

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

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Objectives

The overall objective of this effort is to support DOE with independent system level analyses of various H₂ storage approaches, to help to assess and down-select options, and to determine the feasibility of meeting DOE targets. Specific objectives in Fiscal Year 2008 included:

- Model various developmental hydrogen storage systems.
- Provide results to Centers of Excellence (CoEs) 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

The Hydrogen, Fuel Cells, and Infrastructure Technologies Multi-Year Program Plan technical barriers this project addresses include:

- (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 2007 and 2010 technical targets for on-board hydrogen storage systems:

- System gravimetric capacity: 1.5 kWh/kg in 2007, 2 kWh/kg in 2010
- System volumetric capacity: 1.2 kWh/L in 2007, 1.5 kWh/L in 2010
- Minimum H₂ delivery pressure: 8 atm in 2007, 4 atm in 2010
- Refueling time: 10 min in 2007, 3 min in 2010 (for 5 kg H₂)
- Minimum full flow rate of H₂: 0.02 g/s/kW (2007 and 2010)

Accomplishments

- Updated the storage capacity of the cryo-compressed Gen 2 system with data from Lawrence Livermore National Laboratory.
- Revised analysis of the storage capacity of the cryogenic activated carbon system to reflect 2010 and 2015 delivery pressure targets.
- Determined the intrinsic capacities, thermodynamics, and water and heat management requirements for on-board sodium borohydride (SBH) storage system. Evaluated the overall fuel cycle efficiency of SBH regeneration using flowsheets proposed by Millennium Cell (MCEL) and Rohm & Haas (R&H), and provided input to DOE and the independent Systems Integrator on the go/no-go decision for SBH.
- Conducted systems analysis to determine the intrinsic capacities, thermodynamics, and decomposition kinetics of hydrogen storage in alane slurry. Completed preliminary energy and efficiency analysis of off-board regeneration.
- Conducted preliminary analysis of regeneration of organic liquid carrier and determined the overall fuel cycle efficiency.
- Performed preliminary energy and efficiency analysis of ammonia borane (AB) regeneration using a scheme developed by Los Alamos National Laboratory (LANL). Identified processes that consume significant amount of energy in regeneration and provided feedback to Chemical Hydride CoE.



Introduction

Several different approaches are being pursued to develop on-board hydrogen storage systems with the goal of meeting DOE targets for light-duty vehicular 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 these approaches and to evaluate their potential to meet the DOE targets for on-board applications.

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 will establish performance criteria that may be used, for example, in developing storage system cost models. The models will be refined and validated as data become available from the various developers. We have formed a Hydrogen Storage Systems Analysis Working Group to coordinate our research activities with other DOE analysis projects (such as those of TIAX and the CoEs) 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 hydrogen user (fuel cell system or internal combustion engine for on-board systems, on-board hydrogen storage subsystem for the off-board systems, etc.).

Results

Hydrogen Storage in Alane Slurry

Alane is considered an attractive carrier of hydrogen for on-board storage systems because of its high intrinsic capacity (10 wt% H₂), small heat of formation ($\Delta H \sim 7$ kJ/mol) and fast apparent decomposition kinetics (alane is thermodynamically unstable at room temperature). We investigated several methods of transporting alane in powder and liquid forms and selected the slurry option (70% solid loading in light mineral oil) for initial evaluation. Figure 1 shows the principal components of the on-board H₂ storage system including the fuel tank that stores both the alane slurry and the spent fuel using a volume-

exchange concept, dehydrogenation reactor, slurry pump and heat exchangers. The thermal energy needed for decomposition of alane is provided by a heat transfer fluid (HTF) that flows on the shell side of the reactor. The HTF (XCEL THERM[®]) is heated in a non-catalytic burner that uses hydrogen in the spent anode gas as the fuel and oxygen in the spent cathode air as the oxidant. A buffer tank stores sufficient H₂ to heat the components in the HTF circuit during start-up while providing H₂ to the fuel cell at an arbitrarily chosen 50% of the peak flow rate. The tank also serves to store excess H₂ produced during down-transients and to make up for the shortfall if the reactor cannot meet the H₂ demand during up-transients.

We developed a model to analyze the performance of the dehydrogenation reactor. Avrami-Erofeyev rate expression was used to describe the dehydrogenation kinetics with the rate constants derived from the experimental data obtained at Brookhaven National Laboratory for Ti-doped and undoped fine AlH₃ powders [1]. Our model showed that the reactor needs to operate at 250°C or higher in order to achieve 95% conversion at reasonable liquid hourly space velocity (LHSV of 60 h⁻¹ in Figure 2 is equivalent to a residence time of 1 min in the reactor). The model also indicated that whereas doping significantly destabilizes alane at low temperature, the effect of doping is small at the reactor temperatures needed for acceptable conversion. This is primarily a result of the lower activation energy for doped alane (78 kJ/mol) than for the undoped powder (120 kJ/mol). We also calculate a minimum

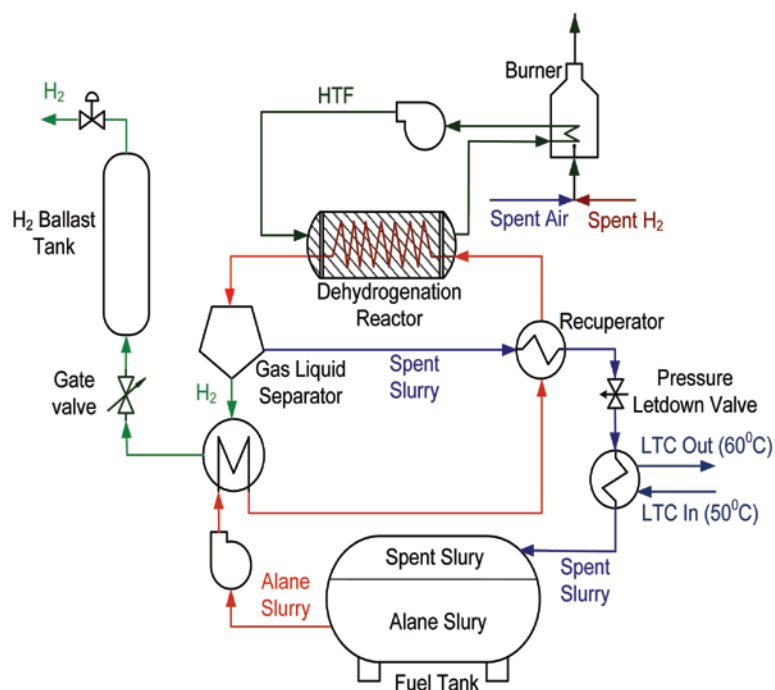


FIGURE 1. Alane Slurry Based On-Board Hydrogen Storage System

heat load of 13.2 kJ/mol that is nearly double the heat of decomposition of AlH_3 at 298 K.

We analyzed the thermal stability of alane stored in the fuel tank and determined its shelf life. Our analysis showed that H_2 loss from undoped alane is limited by its decomposition kinetics and that the peak H_2 loss rate for a fully charged tank with 5.6-kg usable H_2 capacity can be as high as ~ 8 g/h at 50°C with a corresponding $>1,500$ -h autonomy time. Our analysis also showed that H_2 loss from doped alane is limited by heat transfer as well as decomposition kinetics and the estimated autonomy time for a tank with 5.6-kg usable H_2 capacity is 550-1050 W-d at 50°C .

Figure 3 shows the calculated start-up, drive-cycle and the overall efficiency for the on-board storage system. The start-up efficiency is a measure of the H_2 stored in alane that is consumed in bringing the HTF circuit components to their normal operating temperatures. It has been calculated assuming that a vehicle is driven for 100,000 miles over 10 years with

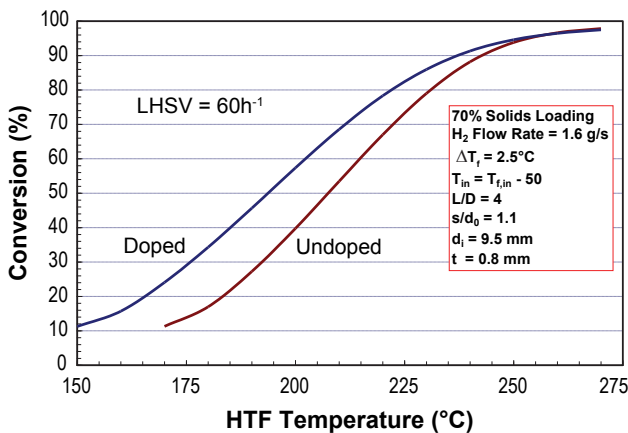


FIGURE 2. Effect of Reactor Temperature on Alane Conversion

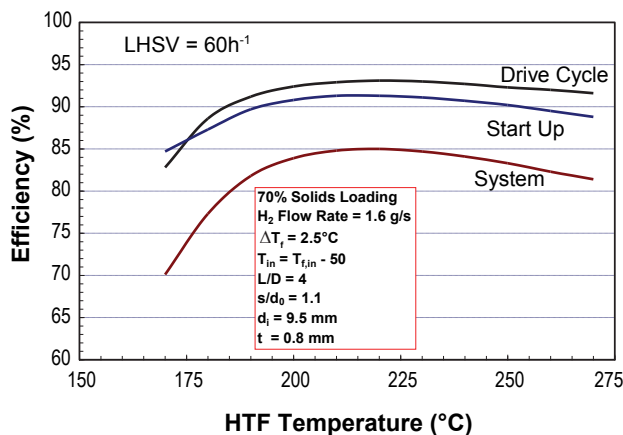


FIGURE 3. Start-Up, Drive-Cycle and System Efficiencies of the Storage System

10,000 cold starts and a fuel economy of 50 miles per gasoline gallon equivalent. The drive-cycle efficiency is defined as the fraction of H_2 released (after startup time) that is available to the fuel cell. The system efficiency – product of the start-up and drive-cycle efficiencies – represents the fraction of stored H_2 that is available for conversion to useful power in the fuel cell. For conditions of highest gravimetric capacity, we estimate a system efficiency of $\sim 80\%$ after accounting for $\sim 13\%$ of stored H_2 being consumed during startup and $\sim 7\%$ of H_2 released in the reactor being consumed in the burner to provide the thermal energy for the endothermic dehydrogenation reaction. Then the estimated usable gravimetric capacity for the system is <4.3 wt% which is less than the 2010 target of 6 wt%; the corresponding usable volumetric capacity is ~ 50 g/L which exceeds the 2010 target of 45 g/L.

Fuel Cycle Efficiencies of Hydrogen Storage Options Requiring Off-Board Regeneration

We analyzed the off-board regeneration processes for several carriers, and determined the energy consumed and the overall fuel cycle efficiency. We compared the calculated well-to-tank (WTT) efficiencies for chemical hydrogen carriers with the WTT efficiencies for physical storage methods (compressed and liquid H_2).

Alane: We surveyed the patent literature and constructed a reference flowsheet for regeneration of alane by a three-step method [2]. As shown in Figure 4, the first step consists of forming alane as an adduct to trimethylamine in the presence of LiAlH_4 catalyst (TMAA). In the second step, TMAA is transaminated in ether to form triethylamine alane adduct (TEAA), and the ether is recycled by vacuum distillation. In the third step, TEAA is decomposed in the presence of LiAlH_4 , and TEA is distilled off under reduced pressure and recycled to step 2; any remaining un-decomposed TEAA is recovered by ether wash and the product alane is vacuum-dried to remove ether residue. We considered two scenarios, one in which the thermal energy needed in the distillation processes is supplied by natural gas combustion, and the other in which it is freely available as low-grade waste heat from industrial sources. We estimate the WTT efficiency as 40.5% with natural gas combustion and 55% if all of the thermal demand can be met with waste heat.

Sodium Borohydride: We analyzed two different pathways for SBH regeneration. The first pathway, proposed by MCEL, recovers Na metal by electrolysis of spent NaBO_2 and NaOH [3], which is converted to sodium hydride and fed to the Schlesinger process for producing NaBH_4 . We considered four options in which the electrolysis steps were carried out with anhydrous or aqueous feed, and with or without H_2 assist at the cell anode. Our analyses showed that the WTT efficiency is in the range of 15 to 23% with Na

recovery being the most energy intensive step. The second pathway, proposed by R&H, is based on direct reduction of NaBO_2 to NaBH_4 using a metal [4]. Our analysis showed that the processes to reduce metal oxide back to metal account for ~75% of total primary energy consumed in the regeneration plant. The overall WTT efficiency for the various metal oxide reduction options analyzed ranged between 12 and 17%.

Organic Liquid Carrier: We constructed a flowsheet for rehydrogenation of N-ethylcarbazole in multi-stage, catalytic, trickle-bed reactors with regenerative intercooling between the stages to achieve a declining temperature profile. Within each stage of reactor, H_2 is introduced at multiple quench locations to maintain a nearly isothermal temperature profile. In this manner, H_2 far in excess of the stoichiometric amount (15-21 times, depending on the number of stages) is used to absorb the heat of reaction (~51 kJ/mol for N-ethylcarbazole). The excess H_2 is recovered downstream of the final stage, recompressed, mixed with compressed makeup H_2 , and recycled. We considered two scenarios, one in which the heat of reaction is discarded as low-grade waste heat and the second in which an organic Rankine cycle is used to produce electricity from the waste heat (~1 kWh/kg- H_2 in liquid carrier). We estimate a WTT efficiency of 60-61% with the first option and a potential 2-3 percentage-point improvement if economics can justify the deployment of the low-temperature organic Rankine cycle.

Ammonia Borane: We constructed and analyzed an engineering flowsheet for regenerating spent AB using the process chemistry being developed at LANL [5]. The flowsheet is based on the concept of achieving high yields by setting up process conditions in which the material to be converted forms the limiting species that is reacted with reagents in excess amounts. We consider

that a single reactor digests spent AB (BNH_2) with thiol and reduces the products with tin metal hydride (MH). Solid AB is recovered as a precipitate whereas thiol is recycled by reacting with formic acid. The MH-COOH product is thermally decomposed to recover the MH while producing CO_2 , which is hydrogenated to yield formic acid [6]. Our analysis indicates that formic acid production is the most energy intensive step, accounting for >40% of the total primary energy consumed in regenerating AB. Depending on the degree of thermal integration, our preliminary estimate of the WTT efficiency for the LANL scheme is 17-34%.

Conclusions and Future Directions

- Although alane is thermodynamically unstable at room temperature, elevated temperatures are needed to achieve >95% conversion in a reasonably compact flow reactor. At these temperatures, doping alane does not appear to accelerate the decomposition kinetics.
- Our preliminary analysis indicates that an alane slurry (70% solid loading) based on-board hydrogen storage system can achieve ~4.3 wt% usable gravimetric capacity and ~50 g/L usable volumetric capacity. These estimates fully account for the energy expended in warming up the storage system from a cold-start, the thermal energy needed to sustain the endothermic dehydrogenation reaction, and the buffer capacity requirements for startup and fast transients. Further work is needed to develop practical methods for preparing the slurry and obtaining data on the decomposition kinetics of alane in slurry form.
- We have obtained preliminary results for fuel cycle efficiencies of some promising hydrogen carriers

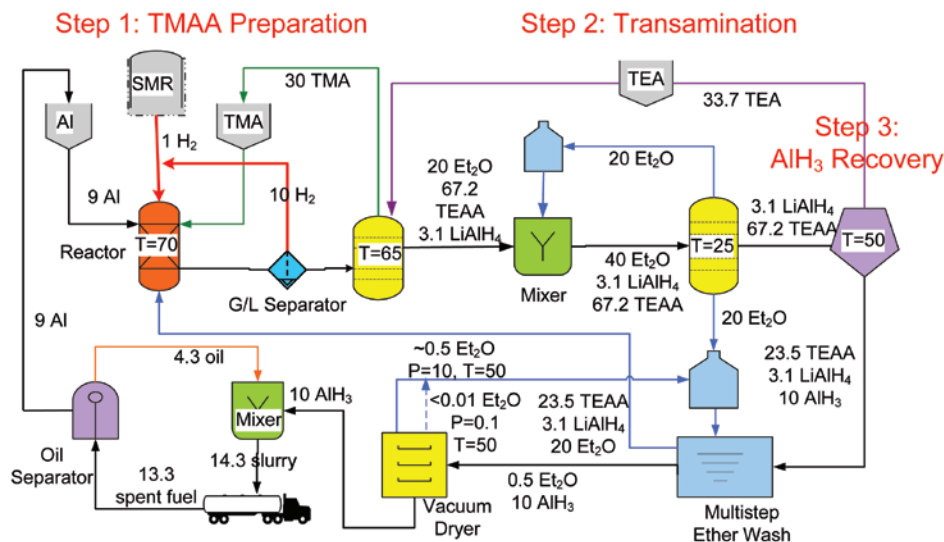


FIGURE 4. Argonne Reference Flowsheet for Regeneration of AlH_3 by Organometallic Route

that require off-board regeneration. We estimate WTT efficiencies between 12 to 23% for the electrolysis routes and the direct reduction methods for regenerating SBH from its hydrolytic product of reaction. Depending on the availability of low-grade waste heat, we estimate a WTT efficiency of 40-55% for regenerating alane by an organometallic route. We estimate a WTT efficiency of ~60% or higher for rehydrogenation of an organic liquid carrier (N-ethylcarbazole) in multi-stage, catalytic trickle-bed reactors with regenerative intercooling. We estimate a WTT efficiency of 17-34% for one of the proposed schemes for regenerating ammonia borane that uses thiol for digestion of spent AB and tin metal hydride as a reductant.

- In FY 2009, we will continue to work with the CoE members to analyze alternative off-board methods of regenerating chemical hydrogen carriers. We will also refine our analyses for improved estimates of WTT efficiencies.
- In FY 2009, we will extend our systems analysis work to include hydrogen storage in metal organic frameworks and in systems with spillover-enhanced sorption.

FY 2008 Publications/Presentations

1. R.K. Ahluwalia, "Sodium Alanate Hydrogen Storage System for Automotive Fuel Cells," *International J. Hydrogen Energy*, Vol. 32, pp. 1251-1261, 2007.
2. R.K. Ahluwalia, T.Q. Hua, and J-K Peng, "Fuel Cycle Efficiencies of Different Automotive On-Board Hydrogen Storage Options," *International J. Hydrogen Energy*, Vol. 32, 3592-3602, 2007.
3. R.K. Ahluwalia and J-K Peng, "Dynamics of Cryogenic Hydrogen Storage in Insulated Pressure Vessels for Automotive Applications," Accepted for publication in *International J. Hydrogen Energy*, 2008.
4. R.K. Ahluwalia and T.Q. Hua, "Analysis of SBH On-Board System," DOE Review Panel for Go/No-Go Decision on Sodium Borohydride Hydrolysis for On-Board Hydrogen Storage, Argonne, IL, 10-11 Sep. 2007.
5. T.Q. Hua and R.K. Ahluwalia, "Off-Board Regeneration of Sodium Borohydride: Analysis of Electrolysis Pathways with Sodium Recovery," DOE Review Panel for Go/No-Go Decision on Sodium Borohydride Hydrolysis for On-Board Hydrogen Storage, Argonne, IL, 10-11 Sep. 2007.
6. T.Q. Hua and R.K. Ahluwalia, "Off-Board Regeneration of Sodium Borohydride: Analysis of Pathways using Metals," DOE Review Panel for Go/No-Go Decision on Sodium Borohydride Hydrolysis for On-Board Hydrogen Storage, Argonne, IL, 10-11 Sep. 2007.
7. R.K. Ahluwalia, T.Q. Hua, and J-K Peng, "On-Board Hydrogen Storage Systems for Liquid Carriers," *Material Science and Technology* 2007, Detroit, MI, 16-20 Sep. 2007.
8. R.K. Ahluwalia, T.Q. Hua, and J-K Peng, "Fuel Cycle Efficiencies of Hydrogen Storage Options Requiring Off-Board Regeneration," Storage Systems Analysis Working Group Meeting, Washington, D.C., 4 Dec. 2007.

References

1. J. Graetz and J. Reilly, "Decomposition Kinetics of AlH_3 Polymorphs," *J. Physical Chemistry B*, Vol. 109, 22181-22185, 2005.
2. J. Murib and D. Horvitz, "Synthesis of Aluminum Hydride and Tertiary Amine Adducts Thereof," *Patent US 3642853*, Feb. 1972.
3. M. Kelly, J. Ortega, O. Moreno, and Y. Wu, "Process for Regeneration of Sodium Borate to Sodium Borohydride," 2006 *DOE Hydrogen Program Review*, Arlington, VA, May 16-19, 2006.
4. A. Chin, L. Klawiter, S. November, and P. Jain "Energy Efficiency of Novel Sodium Borohydride Pathways," Rohm and Haas, 3Q 2007 Milestone Report, Jul. 2007.
5. K. Ott, "Regeneration Chemistries of Spent Fuel from Ammonia Borane," Storage Systems Analysis Working Group Meeting, Washington, D.C., Dec. 4, 2007.
6. J. Anderson, D. Drury, J. Hamlin, and A. Kent, "Process for the Preparation of Formic Acid," *Patent US 4855496*, Aug. 9, 1989.