IV.B.1f Low-Cost Precursors to Novel Hydrogen Storage Materials

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- Innochem, Inc., Boxford, MA
- Electrolytica, Inc., Amherst, NY

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Objectives

- Overall: Develop and advance novel hydrogen storage materials to meet DOE 2010 targets and that have the potential to meet 2015 targets.
- Phase 1 - Define/evaluate novel chemistries and processes for producing chemical hydrides:
  - Emphasize low-cost routes to regenerate sodium borohydride ($NaBH_4$) from spent borate fuel.
- Phase 2 - Identify cost and energy efficient pathways to first-fill and regeneration for ammonia borane (AB) and other borane materials:
  - Continue experimentation leading to selection of single pathway for low-cost $NaBH_4$ and further AB process technology development.
  - Guide selection of a top AB regeneration scheme for experimental studies on most promising alternatives.

Technical Barriers

This project addresses the following technical barriers from the Storage section (3.3) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

(B) System Cost

(R) Regeneration Processes (Cost, Energy Efficiency, Environmental Impacts)

Technical Targets

- **Fuel Cost – Regenerated AB.** Table 1 shows progress against meeting the DOE 2010 and 2015 targets for fuel cost using the AB regeneration scheme developed by Los Alamos National Laboratory (LANL) (thiol-based digestion followed by reduction using tin hydride compounds). Capital recovery and utilities account for 75% of the regeneration cost and are dominated by high mass flow and separation requirements. Several opportunities to reduce cost and energy usage in the LANL process, and thereby lower the fuel cost, have been identified. Additionally, LANL has recently announced a new, much simplified regeneration scheme. Cost estimation for the new scheme is in progress.

TABLE 1. Progress Towards Meeting Technical Targets for Ammonia Borane

Characteristic	Units	2010/2015 Targets	Regenerated AB Status
Fuel Cost	$/gge at pump	2 - 3	7 – 8*

* Based on 250 and 100 mt/day (TPD) H_2 equivalent AB production plants

- **System Storage Cost – First-Fill AB.** The cost for first-fill AB, synthesized using the route developed by Purdue University was estimated to be $9/kg AB. This assumes $5/kg $NaBH_4$ and 10,000 metric tonne per annum (MTA) AB production.

Figure 1 relates AB cost to H_2 cost and shows that, using the above assumptions, it may be possible to meet the 2010 system storage cost target. Sodium borohydride is a dominant component of first-fill AB cost, however, and underscores the importance of developing a lower cost $NaBH_4$ route, especially when the 2015 target is considered.

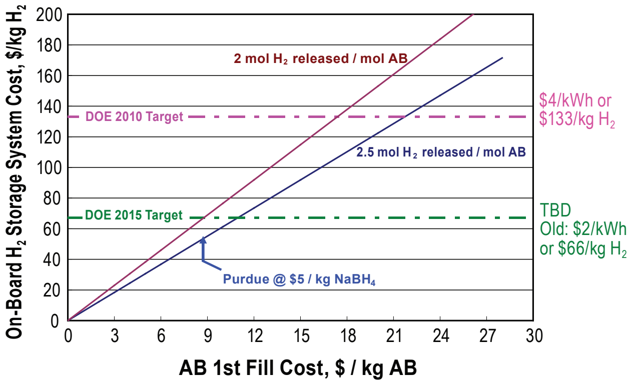

FIGURE 1. First-Fill AB Cost: Impact on Storage System Cost

Accomplishments

- The cost to produce first-fill AB, assuming $5/kg $NaBH_4$ starting material and using the Purdue ammonium formate metathesis route, was estimated at $9/kg AB. This may enable the 2010 target for system storage cost to be met. Sodium borohydride accounts for 75% of the cost to produce make AB, hence, low-cost $NaBH_4$ is critical to meeting the 2015 system storage cost target.
- Alane reduction of borate to borohydride was shown in the laboratory to afford high purities (99+%) and yields (97%). The high material balance closures and lack of intractable by-products point to a recyclable process for lower cost $NaBH_4$ for first-fill AB.
- The baseline cost for regenerated AB using the thiol-based route developed by LANL was estimated at $7–8/kg H_2, compared with the DOE 2010/2015 target of $2–3/gge. Capital recovery and utilities are dominant components of the cost. Several opportunities to lower processing and separation costs have been identified.

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Introduction

This project focuses on identifying and developing viable hydrogen storage technologies using chemical hydrides that have the potential to achieve DOE 2010 and 2015 performance targets for transportation applications. In collaboration with the other Center participants, efforts are directed towards defining and evaluating novel chemistries and processes for producing chemical hydrides. In Phase 1, emphasis was on $NaBH_4$, initially a strong candidate for hydrogen storage because of its hydrogen storage capacity, chemistry, safety, and functionality.

The ability to produce low-cost $NaBH_4$ in an energy-efficient, cost-effective, and environmentally sound manner is critical to the commercial success of virtually any boron-based fuel, including AB. In Phase 2, research continues towards identifying and developing a single low-cost $NaBH_4$ synthetic route for cost-efficient AB first-fill, and conducting baseline cost estimates for first-fill and regenerated AB using a variety of synthetic routes.

Approach

This project utilizes an engineering-guided research and development approach which involves the rapid down-selection of a large number of options (chemical pathways) to a smaller, more manageable number. The down-selection is based on evaluation against a set of fast-fail metrics and can occur before experimentation is initiated. This helps focus efforts and resources on the options with the highest technical and commercial probability of success. A detailed engineering analysis methodology has been established for conducting cost and energy-efficiency calculations. The methodology utilizes a number of inputs and tools (Aspen IPE™, FCHTool, and H2A).

Results

Previously, we reported on the identification of two leading pathways to convert borate to borohydride–metal reduction and carbothermal reduction–based on a comprehensive review of possible pathways, scoring against established metrics, and initial laboratory feasibility studies. Both routes were shown to offer a significant cost reduction and metal usage compared to the current, commercial Schlesinger process, which utilizes four moles of sodium metal to produce one mole of $NaBH_4$.

With the September 2007 No-Go decision for $NaBH_4$ as an on-board hydrogen storage medium, focus was shifted to AB for on-board hydrogen storage and delivery. In Phase 2, the primary objective of this work is to identify cost and energy efficient routes for first-fill AB (storage system cost) and for regenerated AB (fuel cost). Since $NaBH_4$ is a starting material for AB and other boron-based fuels, including several materials currently under consideration by the Metal Hydride Center of Excellence, these materials will require low-cost $NaBH_4$ for initial system fill.

First-Fill AB - Baseline Cost Estimate. In recent years, several attractive routes affording high AB yields have been reported. Purdue and the Pacific Northwest National Laboratory (PNNL) have pursued metathesis routes [1,2]:

$$\text{Purdue: } NaBH_4 + \tfrac{1}{2}(NH_4)_2SO_4 \rightarrow NH_3BH_3 + \tfrac{1}{2}Na_2SO_4 + H_2$$
(>95% yield; THF)

$$NaBH_4 + (NH_4)HCO_2 \rightarrow NH_3BH_3 + NaHCO_2 + H_2$$
(>95% yield; dioxane)

PNNL: $NH_4Cl + NaBH_4 (+NH_3) \rightarrow NH_4BH_4 \rightarrow NH_3BH_3 + NaCl + H_2$
(up to 99% yield)

Ohio State researchers have demonstrated AB formation via base displacement of borane complexes with ammonia [3]:

$$L\text{-}BH_3 + NH_3 \rightarrow NH_3BH_3 + L$$

Initial efforts focused on the Purdue chemistry, specifically the ammonium formate/dioxane route, due to more facile separation of sodium formate by-products from unreacted ammonium formate (compared with the corresponding sulfate salts). A conceptual process flowsheet was developed for this process, and engineering analysis methodology was applied to arrive at an overall cost of \$9/kg AB for a 10,000 MTA sized AB plant. Sodium borohydride pricing of \$5/kg was used as an initial estimate for first-fill AB scales. These results were reviewed and validated by TIAX.

It can be seen from Figure 2 that approximately 80% of the cost to produce AB by this route is due to raw materials, and of this, $NaBH_4$ at \$5/kg accounts for 95% for an overall cost component of 75%. Hydrogen storage media costs based on \$9/kg AB are approximately \$55/kg H_2 (Figure 1). When considered as part of the overall storage system cost, it is clear that $NaBH_4$ pricing significantly lower than \$5/kg is needed if the 2015 target is to be met.

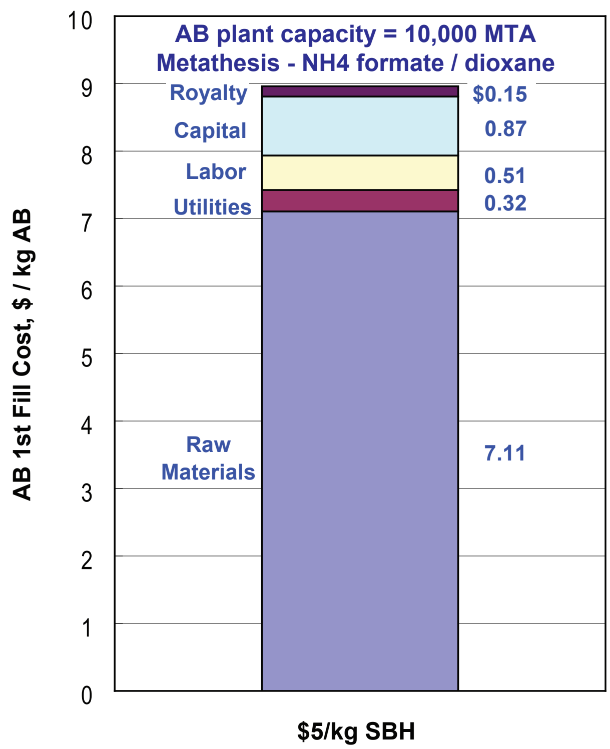


FIGURE 2. First-Fill AB Cost Breakdown – Purdue Scheme

Low-Cost $NaBH_4$ for First-Fill AB. Metal reduction of borate can proceed via a one-step or two-step process as shown below. Recycle of the resulting metal oxide back to the metal in a cost-effective manner is also required.

1-step $NaBO_2 + 2x/y\, M + 2H_2 \rightarrow NaBH_4 + 2/y\, M_xO_y$

2-step $2x/y\, M + 2H_2 \rightarrow 2x/y\, MH_{2y/x}$

$NaBO_2 + 2x/y\, MH_{2y/x} \rightarrow NaBH_4 + 2/y\, M_xO_y$

In Fiscal Year 2009, laboratory studies were re-initiated with the objective of validating prior reactive milling results for, and determining the scalability of, the two-step metal reduction process. The two-step process via metal hydride intermediate offers the advantage of higher yields and lower reaction severities. Much of the work has focused on aluminum as the reductant (ligand-stabilized alanes) in commercially available laboratory-scale ball mills.

$$3\, NaBO_2 + 4\, AlH_3{\cdot}L \rightarrow 3\, NaBH_4 + 2\, Al_2O_3 + 4\, L$$

Table 2 shows the effect of various chemistry parameters on $NaBH_4$ yield. To date, essentially complete mass balance closure has been obtained. Sodium borohydride in high purity (99%) has been isolated, with good yields (97%). Essentially all of the ligand can be recovered, and no intractable by-products have been identified. This points to a recyclable process (Figure 3).

TABLE 2. Effect of Reaction Parameters on $NaBH_4$ Yield

Chemistry (Ball Milling)	Borate Source	$NaBO_2$: **89% $NaBH_4$**, 5% BH $Na_2B_4O_7$ + NaX: **62% $NaBH_4$**
	Alane Adduct	L1: **89% $NaBH_4$**, 5% BH L2: **1% $NaBH_4$**, 29% BH L3: **2% $NaBH_4$**
	Stoichiometry	1.1 eq. AlH_3-L: **60% $NaBH_4$**, 1% BH 2.0 eq. AlH_3-L: **77% $NaBH_4$**, 1% BH
Alternative Approaches	(Slurry-Based Systems)	Borate + AlH_3-L → **29% $NaBH_4$** + 60% BH 89% boron conversion

Results based on ^{11}B nuclear magnetic resonance (NMR) analysis; BH = borane intermediate

In addition to the parameters shown in Table 2, the effects of a variety of milling parameters (i.e., reaction time, ball size, ball-to-powder ratio) have also been investigated. Discrete-element modeling is being used to provide a fundamental understanding of mill motions and energy distribution of particle collisions. Initial results have provided insight into mill operation, scaleup and design, and are helping to guide laboratory studies to identify a scalable process.

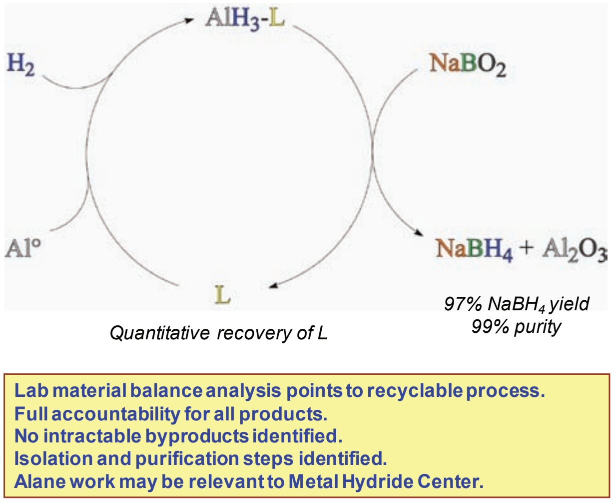


FIGURE 3. Chemical Pathway for Aluminum Reduction of Borate to Borohydride

Carbothermal borate reduction is characterized by the following equation:

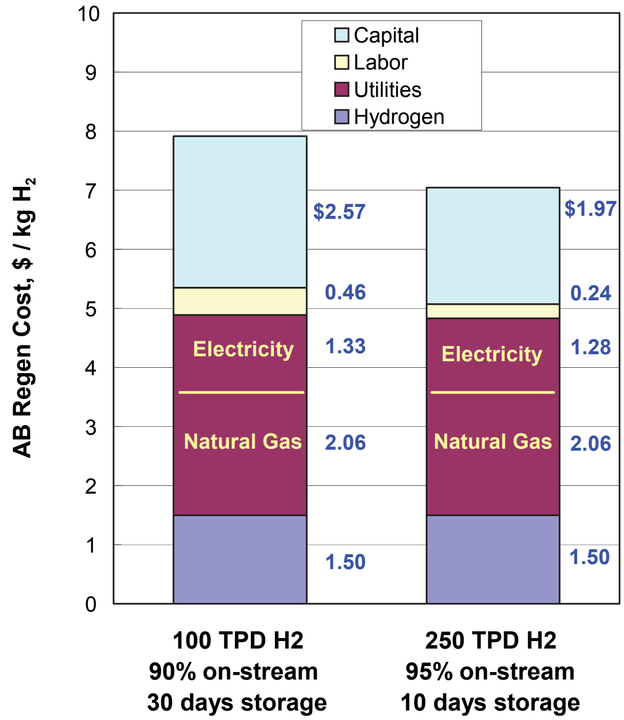
$NaBO_2 + 2CH_4 \rightarrow NaBH_4 + 2CO + 2H_2$ (SynGas byproduct)

Methane (instead of metal) is used as the reductant, thereby eliminating the need for metal oxide recycle and associated cost and energy requirements. High temperatures (generally >1,200°C) are required before these reactions become thermodynamically favorable.

Carbothermal studies utilizing plasma techniques have been undertaken by sub-contractor Idaho National Laboratory (INL). In FY 2009, work was commenced with the objective of reproducing 2007 INL studies which gave 40–50% $NaBH_4$ yield (based on ^{11}B NMR analysis) in a one-step plasma reactor. Additional goals were to gain an understanding of intermediates and byproducts formation and their required separation, reaction quench and heat integration needs, and ultimately identify scaleup options for commercial high temperature operations.

At the time of this reporting, it has not been possible to reproduce past positive results for $NaBH_4$ using the plasma carbothermal process. However, some yet to be identified water-reactive species (possibly boranes, Na, or NaH) have been produced. Assistance is being provided to INL in troubleshooting various equipment and analytical issues, guiding the experimental studies, and in determining an overall mass and boron balances for the system.

AB Regen Baseline Cost Estimate. Center partners LANL, University of Pennsylvania, and PNNL have each developed AB regeneration schemes that have been demonstrated to varying extents. Engineering analysis of the proposed schemes is being provided to the partners to help guide the selection of the most energy-efficient and cost-effective route. LANL's route, based on thiol digestion of the spent fuel followed by reduction to AB using tin hydride compounds, was selected first for analysis.



AB Production, TPD H_2 equivalent	100	250
Baseline AB Regen Plant Cost, $/kg H_2	7.9	7.0
Total Investment, $M	520	1000
Capital	460	850
First Fill Chemicals (dominated by tin)	60	150

FIGURE 4. Cost Breakdown for LANL AB Regeneration Scheme

A conceptual process flowsheet was developed for the LANL process and the same engineering analysis methodology applied for first-fill AB cost estimation was applied. Assuming 225,000 MTA AB production (equivalent to 100 TPD H_2 @ 90% on-stream) and 2.5 mol H_2 release per mol AB, a baseline cost estimate of approximately $8/kg H_2 was calculated. A cost estimate for 250 TPD H_2 equivalent conducted as a sensitivity case resulted in $7/kg H_2. These results were also validated by TIAX.

Cost breakdown for the LANL AB regeneration scheme is shown in Figure 4. Capital recovery and utilities account for 75% of the cost to regenerate AB. This is dominated primarily by high mass flows (dilute solutions, heavy tin reductant) and separation requirements. Several opportunities have been identified to lower the cost and energy requirements for this

process (i.e., minimizing refrigeration, alternatives to distillation, reducing separation requirements). These may enable AB regen costs to approach the DOE 2010/2015 fuel cost target of $2–3/gge.

Additionally, LANL has recently reported a much simplified AB regen route which promises to be more cost-effective and energy-efficient than the thiol-based route. A baseline cost estimate for this approach will be conducted.

Conclusions and Future Directions

Conclusions

- Low-cost $NaBH_4$ as a starting material for first-fill AB is critical to meeting DOE system storage cost targets. At $5/kg $NaBH_4$, the baseline cost estimate for first-fill AB is $9/kg AB (10,000 MTA sized AB plant), which may enable the 2010 target to be met, and significant further reduction in $NaBH_4$ cost will be necessary to be able to meet the 2015 system storage cost target.
- A laboratory-scale process has been demonstrated for reduction of borate to borohydride using alane as the metal reductant. The process affords high yields and high purity $NaBH_4$ and appears to be recyclable. Demonstration of the scalability of this process is a key technical challenge. Other, more scalable routes are also being investigated.
- At $7–8/kg H_2, the baseline cost estimate for AB regenerated using the LANL thiol-based route exceeds the 2010-/2015 target of $2–3/gge. However, several options to reduce the cost have been identified and are being investigated, as is a much simplified regeneration route (also developed by LANL).

Future Directions

- First-fill AB: Conduct baseline cost estimate for PNNL and Shore schemes and refine cost estimates with updated $NaBH_4$ cost.
- Low-cost $NaBH_4$ for first-fill AB: Progress research and development to identify low-cost, scalable process.
  - Metal reduction: demonstrate and select best scalable process.
  - Carbothermal: progress experimental project to validate prior positive results, develop conceptual process and cost.
  - Select single top pathway and further develop process, confirm scalability, update flowsheets and economics.
- Regenerated AB
  - Investigate options to lower cost of LANL regen scheme (reduce mass flow, separation requirements).
  - Conduct baseline cost estimate for new, simplified LANL regen route.

Patents

1. "Process for Production of a Borohydride Compound," A.A. Chin, P. Jain, S.W. Linehan, F.J. Lipiecki, S.G. Maroldo, S.J. November, and J.H. Yamamoto, non-provisional patent application, filed February 23, 2009.

FY 2009 Publications/Presentations

1. "Ammonia Borane 1st Fill and Regeneration Assessments, " A.A. Chin, F. Lipiecki, S. Linehan, N. Allen, R. Butterick, L. Klawiter, S. Nadeau, S. November, FreedomCar Tech Team Meeting, March 19, 2009, Detroit, MI.

2. "Low-Cost Precursors to Novel Hydrogen Storage Materials," S. Linehan, N. Allen, R. Butterick, A. Chin, L. Klawiter, F. Lipiecki, S. Nadeau, S. November, DOE Annual Merit Review, Washington, D.C., May 21, 2009.

References

1. Ramachandran et al, *Inorg. Chem*, 2007, 46, 7810-7817.

2. Heldebrant et al., *Energy & Envir. Science*, 2008, 1, 156-16.

3. Shore et al, WO2007/120511 A2.