and packing density. With these example cases, the program generated conversions 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.

On-Board Fueling System – Preliminary Design

Figure 4 shows a design of an on-board system that contains the following components: fuel tank, reactor, and ancillary equipment to manage gas purity and heat removal. 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 could then 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.

Figure 5 shows an example of simulations obtained with Honeywell UniSim and OLI Electrolytes. The mass balance results show reasonable agreement to what is observed in systems built by MCEL. However, the heat balance shows significant differences from what has been observed. These discrepancies are being discussed with the OLI Systems support group. Some resolution will be implemented depending on the results from OLI Systems recommendations.

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
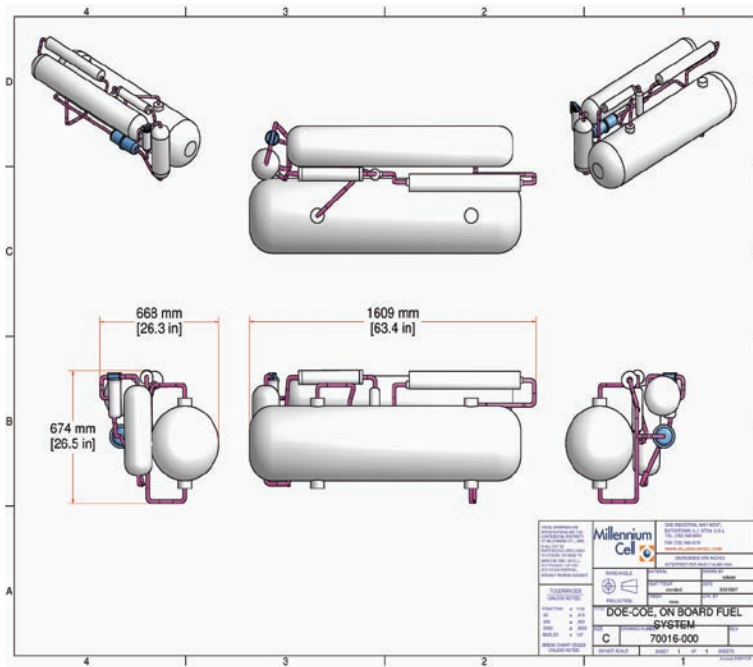
FIGURE 4. Diagram of the Preliminary Design of an On-Board Fueling System Based on Sodium Borohydride (SBH)

50kw HOD process design;				Constants		
				SLPM/kw =	12.5	
Total H2 storged:	10	kg		R =	0.08206	L-atm/deg-mole
Fuel storage:				Fw =	37.833	g/mole
	SBH	30	wt%			
	NaOH	3	wt%			
	flow rate	878.8	g/min			
		52.728	kg/h			
	SBH mol flow	418.1	mol/h			
Fuel density	1.043	kg.l @ 22°C				
Fuel Tank	165.00	Liters				
Targetd H2 flow	625	SLPM (STP) †				
	1674.107	mol/h				
	1.674	kmol/h				
	3.348	Kg/h				
Time for 10kg H2 generation						
	2.987	h				
† Based on 50% Fuel Cell Efficiency						
Heat of reaction	300	Kj/mol				
	125433	kj/h				
% heat loss	50%					
Reactor heat flow	62716.7					
Mixed fuel for reactor processing						
	SBH	20	wt%			

Name	Fuel Storage	H2-H2O Product	Discharged fuel	Reactor Feed	H2	H2O from H2 Stream	Water for Fuel	Fuel	E-1	E-2
Vapour Fraction	0	1	2.66E-04	0	1	0	0	0		
Temperature (C)	20	267.32	267.32	42.00	80.00	80	80	48.087		
Pressure (kPa)	101.326	1288.41	1288.41	1288.41	1288.41	1288.41	47.35	47.35		
Molar Flow (kgmole/h)	2.418654248	3.39	1.29	3.85	1.74	1.66	1.43	3.85		
Mass Flow (kg/h)	52.728	34.36	43.58	78.49	4.53	29.82	25.76	78.49		
Std Ideal Liq Vol Flow (m3/h)										
Heat Flow (kJ/h)	-659602.3404	-390127.90	-651791.09	-1063820.34	-12807.14	-466243.41	-402809.04	-1062411.38	50	-88922.7
Molar Enthalpy (kJ/kgmole)	-272714.6061	-115018.90	-504075.65	-276413.59	-7376.19	-281619.81	-281684.64	-276047.50		

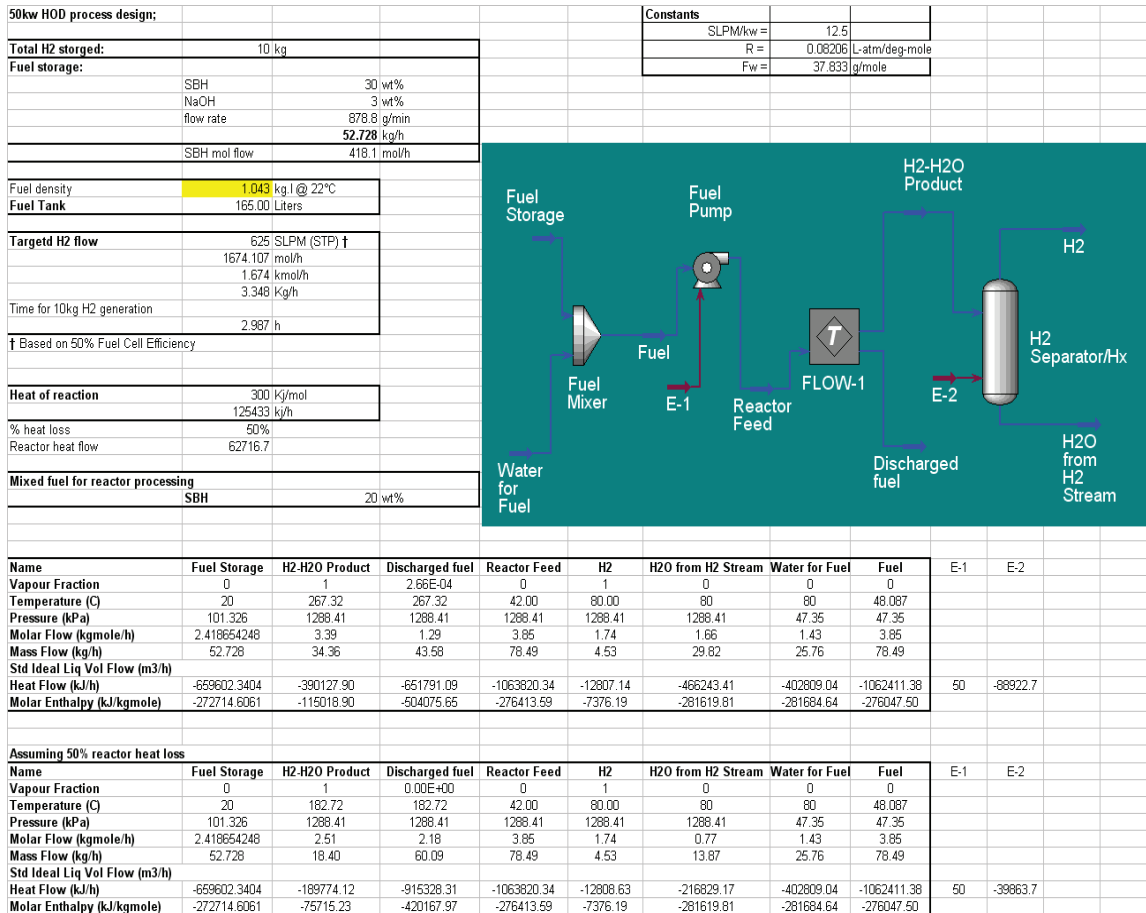| Assuming 50% reactor heat loss										
Name	Fuel Storage	H2-H2O Product	Discharged fuel	Reactor Feed	H2	H2O from H2 Stream	Water for Fuel	Fuel	E-1	E-2
Vapour Fraction	0	1	0.00E+00	0	1	0	0	0		
Temperature (C)	20	182.72	182.72	42.00	80.00	80	80	48.087		
Pressure (kPa)	101.326	1288.41	1288.41	1288.41	1288.41	1288.41	47.35	47.35		
Molar Flow (kgmole/h)	2.418654248	2.51	2.18	3.85	1.74	0.77	1.43	3.85		
Mass Flow (kg/h)	52.728	18.40	60.09	78.49	4.53	13.87	25.76	78.49		
Std Ideal Liq Vol Flow (m3/h)										
Heat Flow (kJ/h)	-659602.3404	-189774.12	-915328.31	-1063820.34	-12808.63	-216829.17	-402809.04	-1062411.38	50	-39863.7
Molar Enthalpy (kJ/kgmole)	-272714.6061	-75715.23	-420167.97	-276413.59	-7376.19	-281619.81	-281684.64	-276047.50		

FIGURE 5. Mass and Energy Balances as Obtained with Honeywell's UniSim Chemical Process Simulator and OLI Electrolyte Systems

concentration, and system pressure were simulated and determined.

- The accuracy of the model reaction kinetics, including both catalytic and thermal hydrolysis, is improved with data from MCEL archives. The updated reaction kinetics account for the different levels of hydration of the resulting sodium borate material, which affects the water availability within the reactor.

- The model program is built with great flexibility to be applicable to different reaction systems.

- Depending on the go/no-go decision at the end of FY 2007, the next phase of the project will involve the construction of an on-board hydrogen generation system, including not only the reactor but all of the components.

FY 2006 Publications/Presentations

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

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