

## IV.E.2 System Level Analysis of Hydrogen Storage Options

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- System gravimetric capacity: 1.8 kWh/kg
- System volumetric capacity: 1.3 kWh/L
- Minimum H<sub>2</sub> delivery pressure: 5 bar
- Refueling rate: 1.5 kg/min
- Minimum full flow rate of H<sub>2</sub>: 0.02 g/s/kW

### FY 2011 Accomplishments

- Analyzed the gravimetric and volumetric capacities of Type-3 and Type-4 two-tank compressed hydrogen (cH<sub>2</sub>) physical storage systems.
- Updated the on-board and off-board analyses of the activated carbon (AX-21) system with adiabatic liquid hydrogen (LH<sub>2</sub>) refueling and cryogenic liner fatigue considerations.
- Conducted the on-board and off-board analyses of the metal-organic framework (MOF-5) system (powder and pellets) with adiabatic LH<sub>2</sub> refueling. Determined the intrinsic capacities, thermodynamics, dormancy, H<sub>2</sub> refueling dynamics, and discharge dynamics.
- Updated system analysis of on-board hydrogen storage systems that use ammonia borane (AB) in ionic liquids (IL) as the hydrogen storage medium.
- Performed off-board analysis of AB regeneration using hydrazine. Identified processes that consume significant amounts of energy in regeneration and provided feedback to stakeholders.
- Revised off-board analysis of alane regeneration using the three-step organometallic approach. Identified processes that consume significant amounts of energy in regeneration and provided feedback to stakeholders.

### Fiscal Year (FY) 2011 Objectives

The overall objective of this effort is to support DOE with independent system level analyses of various H<sub>2</sub> storage approaches, to help to assess and down-select options, and to determine the feasibility of meeting DOE targets. Specific objectives in FY 2011 included:

- Model various developmental hydrogen storage systems.
- Provide results to Hydrogen Storage Engineering Center of Excellence (HSECoE) for assessment of performance targets and goals.
- Develop models to “reverse-engineer” particular approaches.
- Identify interface issues, opportunities, and data needs for technology development.

### Technical Barriers

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

- (A) System Weight and Volume
- (B) System Cost
- (C) Efficiency
- (E) Charging/Discharging Rates
- (J) Thermal Management
- (K) System Life Cycle Assessments

### Technical Targets

This project is conducting system level analyses to address the DOE 2015 technical targets for on-board hydrogen storage systems:



### Introduction

Several different approaches are being pursued to develop on-board hydrogen storage systems with the goal of meeting the DOE targets for light-duty vehicle applications. Each approach has unique characteristics, such as the thermal energy and temperature of charge and discharge, kinetics of the physical and chemical process steps involved, and requirements for the materials and energy interfaces between the storage system and the fuel supply system on the one hand, and the fuel user on the other. Other storage system design and operating parameters influence the projected system costs as well. We are developing models to understand the characteristics of storage systems based on the various approaches, and to evaluate their potential to meet the DOE targets for on-board applications including the off-board targets for energy efficiency.

## Approach

Our approach is to develop thermodynamic, kinetic, and engineering models of the various hydrogen storage systems being developed under DOE sponsorship. We then use these models to identify significant component and performance issues, and to assist DOE and its contractors in evaluating alternative system configurations and design and operating parameters. We establish performance criteria that may be used, for example, in developing storage system cost models. We refine and validate the models as data become available from the various developers. We work with the Hydrogen Storage Systems Analysis Working Group to coordinate our research activities with other analysis projects to assure consistency and to avoid duplication. An important aspect of our work is to develop overall systems models that include the interfaces between hydrogen production and delivery, hydrogen storage, and the fuel cell or internal combustion engine hydrogen user.

## Results

### Physical Storage

We expanded our analysis of  $cH_2$  physical storage to include systems that may use two smaller, equal tanks that are in close communication (equalized pressures) and do not require duplicate controls. There is only a small weight (5-10%) and volume (<3%) increase in going from single-tank to two-tank systems; the penalty would be larger if the two tanks are not in close communication and require duplicate balance-of-plant components.

### Hydrogen Storage in Metal-Organic Frameworks (MOF-5)

We conducted an analysis of on-board hydrogen storage in MOF-5 (Basolite Z 100-H) powder ( $130 \text{ kg.m}^{-3}$ ) and pellets ( $310\text{-}790 \text{ kg.m}^{-3}$ ). Figure 1 shows the principal components of the reference on-board hydrogen storage system with adiabatic refueling, in which the MOF tank is evaporatively cooled during refueling with  $LH_2$ . During discharge, the heat of desorption and any temperature swing in the sorbent bed is provided by recirculating the hydrogen through a small ex-tank heat exchanger. The composite pressure vessel consists of T700S carbon fiber (2,550 MPa tensile strength) wound on an Al 6061-T6 alloy liner, and it is thermally insulated with multi-layer vacuum super insulation in a 3-mm-thick Al 6061-T6 alloy vacuum shell. We conducted fatigue analyses to estimate the required liner thickness to meet the target life of 5,500 pressure cycles (Society of Engineers [SAE] J2579 requirement). The thickness of the insulation was determined so as to limit the heat transfer rate from the ambient to 5 W. A geodesic winding algorithm was employed to determine the optimal dome shape for the composite vessel and the carbon fiber thickness required for a 2.35 safety factor (SAE requirement) at the peak storage pressure.

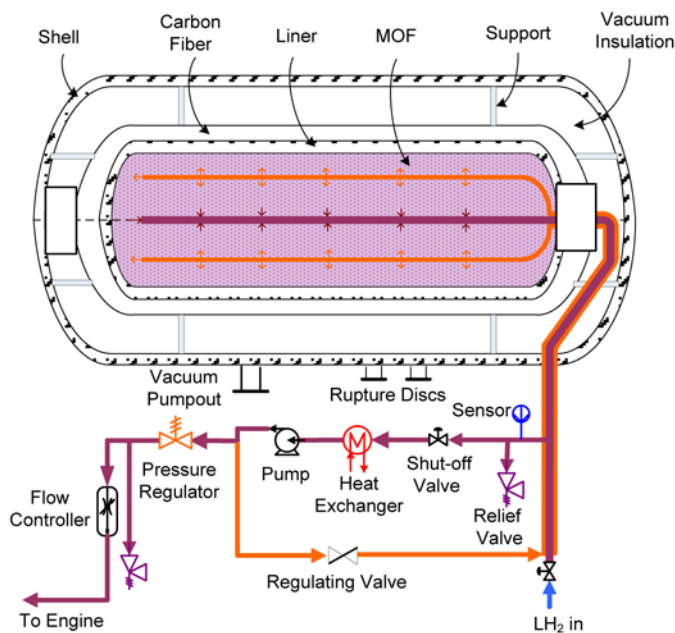


FIGURE 1. On-Board MOF-5 Storage System with  $LH_2$  Refueling

We modeled the MOF-5 powder ( $130 \text{ kg.m}^{-3}$ ) hydrogen adsorption isotherms by fitting the low-temperature data of Zhou et al. [1] and Sudik et al. [2] to the Dubinin-Astakhov (D-A) equation. We used solution thermodynamics to evaluate the integral enthalpy of adsorption. We modeled the MOF-5 pellets ( $310\text{-}790 \text{ kg.m}^{-3}$ ) hydrogen adsorption isotherms by fitting the data of Sudik et al. [2] to the D-A model. We incorporated the fitted isotherms in our system model to estimate the gravimetric and volumetric capacity for 5.6 kg recoverable  $H_2$  at 5-bar minimum delivery pressure and  $1.5\text{-kg.min}^{-1}$  refueling rate. Figure 2 shows the calculated system capacities for powder and pellets. The optimal pressure and temperature for maximum gravimetric capacity are 100-120 bar and  $\sim 60 \text{ K}$  for powder and  $310 \text{ kg.m}^{-3}$  pellet bulk density, and  $\sim 100 \text{ K}$  for  $510 \text{ kg.m}^{-3}$  pellet bulk density. The gravimetric capacity peaks at 6.6 wt% for powder, 4.8 wt% for  $310 \text{ kg.m}^{-3}$  pellets, and 3.3 wt% for  $510 \text{ kg.m}^{-3}$  pellets. The optimal temperature for maximum gravimetric capacity is lower than the temperature at which recoverable excess uptake is at a maximum. The system volumetric capacity increases with pressure for  $130\text{-}310 \text{ kg.m}^{-3}$  bulk density, but does not reach the  $40 \text{ g.L}^{-1}$  2015 target. The maximum volumetric capacity for powder is achieved at 150-250 atm, but at those pressures, a higher volumetric capacity can be achieved without using the sorbent. The volumetric capacity for the  $510 \text{ kg.m}^{-3}$  pellet bulk density decreases with increasing pressures above 100 atm as a result of the lower recoverable excess adsorption. For hydrogen storage in MOF-5 powder (150 atm, 60 K), the containment (liner, carbon fiber, and shell), the storage medium, and the balance-of-plant components account for 44%, 24% and 31%, respectively. The system has a volumetric efficiency of 69%, and 20% of

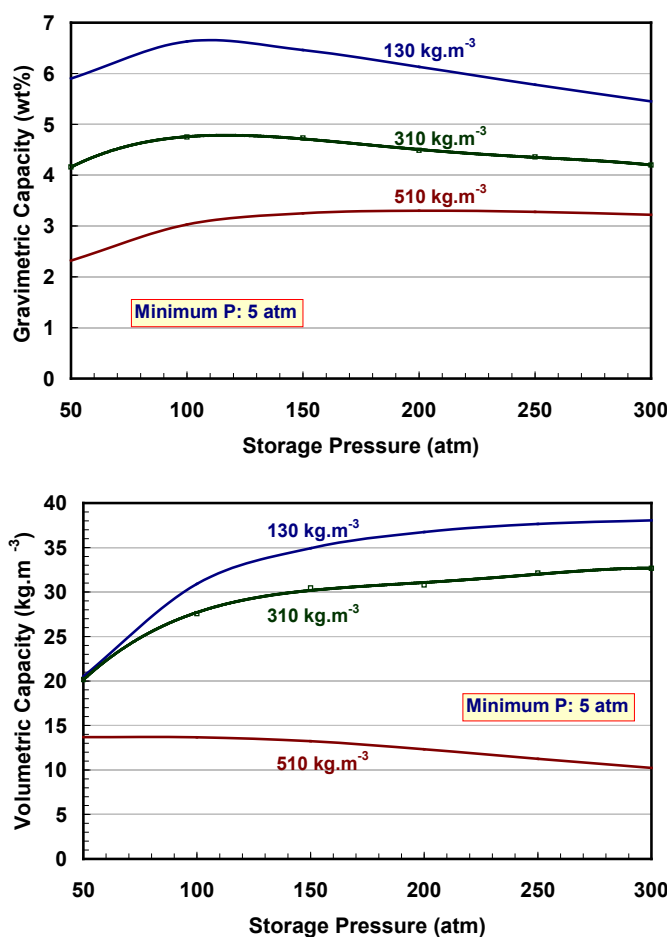


FIGURE 2. Usable Gravimetric and Volumetric Capacities of MOF-5 Powder and Pellets

the system volume is due to the vacuum insulation and the balance-of-plant components.

Analysis of the refueling dynamics showed that the total cooling load is 2, 2.1, and 3.9 MJ (maximum, from completely empty to completely full) for 130, 310 and 510 kg.m<sup>-3</sup> bulk density, respectively. The heat of hydrogen adsorption accounts for 41-53% of the total cooling load; the thermal mass and the pressure-volume work of compressing the hydrogen in the tank account for the balance of the cooling load. Recoverable adsorption accounts for less than 10% of the 5.6-kg usable H<sub>2</sub> in the system with MOF-5 powder or 310 kg.m<sup>-3</sup> pellets. For discharge, we estimated that the required bed permeability is 10<sup>-14</sup> to 10<sup>-13</sup> m<sup>2</sup> for 1 psi in-bed pressure drop and 20 charge and discharge tubes. The initial measurement [3] is 5.4 x 10<sup>-13</sup> m<sup>2</sup> for the 360 kg.m<sup>-3</sup> density pellet. We estimated that the required bed thermal conductivity for 10 U tubes is 0.04–0.05 W.m<sup>-1</sup>.K<sup>-1</sup>. The measured conductivity for powder and pellets is 0.088 W.m<sup>-1</sup>.K<sup>-1</sup> and ~0.6 W.m<sup>-1</sup>.K<sup>-1</sup> for 500 kg.m<sup>-3</sup> pellets with 10 wt% graphite flakes added to MOF-5.

We determined the dormancy capability of the MOF-5 system as a function of temperature, pressure, and the

amount of hydrogen stored at the start of the dormancy period. We estimated the minimum dormancy by analyzing the worst-case scenario, in which a MOF tank is fully charged with H<sub>2</sub> at 150 atm at 60 K, and it is then parked for an extended time. Assuming that the relief valve is set at 25% above the design pressure, H<sub>2</sub> would begin to vent after 6 W.d of cumulative heat transfer (1.2 days at 5 W heat in-leakage rate). In this scenario, the calculated peak H<sub>2</sub> loss rate is 1.9 g.h<sup>-1</sup>.kg<sup>-1</sup> for 5 W in-leakage rate. This rate decreases as H<sub>2</sub> vents from the tank. Also, the peak H<sub>2</sub> loss rate decreases to 0.3 g.h<sup>-1</sup>.kg<sup>-1</sup> if the tank is initially 25% full, and there is no loss of H<sub>2</sub> if the tank is less than 15% full, or with minimal daily driving.

### Chemical Storage

We conducted an on-board analysis for hydrogen storage in a 50:50 (by weight) liquid mixture of AB and an IL, bmimCl (1-butyl-3-methylimidazolium chloride, C<sub>8</sub>H<sub>15</sub>ClN<sub>2</sub>). This AB solution is a stirrable, viscous liquid at room temperature, with a freezing point below -10°C. However, the solution foams once H<sub>2</sub> is released from the AB in the exothermic process; the foam begins to convert to a white solid after releasing 1 H<sub>2</sub>-equiv, with the entire mixture becoming solid after releasing 2 H<sub>2</sub>-equiv [4]. Assuming that an alternative IL (or a mixture of ILs) is found such that the solution does not foam or solidify, we developed a conceptual on-board dehydrogenation reactor model using the kinetic data for the AB-bmimCl mixture. The main challenge is to control the peak temperature in this exothermic process, as too high a temperature may lead to undesirable side reactions, as well as issues of solvent stability and AB conversion (complete AB conversion would impede regenerability). The reactor temperatures can be controlled by using a heat transfer coolant, product recycle, or a combination of the two. The reactor model was set up to yield 1.6 g/s of H<sub>2</sub> at 100% conversion (2.35 H<sub>2</sub>-equiv) using ethylene glycol as the coolant with a 10°C temperature rise through the reactor. The peak reactor temperature is a function of the solution inlet temperature and the recycle ratio. For a specified conversion, it may not be possible to control the peak temperature adequately by just reducing the inlet temperature.

In our simulations, we varied the coolant flow rate (100°C coolant inlet temperature) to control the reactor outlet temperature. For a fixed reactor outlet temperature (200°C), Figure 3a presents the reactor inlet and peak temperatures as functions of the recycle ratio for 100% conversion, and 100 h<sup>-1</sup> (square symbols) and 200 h<sup>-1</sup> (triangle symbols) space velocities (liquid hourly space velocity, LHSV). Figure 3a shows that the reactor inlet temperature decreases with decreasing recycle ratio (R), and drops below 130°C at R = 0.62, at which inlet temperature 100% conversion cannot be achieved. The results in Figure 3a also indicate that the reactor temperatures are insensitive to space velocities over the range of LHSV considered. The reactor outlet temperature has only a

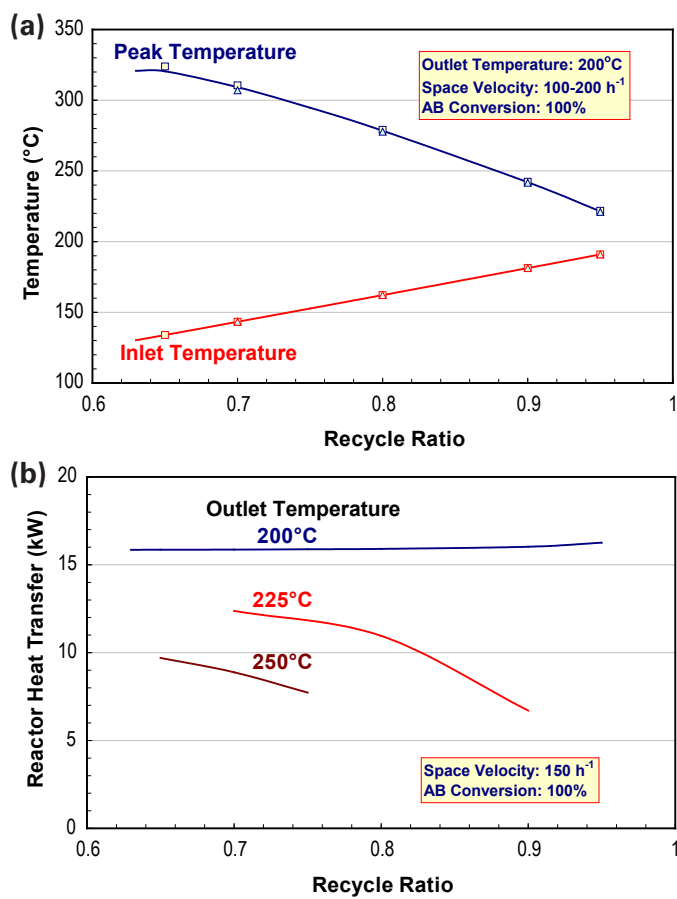


FIGURE 3. Performance of On-Board AB reactor

small effect on the reactor peak and inlet temperatures; the heat transfer, however, is affected by the reactor outlet temperature and the recycle ratio. The reactor heat transfer decreases as the outlet temperature is allowed to rise (see Figure 3b). Finally, we note that whereas high recycle ratios help in limiting the operating temperatures, the inlet flow rate and, therefore, the pumping power increases non-linearly with increasing R.

Our modeling results indicate that the peak rate of H<sub>2</sub> loss from the exothermic decomposition of AB/IL in the storage tank depends on the heat transfer coefficient (assumed 15 W.m<sup>-2</sup>.K<sup>-1</sup> for natural convection) in addition to the Avrami kinetics and the ambient temperature. Based on the 75-110°C kinetics data, we estimate that H<sub>2</sub> loss rate from a full tank significantly exceeds the DOE target (0.05 g.h<sup>-1</sup>.kg<sup>-1</sup>) at >50°C ambient temperature, but is lower than the target at <30°C ambient temperature. The loss rates are proportionally lower with partially full tank. Also, the maximum cumulative loss is limited to 1 H<sub>2</sub>-equiv since the kinetics of the second decomposition step that releases H<sub>2</sub> beyond 1 H<sub>2</sub>-equiv is slow at low temperatures.

We calculated that the AB/IL system has a gravimetric capacity of 4.9 wt%, which is below the 2015 target, and a volumetric capacity of 49.5 g.L<sup>-1</sup>, which exceeds the 2015

target. The AB/IL solution accounts for 63% of the system weight and 79% of the system volume.

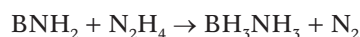
### Off-Board Regeneration of Alane

We updated and analyzed two engineering flowsheets for converting spent Al to alane by a three-step method, using information available in the literature as well as recent unpublished experimental data obtained at Brookhaven National Laboratory [5,6]. Figure 4 shows one of the two flowsheets. In the first step, dimethylethylamine reacts with pressurized hydrogen gas and Ti-catalyzed Al in diethyl ether to form dimethylethylamine alane adduct. The second step involves transamination of the adduct by triethylamine to form triethylamine alane adduct which is less stable and can be thermally decomposed in a final step to yield alane. All reagents, except aluminum and hydrogen, are recovered and recycled. In the second flowsheet, trimethylamine replaces dimethylethylamine in the first step to form trimethylamine alane adduct. Most of the process steps in this flowsheet are similar to those in the first flowsheet, with a few exceptions.

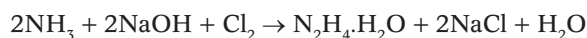
We estimated that the well-to-tank (WTT) efficiency of the first flowsheet is 24%, which increases to 42% if low-temperature waste heat is freely available from an external source. The corresponding efficiencies in the second flowsheet are 23 and 37%, respectively. The estimated greenhouse gas emissions in both flowsheet are ~32 kg CO<sub>2</sub>-equiv/kg-H<sub>2</sub>, which reduce to ~22 kg CO<sub>2</sub>-equiv/kg-H<sub>2</sub> if free waste heat is available.

### Off-Board Regeneration of AB using Hydrazine

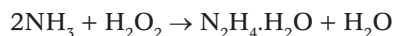
We analyzed the off-board regeneration process for ammonia borane in a single-pot scheme, in which the spent AB is reacted with hydrazine (N<sub>2</sub>H<sub>4</sub>, limiting reagent) in liquid ammonia [7].



Two flow sheets were constructed to close the cycles by considering the commercial processes (Bayer Ketazine and PCUK) for producing hydrazine. The Bayer Ketazine process requires large amounts of electricity to produce NaOH and Cl<sub>2</sub>, which are the feed materials for hydrazine production.

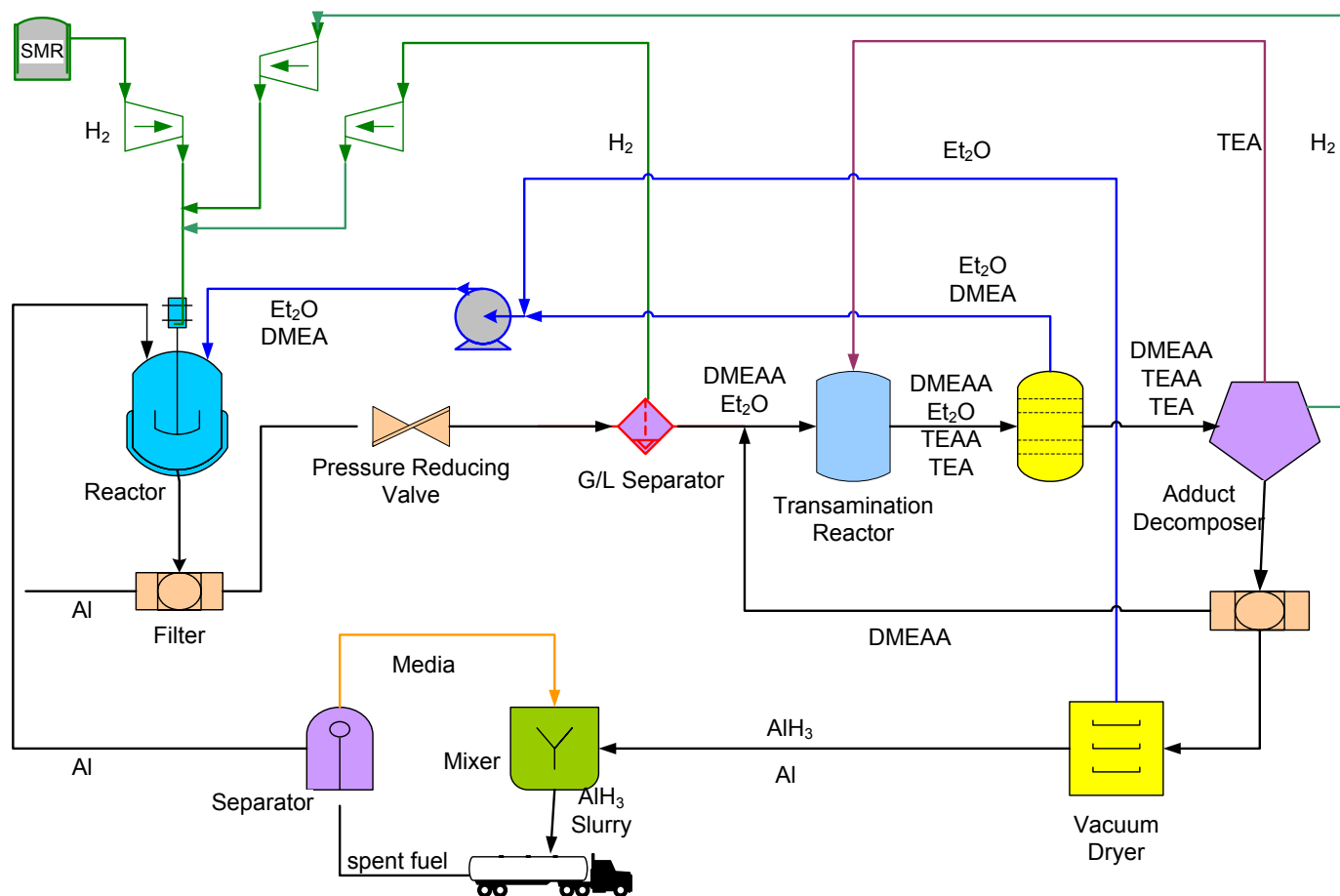


The PCUK process consumes a large amount of steam in making hydrogen peroxide.



We estimated that the WTT efficiency for AB regeneration is 12% via the PCUK pathway and 8% via the Bayer Ketazine pathway. We also estimated that the total greenhouse gas emissions are 63 and 101 kg CO<sub>2</sub>-equiv/kg-H<sub>2</sub> for the PCUK and Bayer Ketazine pathways, respectively.





DMEAA - dimethylethylamine alane; DMEA - dimethylethylamine; TEAA - triethylethylamine alane adduct; TEA - triethylamine; SMR - steam methane reformer

FIGURE 4. Process Flowsheet for Regeneration of Alane using Dimethylethylamine

## Conclusions and Future Directions

- We project that an on-board MOF-5 system with adiabatic LH<sub>2</sub> refueling and 5.6 kg recoverable H<sub>2</sub> can achieve 6.5 wt% gravimetric capacity and 34.9 g.L<sup>-1</sup> volumetric capacity at 150 atm. The loss-free time and hydrogen loss rate are functions of the amount of hydrogen stored and the pressure and temperature at the start of the dormancy event.
- Assuming that an alternative IL (or a mixture of ionic liquids) is found such that the AB/IL solution does not foam or solidify upon releasing hydrogen, we calculate that the AB/IL system has a gravimetric capacity of 4.9 wt% and a volumetric capacity of 49.5 g.L<sup>-1</sup>. We estimate that the H<sub>2</sub> loss rate from a full tank significantly exceeds the DOE target (0.05 g.h<sup>-1</sup>.kg<sup>-1</sup>) at >50°C ambient temperature, but it would meet the target at <30°C ambient temperature.
- We estimate WTT efficiencies of 8-12% for regenerating AB using hydrazine in liquid ammonia in the single pot scheme developed at Los Alamos National Laboratory. We estimate WTT efficiencies of 24-42% for regenerating alane by a three-step organometallic

approach using dimethylethylamine or trimethylamine as the primary amine to form an amine alane adduct.

- In FY 2012, we will update our analysis of alane slurry storage with new kinetics data from Brookhaven National Laboratory for micrometer-sized alane.
- In FY 2012, we will analyze hydrogen storage in a generic sorbent system with an arbitrary heat of adsorption, and for the LiNH<sub>2</sub>:MgH<sub>2</sub> on-board reversible metal hydride system.
- Also in FY 2012, we will further extend our systems analysis work on physical, sorbent, and metal-hydride storage methods.

## FY 2011 Publications/Presentations

- R.K. Ahluwalia, T.Q. Hua, J.K. Peng, S. Lasher, K. McKenney, J. Sinha and M. Gardiner, "Technical Assessment of Cryo-Compressed Hydrogen Storage Systems with Automotive Applications," International Journal of Hydrogen Energy, 35 (2010), 4171-4184.
- T.Q. Hua, R.K. Ahluwalia, J.K. Peng, M. Kromer, S. Lasher, K. McKenney, K. Law and J. Sinha, "Technical Assessment

of Compressed Hydrogen Storage Systems with Automotive Applications,” *International Journal of Hydrogen Energy*, 36 (2011), 3037-3049.

3. R.K. Ahluwalia, T.Q. Hua and J.K. Peng, “On-Board and Off-Board Performance of Hydrogen Storage Options,” Accepted for publication in *International Journal of Hydrogen Energy* (2011).

4. T.Q. Hua and R.K. Ahluwalia, “Alane Hydrogen Storage for Automotive Fuel Cells – Off-Board Regeneration Processes and Efficiencies,” Submitted to *International Journal of Hydrogen Energy* (2011).

5. R.K. Ahluwalia and T.Q. Hua, “Hydrogen Storage in Ammonia Borane Dissolved in an Ionic Liquid,” Submitted to *International Journal of Hydrogen Energy* (2011).

6. T.Q. Hua, R.K. Ahluwalia, J.K. Peng, M. Kromer, S. Lasher, K. McKenney, K. Law and J. Sinha, “Technical Assessment of Compressed Hydrogen Storage Systems with Automotive Applications,” Argonne National Laboratory Report, ANL-10/24, September 2010.

7. R.K. Ahluwalia, T.Q. Hua, J.K. Peng and M. Kromer, “Performance and Cost Analyses of Type 3 and Type 4 Compressed Hydrogen Tanks,” Storage System Analysis Working Group, Washington, DC, June 2010.

8. T.Q. Hua and R.K. Ahluwalia, “Process Efficiency for Regeneration of Ammonia Borane,” AIChE 2010 Midwest Regional Conference, Illinois Institute of Technology, Chicago, September 2010.

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10. R.K. Ahluwalia, T.Q. Hua and J.K. Peng, “On-board Storage System Analysis,” Storage System Analysis Working Group, NREL, Colorado, January 2011.

11. T.Q. Hua, R.K. Ahluwalia and J.K. Peng, “Off-board Storage System Analyses,” Storage System Analysis Working Group, NREL, Colorado, January 2011.

12. R.K. Ahluwalia, J.K. Peng and T.Q. Hua, “Cryo-Compressed Hydrogen Storage: Performance and Cost Review,” Compressed and Cryo-Compressed Hydrogen Storage Workshop, Arlington, VA, February 2011.

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2. A. Sudik, et al., “Achieving Optimal Hydrogen Storage in MOF-5,” 2010 Annual AIChE Meeting, Salt Lake City, UT.

3. A. Sudik, Private Communication 2011.

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5. Lacina D., Wegrzyn J., Reilly J., Celebi Y., Graetz J. Regeneration of aluminum hydride using dimethylethylamine. *Energy Environ. Sci.* 2010; 3:1099–1105.

6. Lacina D., Reilly J., Celebi Y., Wegrzyn J., Johnson J., Graetz J. Regeneration of aluminum hydride using trimethylamine. *J Physical Chemistry C* 2011.

7. Nakagawa T., Shrestha R., Davis B., Diyabalanage H., Burrell A., Henson N., Semelsberger T., Stephens F., Gordon J., Ott K., Sutton A. Chemical hydrogen storage R&D at Los Alamos National Laboratory. DOE Hydrogen Program Annual Review, Washington, D.C.; 2010.