PNNL Research as Part of the DOE Chemical Hydrogen COE

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Overview

Timeline
• Project Start: 3-15-05
• Project End: 9-30-09
• Complete: ~40%

Budget
• FY06: $1200K
• FY07: $1700K

Barriers Addressed
• System weight & volume for 2010
• H₂ release rate
• Thermal management
• Fuel cost: regeneration

Partners
Objectives

• Investigate chemicals that promise to meet DOE goals
  – Storage density → RELEASE (pathways/thermodynamics)
  – H₂ release rate → RELEASE (kinetics)
  – Fuel cost → REGENERATION

• Principal focus on solid ammonia borane (AB)
  – 19.6 wt%, 0.16 kg/L H₂ on a material basis
  – 13.1% quantitatively demonstrated and working to higher levels

• Coordinate efforts Center-wide on engineering
Team & Collaborations


• Center Collaborations:
  – Ammonia Boranes: LANL, Penn, UW, Alabama
  – Engineering: Rohm & Haas, Millennium Cell, LANL
  – Fuel Stability: Rohm & Haas
  – Fuel Regeneration: LANL, Rohm & Haas, Penn, UC Davis, Alabama
  – Catalysis: LANL, Penn, UW
  – Computational Chemistry: Alabama

• IPHE Collaborators: Oxford University, Industrial Research Limited, National University of Singapore, University of Birmingham, Rutherford Appleton Labs, LANL

• Additional international collaboration through IEA Task 22

• Environmental Molecular Sciences Laboratory
  – Computational Chemistry Grand Challenge in Hydrogen Storage
  – High Field NMR Facility

Collaboration is critical to meeting Center objectives
Approach

• **Release**
  - Maximize $\text{H}_2$ from fuel to obtain high capacity
  - Maintain balance with spent fuel → need a composition that is regenerable
  - Different approaches to control release and obtain high rates
    - Thermally driven release
    - Additives
    - Scaffolds
  - Understand the impact of working with exothermic release → safety

• **Regeneration**
  - Minimize energy and cost
  - Determine best route for digestion of solid spent fuels
  - Determine how to economically reduce boron centers

• **State-of-the-art scientific instrumentation and computational chemistry tools**
  - High Field NMR Facility
  - TGA/DSC - thermochemistry
  - Spectroscopic tools: Raman, IR, XAFS, others
  - High resolution X-ray diffraction
  - Molecular Science Computing Facility (MSCF)

• **Consider the system: use engineering tools to help direct research activities and identify pitfalls**
  - Component & process models
  - Semi-continuous & continuous bench-scale investigations

Data being collected for Center down-selection process at the end of FY07
Approach: Solid AB

ENERGY EFFICIENCY & FUEL COST

PROCESS CHEMISTRY FOR REGENERATION

H₂ RELEASE MECHANISM

SPENT FUEL COMPOSITION

ADDITIVES

KINETICS

REACTOR/PROCESS MODELS & FLOW SYSTEMS

THERMOCHEMISTRY

FUEL STABILITY & SAFETY

THERMAL MANAGEMENT

SCAFFOLDS
Progress

• Release
  – Now understand the mechanism for the onset of release
    • Series of experiments with high field $^{11}$B NMR
    • Confirmed nucleation and growth mechanism
    • Diammoniate intermediate is key to release
      • Mechanism valid up to ~ 120°C
    – Identified additives that accelerate release
    – Shown that AB is stable at 50/60°C and that impurities have a large impact on release
    – Explored higher loading in silica MCM-41 scaffolds

• Regeneration
  – Demonstrated complete digestion of solid spent fuel
  – Theory used to identify better digestion approaches
  – Theory used to build case for reduction approaches

• Engineering Assessment
  – Used bench scale kinetics to understand impact of 2010 rate requirement on reactor dimensions
  – Preliminary consideration of fuel morphology indicates capacity targets likely within reach
800 MHz $^{11}$B NMR: Solid AB

- Peaks sharpen at 20 min. indicating mobile phase
- Feature at -(10-15) ppm is key to understanding mechanism

_PNNL: W. Shaw, T. Autrey, J. Linehan_

**Impact:** NMR teaches rate enhancement approaches
Transition from Nucleation to Growth

- Multiple triplets indicates series of -BH$_2$- in slightly different chemical environments: oligomers nucleated by DADB
- DADB is the reaction initiator

**PNNL:** W. Shaw, T. Autrey, J. Linehan

**Key result:** DADB is key to increasing rate
Additives Increase Release Rate

Additives reduce the induction period
- Neat DADB → fastest kinetics
- BH\(_4^-\) & NH\(_4^+\) improve kinetics
- NH\(_4\)Cl is slightly better than DADB at 5% loading
- Acidic character appears to be important for the additive → consistent with mechanistic work

Key result: additives to AB formulation accelerate release
Stability & Exothermic Release

- DOE target for 2015: fuel needs to be stable at 60°C
- Solid ammonia borane shows an induction period before release
- Isothermal DSC data [Wolf et al., Thermochimica Acta 343, (2000) 19] can be used to extrapolate release trends to lower temperatures
- Adiabatic assumed as a worst case
  - Fuel predicted to be stable for ~ 100 hrs. at 60°C
  - Greater stability at lower T

Avrami Kinetics

\[ X = 1 - \exp[-(kt)^n] \]

PNNL: S. Rassat, T. Autrey

2006: conservative model predicted stability issues for storage at 50-60°C
Measured Stability at 60°C

- Solid ammonia borane
  - Source A unstable
  - Source B stable
- Source B had a significantly higher purity than source A
- If source A is dissolved and recrystallized, it becomes significantly more stable
- Adiabatic hold experiments indicate that the modeling approach was conservative within the range of formulations examined

*Key Finding: fuel purity is critical for stability at 60°C*
Scaffolds: Higher AB Loading

Key result: scaffolds allow tuning of thermodynamics and kinetics

- $^{11}$B NMR and DSC suggest di-H-bonds are disrupted at lower temperature
- 1:1 AB to scaffold releases hydrogen at 50°C
- Higher AB loading may offer best trade off between tuned thermodynamics and fuel stability

**PNNL: A. Karkamkar, W. Shaw, T. Autrey**
Regeneration of Ammonia Borane

- RECLAMATION
  - Spent fuel is off-boarded at fueling station
  - Transported to large-scale regeneration facility

- DIGESTION (& DISPROPORTIONATION)
  - First step is to dissolve the fuel
  - Fuel has to be digested to allow chemical manipulation

- REDUCTION & DISPROPORTIONATION
  - Reduction is required to get H\textsubscript{2} back into the spent fuel
  - Disproportionation allows recovery of ammonia borane

REGENERATED FUEL VIA MULTI-STEP PATHWAY
Digestion with Disproportionation

- **Digestion:** $t$-BuOH digests compounds analogous to spent AB fuel
- **Disproportionation:** $B(\text{Ot-Bu})_3$ and AB are formed over time from initial product
- There is competition between AB and $H_2$ formation
  - MeOH favors $H_2$
  - $t$-BuOH favors AB

$$1/3 \ (\text{BHNH})_3 + 2 \ ROH \rightarrow (RO)_2BH + NH_3 \ (\text{wanted})$$
$$ (RO)_2BH + 1/3NH_3 \rightarrow 2/3(RO)_3B + 1/3BH_3NH_3 \ (\text{wanted})$$
$$ROH + (RO)_2BH \rightarrow (RO)_3B + H_2 \ (\text{unwanted})$$

**Impact:** B-H recovered through one pot digestion and disproportionation

*PNNL: D. Heldebrant, J. Linehan, D. Camaioni*
Digestion: Effect of Ammonia Addition and Alcohol Substitution

- 6-fold increase in B-H recovery with NH₃ overpressure
- MeOH gives little NH₃BH₃ → B-H loss dominates
- B(Ot-Bu)₃ co-product → B-OR bonds may be difficult to reduce

**PNNL: D. Heldebrant, J. Linehan, D. Camaioni**

**Impact:** ammonia speeds digestion & increases yield of NH₃BH₃ 6-fold
Theory: A Guide to the Best Digestion Strategy

Rxn 1: \((\text{RO})_3\text{B} + \text{H}^- \rightarrow (\text{RO})_3\text{BH}^-

<table>
<thead>
<tr>
<th>Alkyl</th>
<th>B-O (Å)</th>
<th>O-B-O</th>
<th>B-O-C</th>
<th>(-\Delta H_1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glyceryl, I</td>
<td>1.43, 1.39</td>
<td>113°, 122°</td>
<td>82°, 93°</td>
<td>115</td>
</tr>
<tr>
<td>Cyclohexa-1,3,5-triyl, II</td>
<td>1.39</td>
<td>118°</td>
<td>101°</td>
<td>100</td>
</tr>
<tr>
<td>Methanetrimethyl, III</td>
<td>1.39</td>
<td>118°</td>
<td>100°</td>
<td>96</td>
</tr>
<tr>
<td>Triphenyl, IV</td>
<td>1.37</td>
<td>120°</td>
<td>126°</td>
<td>87</td>
</tr>
<tr>
<td>Trimethyl</td>
<td>1.37</td>
<td>120°</td>
<td>121°</td>
<td>51</td>
</tr>
</tbody>
</table>

PNNL: D. Camaioni, J. Li

Impact: strained B-O bonds are 36-64 kcal easier to reduce than B(OMe)_3
Engineering Assessment
Toward Meeting the DOE Rate Targets
Bench Scale Kinetics → Reactor Size

Neat AB, Gas Burette Tests

Data vs. DSC-Based Model

Impact: DOE rate target can be achieved with modest sized reactor
Engineering Assessment
Impact of Solid Fuel on Capacity

- Loosely packed AB powder cannot make the 2010 system target
- 2010 system target may be attainable with pellets
  - How is release impacted by pellet size?
  - What packing density is realistic?
- 2015 system target is not attainable with a pellet-based approach
- Game changers:
  - Ultra-low voidage approach
  - More H₂ from AB

PNNL: S. Rassat, T. Autrey, A. Karkamkar

Volumetric capacity target looks possible with an engineered morphology
Higher Temperature Preliminary Data

- New gas burette apparatus allows release at higher temperature
- Working to higher temperature to further increase rate and capacity
- Wt% > 16% H$_2$
- Max rate > 3 gH$_2$/s/kg AB
- Virtually no induction period observed at higher temperatures

Key result: higher temperature could be the key to capacity & rate
Future Work: Release

• Continue to drive up Capacity
  – Higher temperature → > 2 equivalents (mechanism still poorly understood)
  – Volumetric: fuel morphology & low voidage formulations

• Continue to drive up Rate
  – Higher temperature → faster kinetics
  – Additives – enhance release and maintain stability
  – Need to understand kinetics of H₂ release after 1st equivalent

• Quantitative measurement of H₂ purity

• Scaffolds: different surface chemistry to tune thermodynamics, kinetics while maintaining fuel stability

• Reactor and process concepts for solids: keep working toward evaluation based on systems rather than materials
  – Apparatus being assembled for continuous processing
  – Examine impact of engineered solids on release
  – Component and process model development
Regeneration: Future Work

• Drive to better efficiency
• Develop strategies that destabilize the bonds formed during digestion and offer good access to the B center for reduction
  – Theory indicates destabilization using polyols & phenols
  – Need to look at -SH in addition to -OH digestions
• Incorporate reduction pathways
  – Rohm & Haas efficiency analysis has shown that Zn may be an economical metal route to sodium borohydride
    • PNNL synthesizing ZnH$_2$ in support of experimental program
    • PNNL will examine ZnH$_2$ for reduction of spent ammonia borane
  – Theory driving renewed interest in transfer hydrogenations
  – New pathway proposed by Dan Dubois at PNNL
    • Activates H$_2$ for reduction reactions
    • Theory suggests reduction of borate esters feasible
    • Use on B-O bonds directly or for regeneration of other hydrides
• Engineering analysis
  – Conceptual design & preliminary flow sheeting
  – Efficiency & cost analyses
Future Regeneration
Catalytic Activation of H$_2$ for Reduction

**Dubois et al. Organometallics (2006)**

$L_4M^+ + H_2 + t$-BuO$^-$ → $L_4M$-$H + t$-BuOH

$L_4M$-$H + BEt_3 → L_4M^+ + H-BEt_3^-$

Theory: $\Delta G = -14$ kcal/mol

$(PhO)_3B + H-BEt_3^-$ → $(PhO)_3B$-$H^-$ + B$Et_3$

- Cannot reduce with H$_2$ alone
- Couple catalysis to acid-base chemistry to drive reaction
- Working on one pot reaction

Goal: $H_2 + Base + (RO)_3B^{\text{Cat}} \rightarrow (RO)_3B$-$H^- + Base$-$H^+$

**PNNL: D. Dubois, J. Linehan, D. Camaioni, D. Heldebrant**

**Impact:** route demonstrated by Dubois et al. should reduce B(OPh)$_3$
Summary: Release

• Neat AB appears to be the front runner at present
  – Mechanism of release is pretty clear for 1st Equivalent
  – Temperature can be used to control rate
  – Demonstrated release of up to 16+ wt% (preliminary) for material
  – Need more kinetics studies on 2nd+ equivalents
  – Fuels can be formulated for long term stability at 60°C (2015 target)
• Additives have been identified that greatly accelerate the rate of release
  – Need to determine if there are additives that allow increased rate at release temperature, but stable fuel at 60°C
  – Scaffolds are still of great interest, but additional work needs to be done to be sure stable fuels are possible
• Simple engineered forms have potential to meet the 2010 gravimetric and volumetric targets for a system
• Based on the 2010 maximum rate target, reactor sizes look to be reasonable
Summary: Regeneration

• Shown how theory is guiding digestion and reduction work at PNNL
  – Need to destabilize borate ester co-products and look at –SH
  – Two ideas on reduction pathways to be examined over the next year
• Digestion & disproportionation with B-H recovery has been demonstrated
• Ammonia overpressure dramatically impacts B-H recovery
• Engineering analysis will start now that regeneration routes are emerging
# Summary Table
(Solid Ammonia Borane)

<table>
<thead>
<tr>
<th>Temp (°C)</th>
<th>Weight % H₂</th>
<th>Vol. Cap. (kg/L) (loose powder)</th>
<th>Max. Rate (gH₂/s/kg)</th>
<th>kg AB in Reactor for 2010 rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>60 (1:1 Scaffold)</td>
<td>3.2</td>
<td>3.2</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>86.5</td>
<td>5.5</td>
<td>5.5</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>120</td>
<td>6.5</td>
<td>7</td>
<td>0.021</td>
<td>1</td>
</tr>
<tr>
<td>140</td>
<td>---</td>
<td>&gt;13</td>
<td>0.039</td>
<td>1.8</td>
</tr>
<tr>
<td>155</td>
<td>---</td>
<td>&gt;16</td>
<td>0.048</td>
<td>&gt;3</td>
</tr>
</tbody>
</table>

All numbers provided above are MATERIAL values. DOE targets are based on system:
- 2010 Gravimetric Capacity of 6%
- 2010 Volumetric Capacity of 0.045 kg/L
- 2010 Rate of 0.02 gH₂/s/kW