

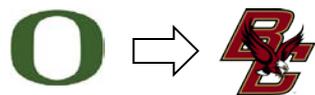
Project ID: ST104



Novel Carbon(C)-Boron(B)-Nitrogen(N)- Containing H₂ Storage Materials

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Department of Chemistry, Boston College
2014 Annual Merit Review Meeting
Washington DC
June 17, 2014

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Synthesis
Catalysis



Characterization



Theory



Fuel Cell Operation

Overview

Timeline

Project start date: March 5, 2012

Project end date: March 4, 2015

Budget

Total Project Value: \$2,526,606

Cost Share: \$505,664

DOE Share: \$2,020,942 (includes
\$862,000 in FFRDC funds)

DOE Funding Spent* (not including FFRDC
funds): \$602,356

* as of 3/31/2014

Technical Barriers (Vehicular)

- A. system weight and volume
- C. efficiency
- D. durability/operability
- E. charging/discharging rates
- J. thermal management
- R. regeneration processes
- S. by-product/spent material removal

Project Team



Shih-Yuan Liu
Frank Tsung



Tom Autrey
Abhi Karkamkar
Mark Bowden
Sean Whittemore
Kriston Brooks



David Dixon



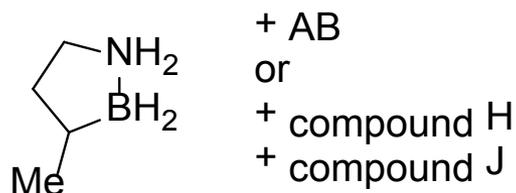
Paul Osenar
Jim Sisco

Outline

- Relevance (Potential Impact & Objectives)
- Collaboration & Coordination
- Approach to performing work
- Recommendations (AMR Reviewers and Protonex)
- Accomplishments & Progress
- Future Work

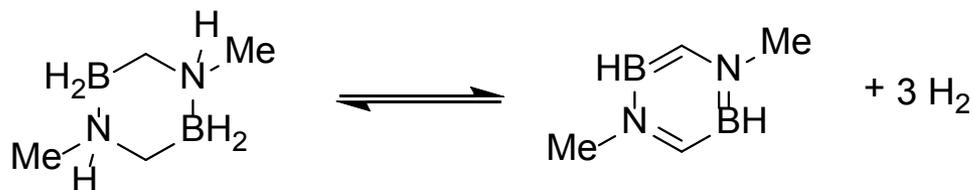
Project Relevance (Potential Impact)

i) Liquid phase fuel blends



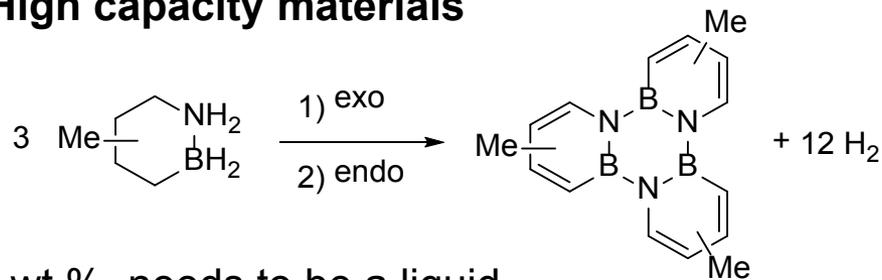
>5.4 wt.%, liquid phase

ii) Reversible materials



3.4-5.3 wt.%, potential onboard reversible material

iii) High capacity materials

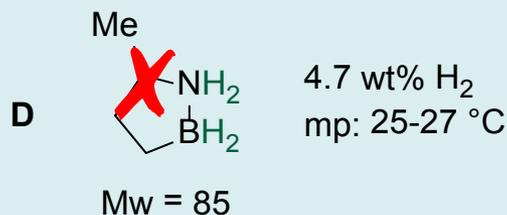
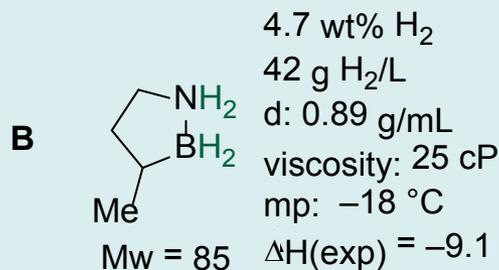
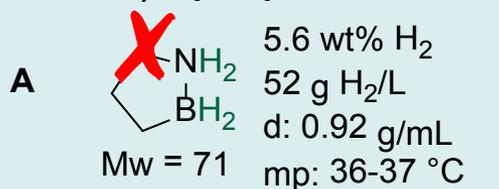


>8 wt.%, needs to be a liquid

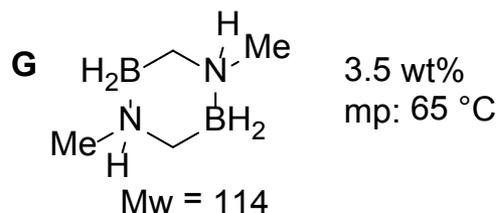
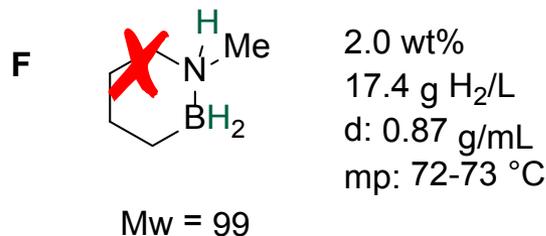
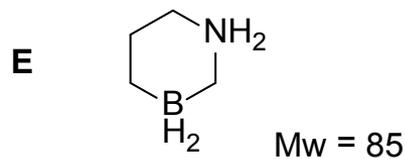
Project Objectives

Develop novel chemical H₂ storage materials that have the potential to enable non-automotive applications and meet the 2017 DOE targets for vehicular applications with focus on three classes of materials:

i) liquid phase

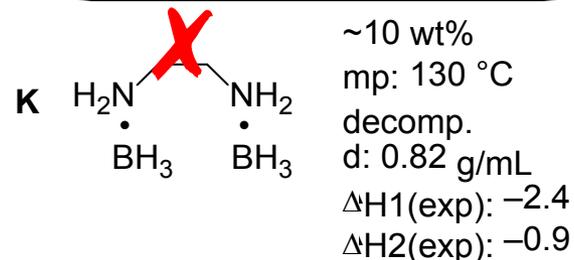
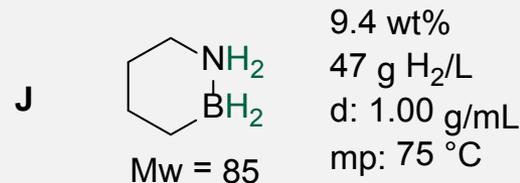
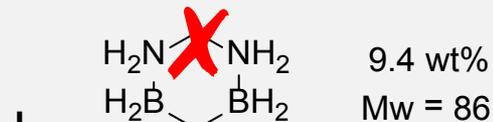
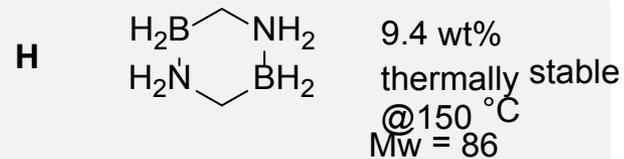


ii) potential reversible



energy values in kcal/mol

iii) high capacity



Collaboration and Coordination

Team members and roles:

Boston College (BC):

- synthesis and development of CBN H₂ storage materials
- NEW expertise: heterogeneous catalysis

Pacific Northwest National Laboratory (PNNL):

- experimental characterization of materials (thermodynamics, kinetics, thermal stability, H₂ purity)
- modeling (flow sheet for first fill & regen, COMSOL for reactor design for coupled exo/endo materials)

The University of Alabama (UA):

- computational chemistry (thermodynamics, physical properties, mechanisms)

Protonex:

- fuel cell system integration for chemical hydrogen storage materials
- expertise and advisors for non-automotive market applications (portable power)

Coordination: Liu (BC) is project lead (quarterly conference calls among all partners) many examples of more frequent 2-way exchange of information.

Outside collaborations

Kriston Brooks (PNNL) has kept us up to date on progress and direction in the HSECoE
Ben Davis (LANL) exchange information on liquid carriers, techniques and approaches
Craig Jensen (Hawaii) information of homogeneous catalysts for liquid carriers
Qiang Xu (AIST) information of heterogeneous catalysts for liquid carriers

Questions related to commercialization: *provide guidance for research directions for portable power*

- What is the estimated cost of production for Compound **B**?
→ **Task 3**
- What is the long term stability of Compound **B**?
→ **Tasks 1b and 1c**
- What are environmental influences?
- What are the hazards of Compound **B** and its spent fuel? Hazard Class? Flash Point? Shipping logistics?
→ **Task 1d**
- What is the dependence of decomposition rate on temperature?
→ **Task 1b**
- Is the decomposition reaction exothermic? What is the heat of reaction?
→ **Tasks 1b, 1c, 1e**
- Can Compound **B** be decomposed in a fixed bed reactor (in a single pass, at high conversion)? Do we need new heterogeneous catalysts?
→ **Task 2**

See Reviewer-Only slides for specific details

Approach

Tasks (Approach is focused of 5 integrated tasks)

- 1) Synthesis and characterization (BC, PNNL)
- 2) Characterization of materials (PNNL)
- 3) Theory (UA)
- 4) Scale-Up Synthesis/Analysis (BC, PNNL)
- 5) Material property targets for small power applications (Protonex)

Project takes advantage of using the combined expertise of all partners. BC has the experience and facilities to carry out the synthesis and catalytic hydrogen release in new CBN materials and works in collaboration with PNNL, with the experience and facilities to characterize the new materials (kinetics, thermodynamics, thermal stability, volatile impurities). UA has the experience in computational methods to predict new material properties, e.g., vapor pressure and volatility, initial predictions that help to guide materials 'selection', thermodynamics used in modeling, and mechanistic studies to help us down select to most feasible pathway for hydrogen release. Protonex has the experience and facilities to work with chemical hydrogen storage materials for portable power applications and is consulted regularly to discuss the results of the characterization, catalysis and modeling studies.

2013 AMR Reviewer Recommendations

provide guidance for research directions

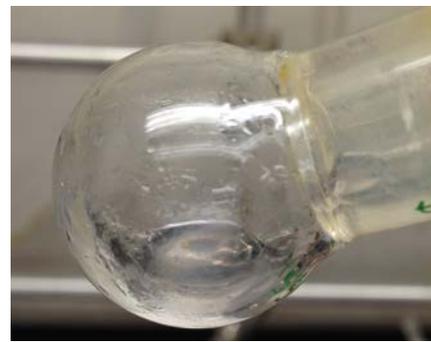
- Project focus should be re-directed toward the development of a compound that will meet the DOE H₂ storage LDV targets.
- *investigate hydrogen release from CC backbone of CBN and increasing efficiency through coupled endothermic and exothermic hydrogen release (target >8 wt% H₂)*
- The project team should carefully examine the fuel blends issue with respect to regeneration if the main focus going forward is vehicular application.
- *Investigate liquid fuel blends of compound B and ammonia borane to maximize hydrogen and minimize borazine (target liquid carrier with ≥5.4 wt% H₂). Show that the path to regeneration is reasonable*
- The scope of tasks and planned activities is sound at this time (for completing Phase I and transitioning into Phase II). The team should devote more time to searching for and identifying impurities released during the hydrogen desorption under conditions needed to operate fuel cells, as well as looking at intrinsic degradation and thermal stability.
- *(i) quantify volatile impurities, (ii) measure vapor pressure of starting material and spent fuel – use to benchmark theory. (iii) measure thermal stability at 50 °C and use to guide theory.*

Accomplishments: Fuel Blends of B + AB leads to improved materials properties

- experimentally determined H₂ storage capacity is 6 wt% for a **B : AB = 2:1** blend
pure compound B has a H₂ capacity of 4.7 wt%
- spent fuel product mixture is a liquid after cooling to room temperature
- spent products are consistent with trimerization incorporating AB units. Suppressed borazine (B₃N₃H₆) formation.



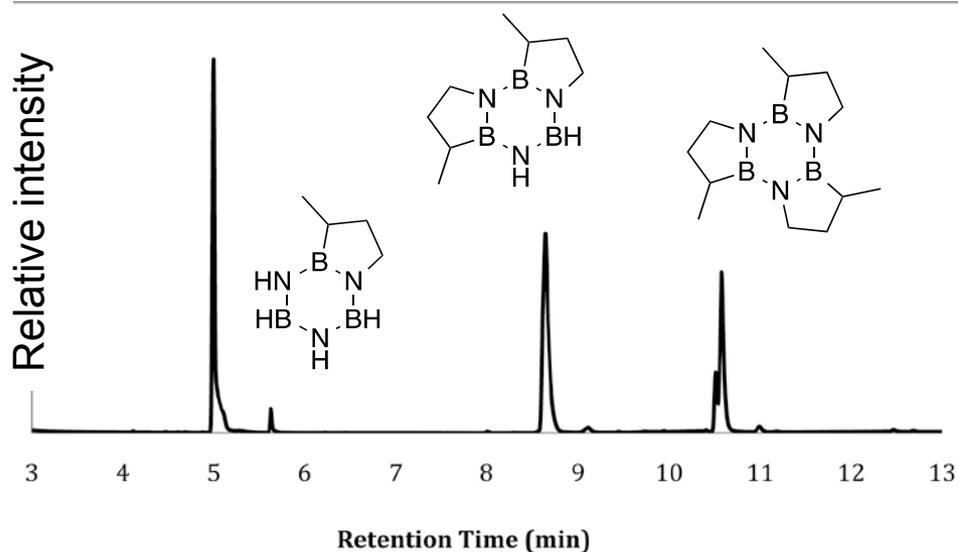
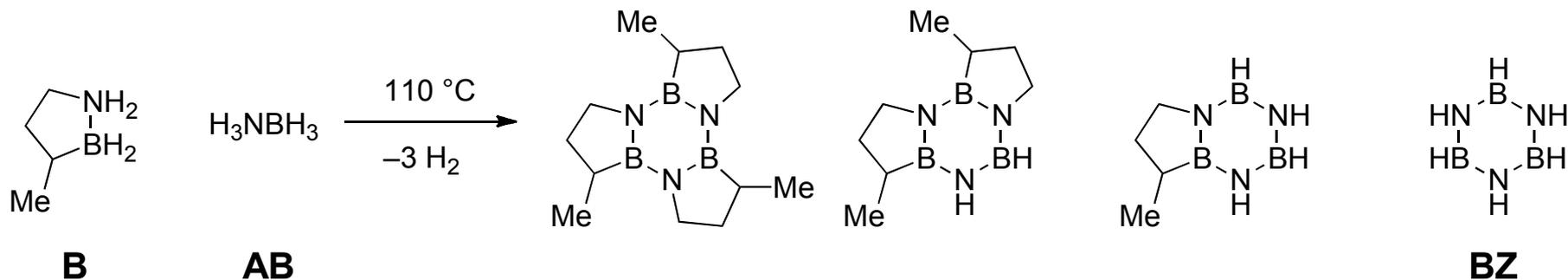
fuel blend BEFORE desorption
(single phase at <80 °C)



fuel blend AFTER desorption
at 25 °C

Fuel blends (B + AB) leads to increased H₂ storage density, faster rates, and liquid spent fuel products.

Accomplishments: Higher Molar Ratio of B/AB Leads to Decreased Borazine (BZ) Formation

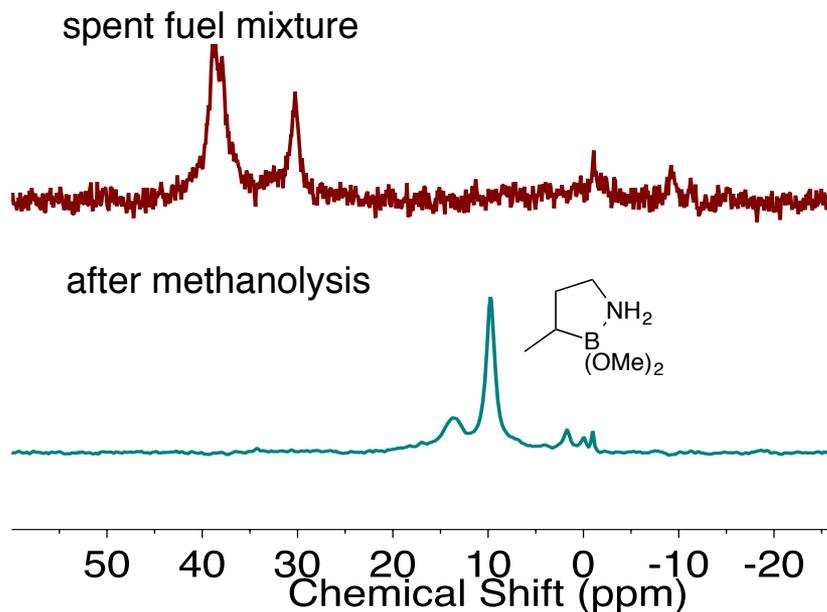
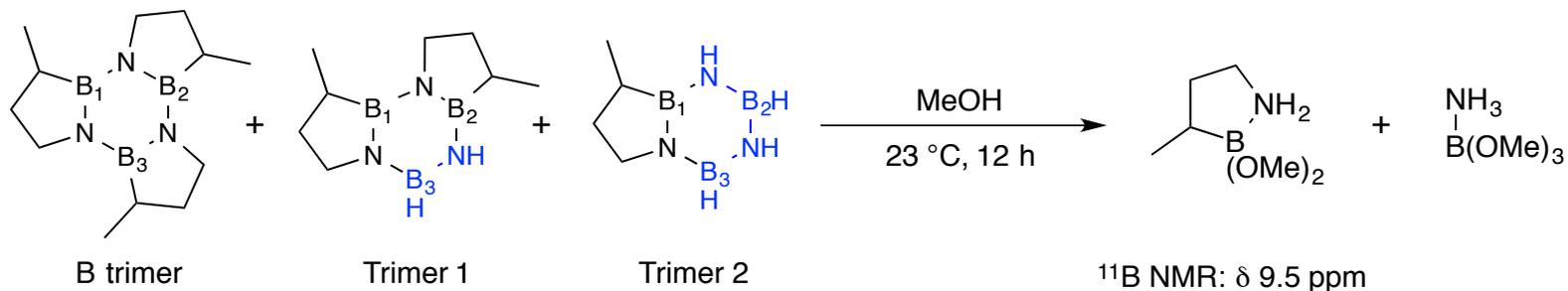


B/AB molar ratio	wt% H ₂	n-Fold reduction in BZ
0:1	12	0
1:1	7.0	6
2:1	6.0	15
3:1	5.7	21
4:1	5.4	46

GC trace of spent fuel from 2:1 **B:AB** mixture

Blends of B & AB reduce borazine formation. Spent fuel remain liquids due to the nature of mixtures (a single compound is more prone to precipitation)

Progress: Regeneration of Spent Fuel Blends

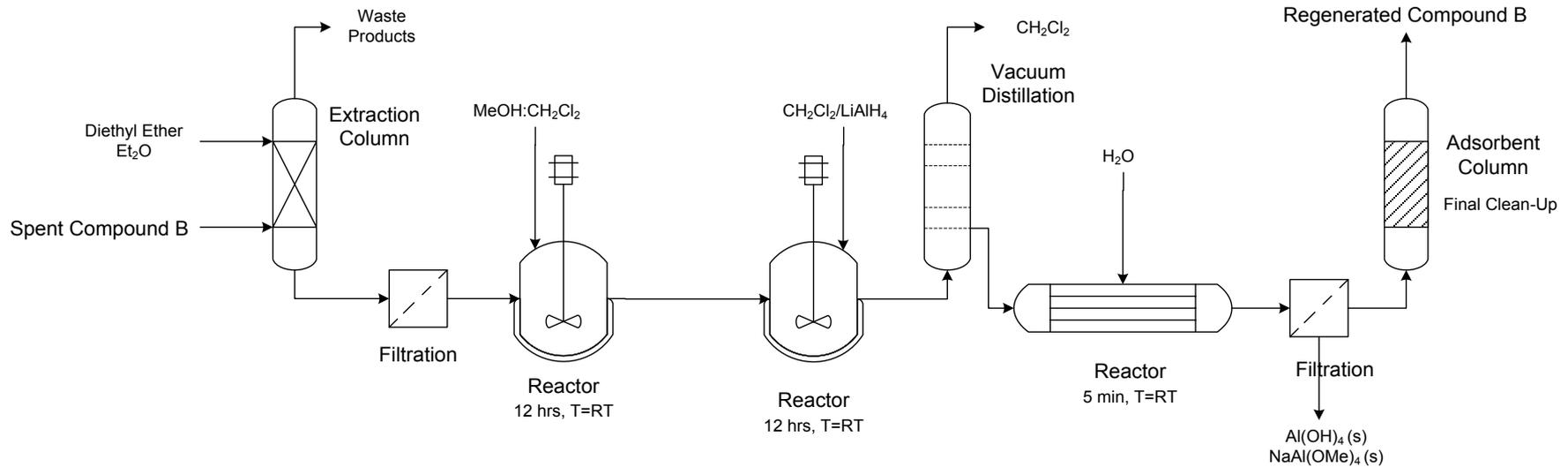


CBN Compound	Trimer B	Trimer 1	Trimer 2
B ₁	41.7	42.1	39.9
B ₂	41.1	40.7	32.7
B ₃	40.5	32.0	31.3

*calculated chemical shifts were provided by UA

Mixture of spent fuel compounds readily converted to 2 methyl borates that can be treated with a hydride (e.g., LAH) to regenerate the liquid fuel blend.

Progress: Regeneration of Spent Fuels

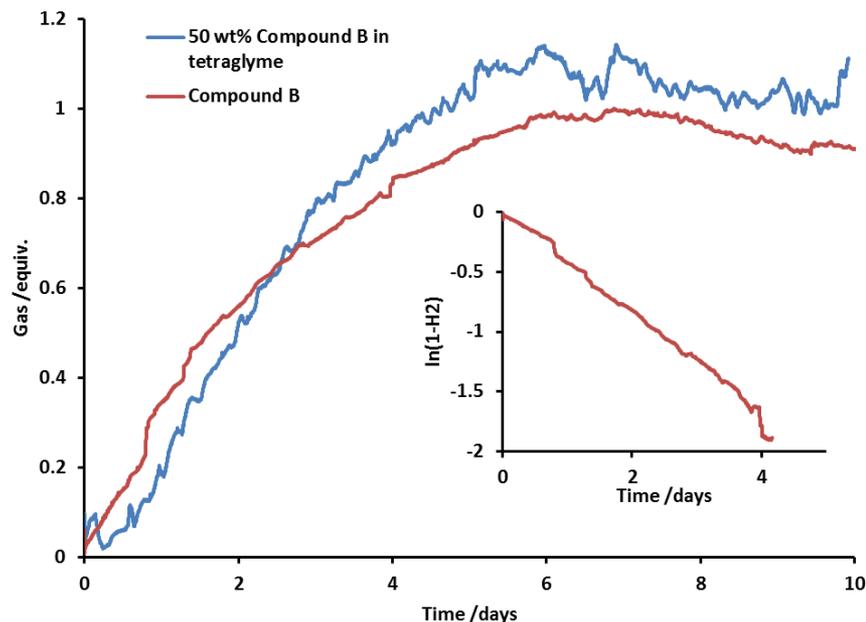


- Basic flow sheet modeling for LiAlH_4 process. Regeneration of spent fuel digested with methanol.
- next steps: add in conversions and flow rates to size the equipment for capital expenses. estimated cost of raw materials for the operating expenses

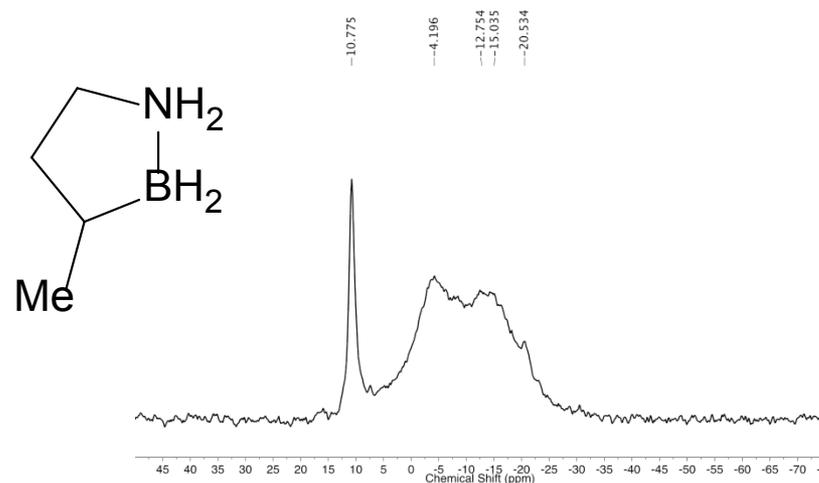
Preliminary flow sheet modeling provides comparison of regen pathways for comp'd B (as well as J). Provides input for more detailed cost analysis

Accomplishment/Progress: Thermal Stability Compd B¹⁴

Gas buret, 50 °C



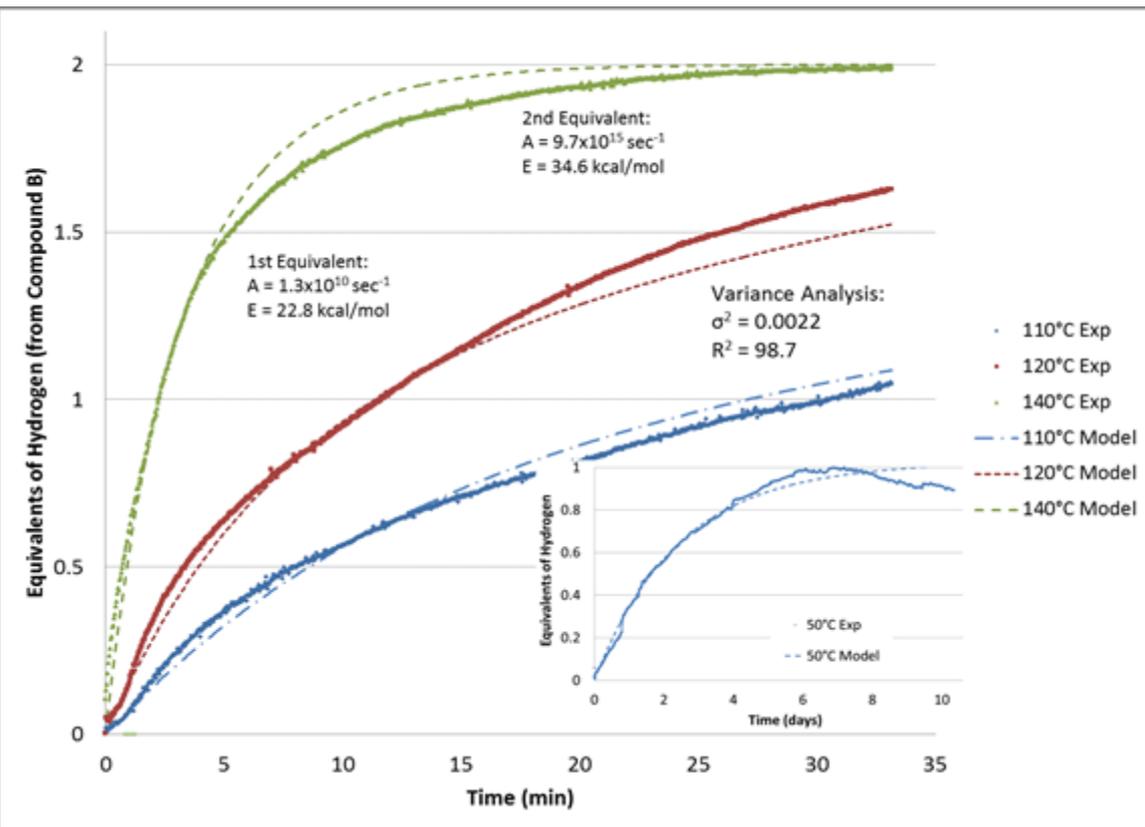
¹¹B NMR after H₂ release shows mixture of cycloborazanes



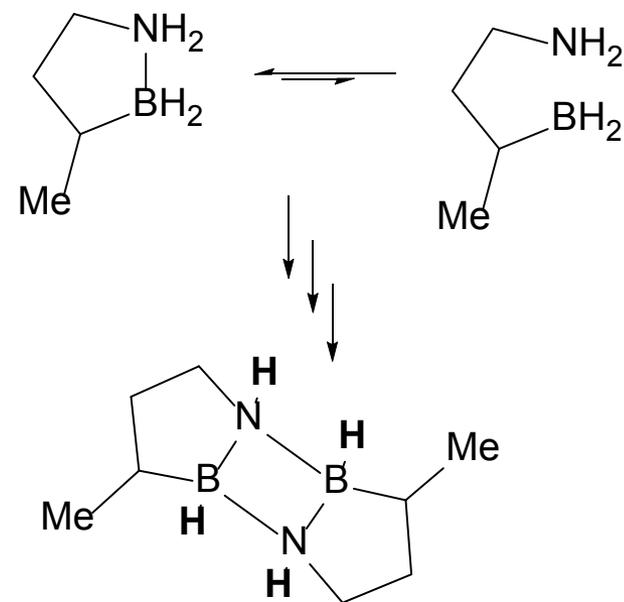
- *Partial* release of H₂ at 50 °C from Compound B (2.3 wt% H₂)
- Decomposition 1st-order (not bi-molecular)
- stable cycloborazane (-BH-NH-) intermediates (2.4 wt% H₂)

Compound B and blends of Compound B do not demonstrate sufficient thermal stability for vehicular or non-vehicular applications (Protonex) 2.4 wt% not sufficient H₂ density and 4.7 wt% not sufficiently stable)

Accomplishment/Progress: Thermal Stability Compd B



Tentative mechanism

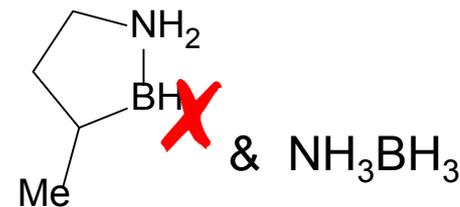


- Temperature dependent rates suggest two consecutive unimolecular decomposition steps.
- Experimental activation barriers are close to predicted B-N BDE.

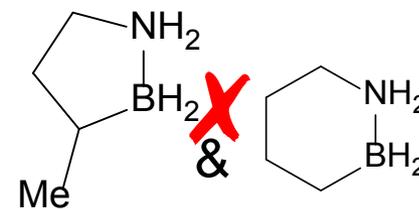
If 'thermal stability' is related to B-N bond energy, then we need to increase the BDE of B-N. Need more mechanistic work.

Summary (CBN cyclopentanes)

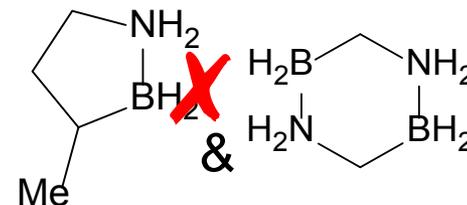
- Liquid blends of AB and B. Target 5.4 wt% H₂
 - reduction of borazine is significant; >40X in liquid B compared to neat AB. (*RGA and GCMS results*)
 - rate is faster in blends than either neat B or AB (*gas buret results*)
 - regen is same path (*regen for compd B works for blends of AB & B*)
 - flow sheet model developed for compd B is adaptable for compd J.
 - thermal stability (additives, e.g., PVP, J, H, did not improve stability)



- Blends of J & B. and H & B (Target 7 wt% H₂)
 - no volatile impurities detected (*RGA*)
 - 1:1 blend (only partially liquid)
 - compound J does not increase thermal stability of B

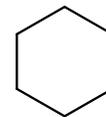
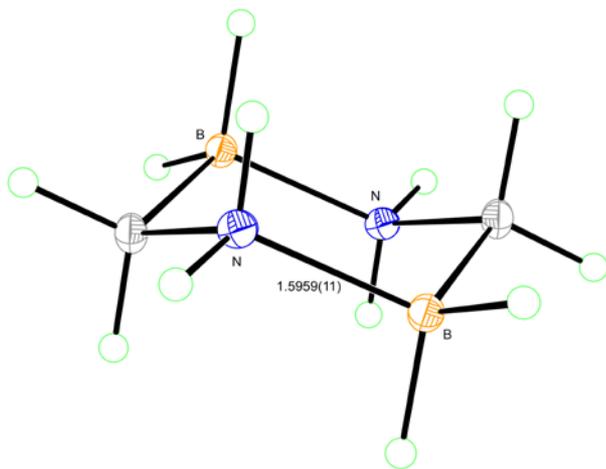
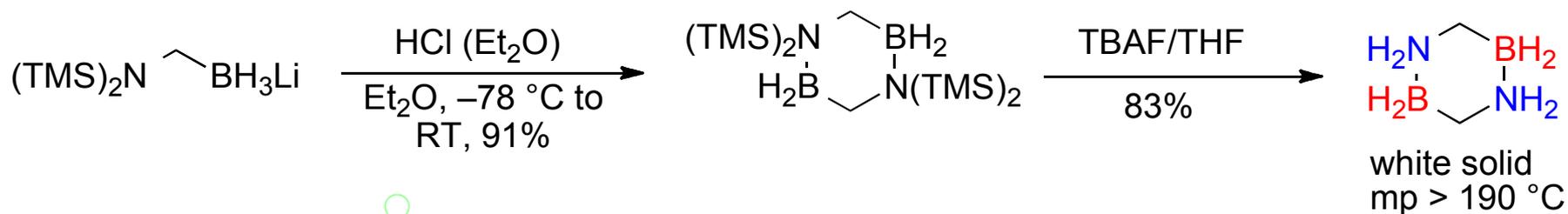
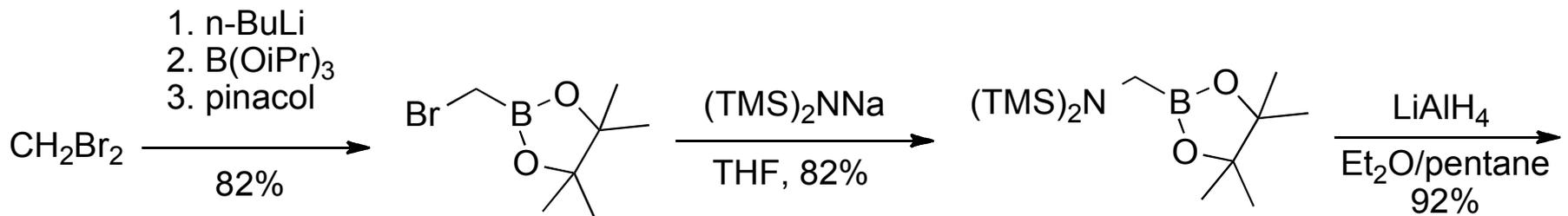


No-Go on liquid blends B

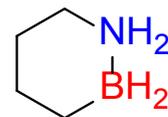


We will measure the relative stability of B + AB blend at 50 °C and finish up the work on blends of B by publishing results & conclusions.

Progress on CBN cyclohexanes : Synthesis Compound H



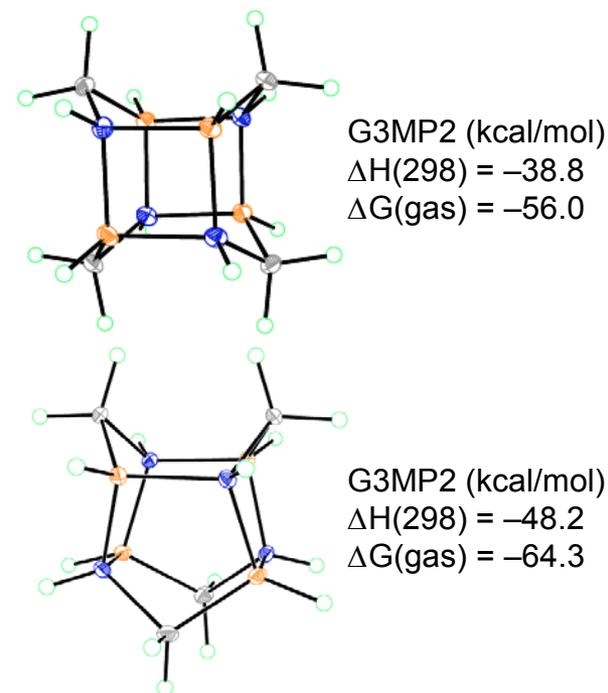
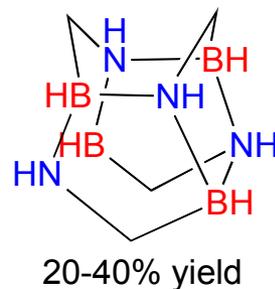
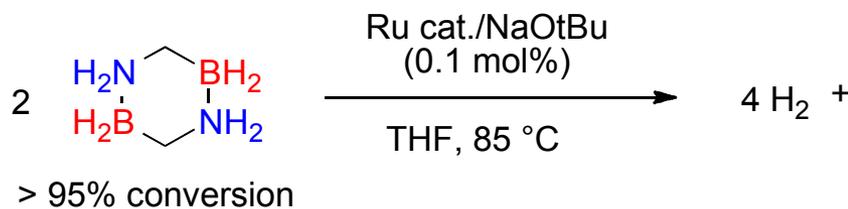
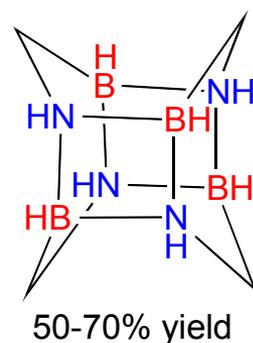
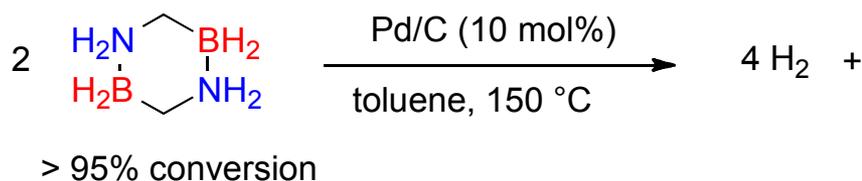
mp: 4-7 °C



mp: 75-77 °C

“First Fill” synthesis for Compound H has been improved (overall yield has doubled from the original 22% to 46%) and structure was unambiguously determined

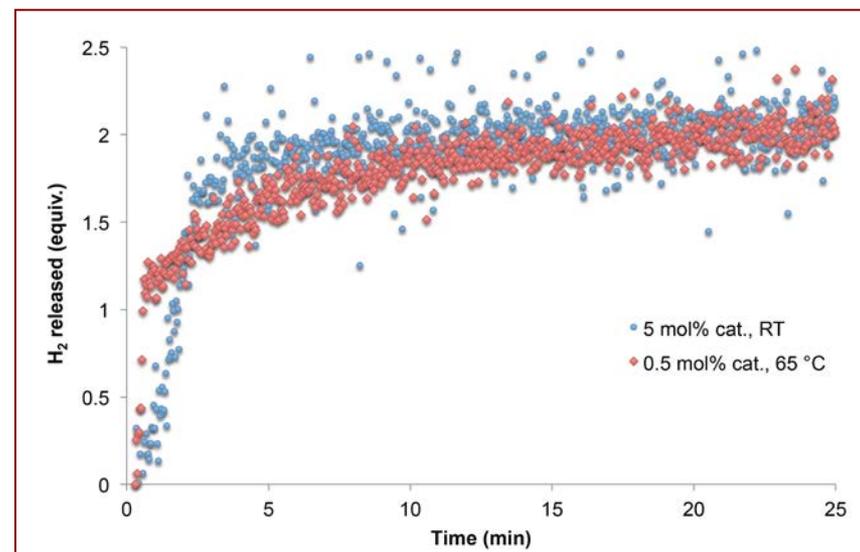
Progress (CBN cyclohexanes): Characterization Compound H ¹⁸



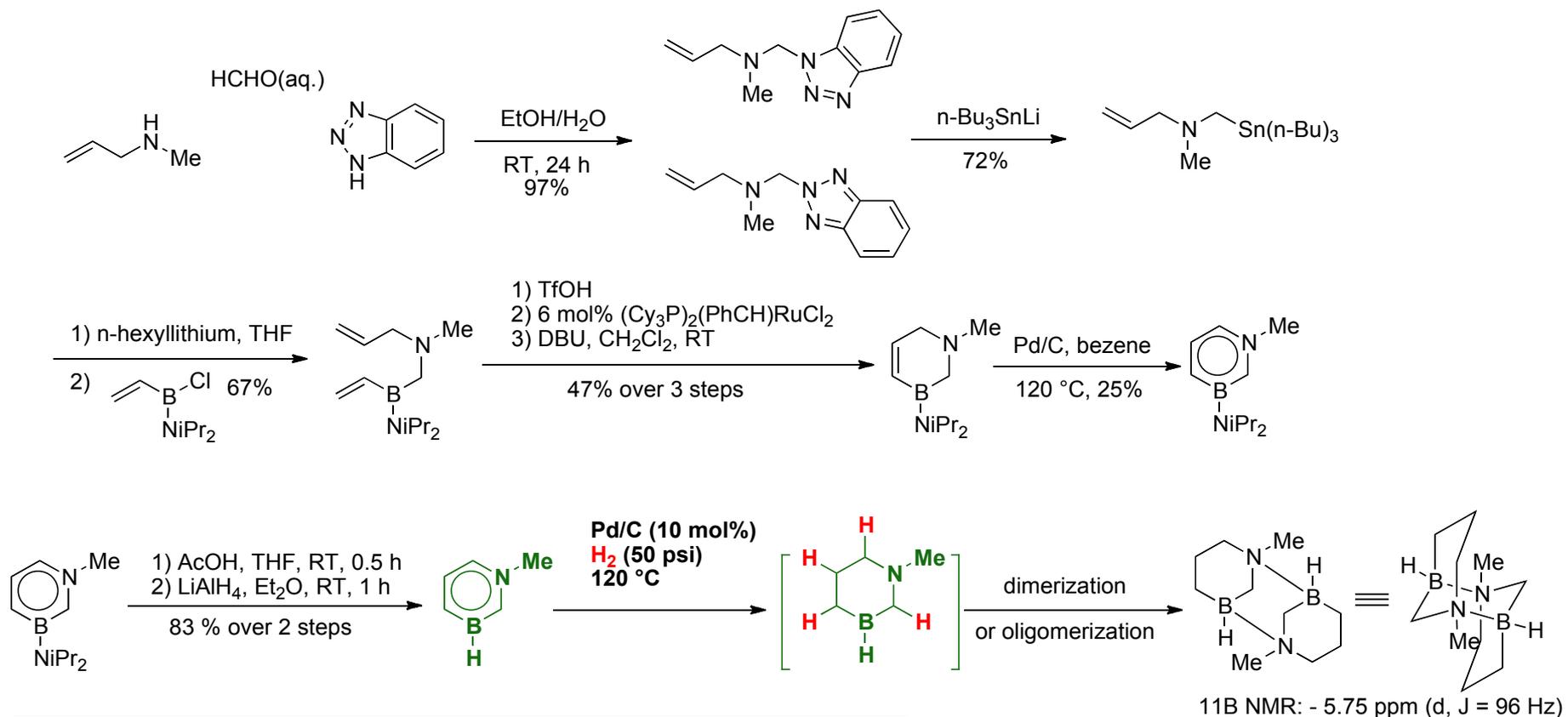
Compound H is very stable in neat form and in solution: no decomposition was observed up to 150 °C.

H₂ desorption can be accomplished at room temperature in 5-10 minutes in the presence of a catalyst.

More H₂ needs to be desorbed to reach full capacity of compound H.

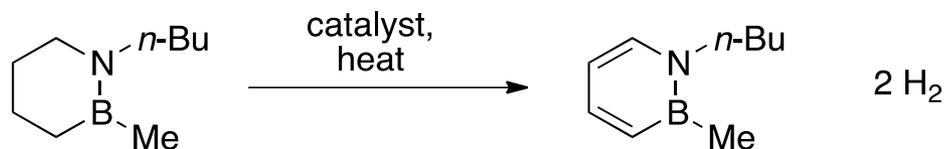


Accomplishments: Synthesis of Compound E



Spent fuel material of compound E prepared & absorption of 2 equiv. of H₂ observed.

Reaction is *partially* reversible – however - dimerization prevented further recharging.

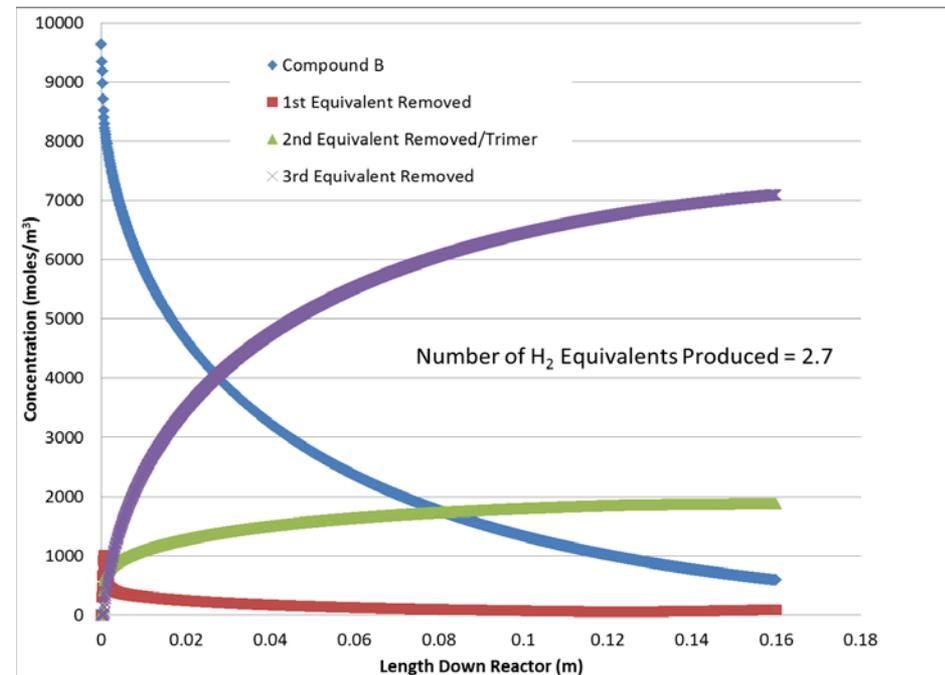
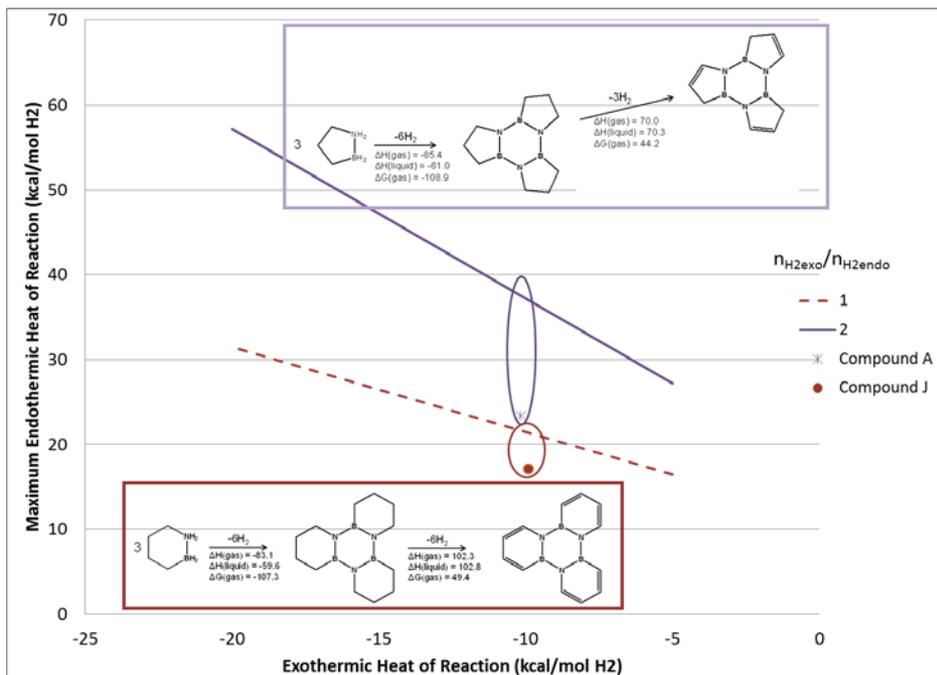


Catalyst screening

Catalyst	Hydrogen Evolution	
	Cyclohexane	B-N heterocycle
0.5 wt % Pt/Al ₂ O ₃	Yes	No
10 wt % Pt/C	Yes	No
5 wt % Pd/Al ₂ O ₃	Yes	No
10 wt % Pd/C	Yes	Yes
5 wt % Pd/SiO ₂	Yes	No

Only select catalysts are active for C-H activation. Need more exhaustive screening of catalysts.





Zero Order Analysis

- Use calculated reaction thermodynamics and determine if generated H₂ needs to be burned to provide required heat for H₂ release from carbon backbone.
- Results: Compound J can meet 90% on-board efficiency

One-Dimensional Analysis

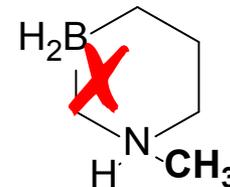
- Include reaction kinetics (from slide 15 and from BC for endothermic step) and acceleration of flow due to H₂ generation
- 2.7 equivalents H₂ produced with a maximum T ~ 400°C

Heat generated from exothermic reaction can be used for endothermic reaction resulting in higher H₂ storage capacity

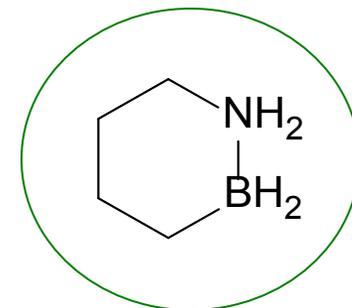
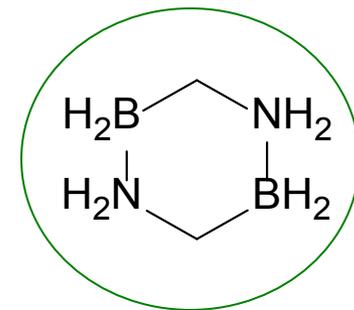
Summary (CBN cyclohexanes)

- Compound **E**
 - Only *partially* reversible
 - Dimer formation prevents full potential

No-Go on Compound E (E')

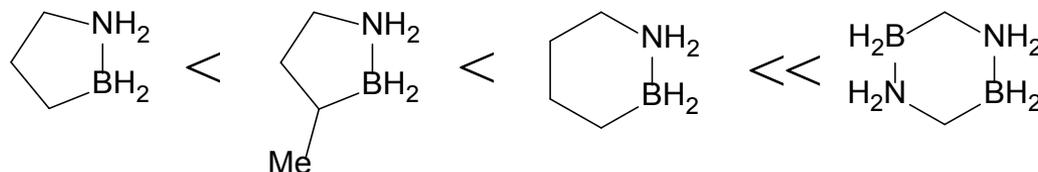


- Compound **H**
 - No volatile impurities detected
 - Thermally stable at 150 °C
- Compound **J**
 - Thermally stable at 50 °C
 - No volatile impurities detected
 - Melts at 75 °C and remains liquid during H₂ release



Summary (Lessons Learned)

- **Fuel blends are desirable** if the goal is to maintain a liquid phase. *Recall it is difficult to crystallize a pure compound when it is mixed with other species.* However, need to be clever to maintain straightforward regen. E.g., spent AB and spent B can be regenerated by same pathways in parallel.
- **Coupling endothermic and exothermic reaction pathways increases on-board efficiency.** *Use the heat from the exothermic step to heat up your reactor so you don't have to burn H_2 to heat up your reactor for the endothermic step.*
- **BN cyclohexanes are more thermally stable than CBN cyclopentanes.** Is this due to B-N bond strength or hydricity of B-H bond?

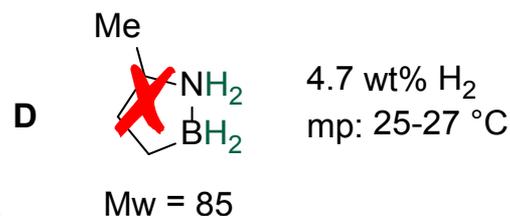
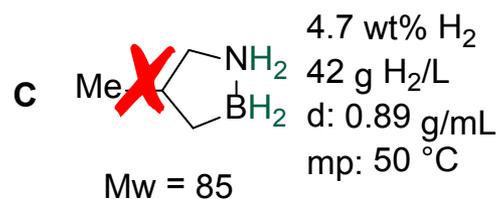
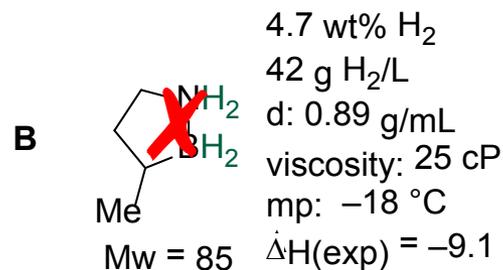
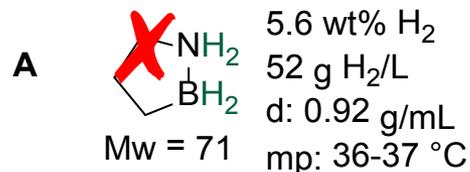


Compd **A** < Compd **B** < Compd **J** << Compd **H**

Down-Selection (4/14)

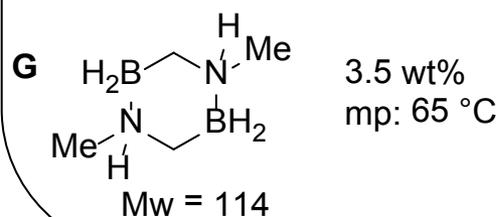
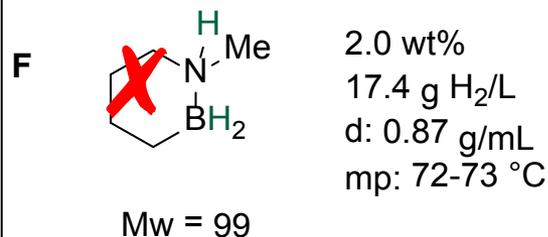
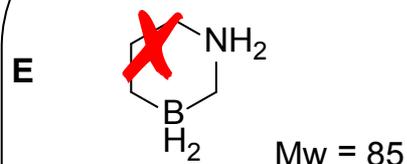
CBN cyclopentanes

i) liquid phase



CBN cyclohexanes

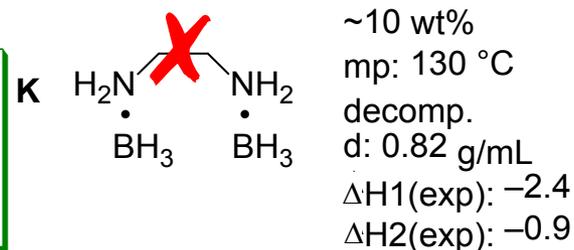
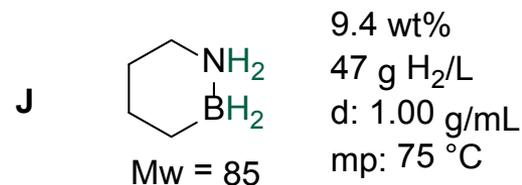
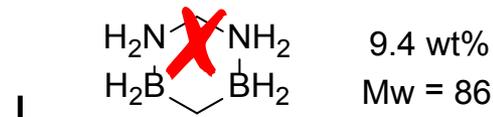
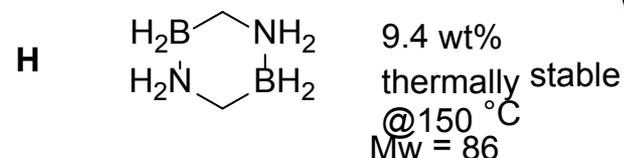
ii) potential reversible



energy values in kcal/mol

**Down selected to 3
compounds for future
work.**

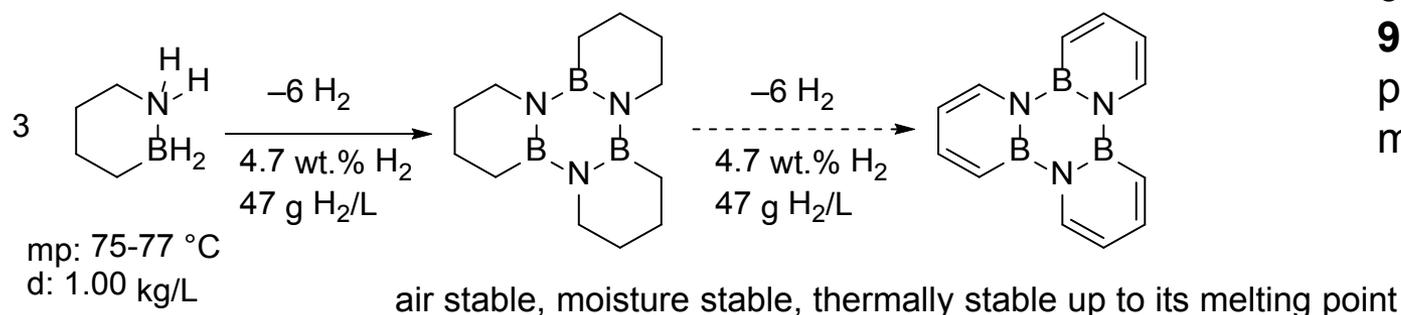
iii) high capacity



Future Work (Compounds J, G & H)

Why CBN cyclohexanes? They are solids at room temperature, vehicle targets are a challenge, but non-vehicular targets are within reach given the distinct advantages: (i) thermally stable, (ii) lower vapor pressure, no volatile impurities, (iii) increased on-board efficiency with coupled exo/endo H_2 release.

I. Compd J (4.7-9.4 wt% H_2). becomes liquid $>75^\circ C$.



overall potential:
9.4 wt.%; 94 g H_2 /L,
potential **liquid phase**
material at operating T

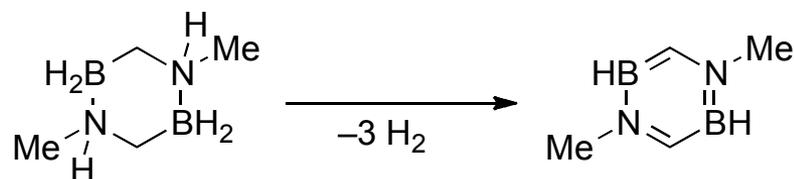
Work focus and questions to be addressed:

- develop catalysts for release of H_2 from carbon backbone.
- measure temperature dependent kinetics for exothermic release to provide input into COMSOL model of exo/endo hydrogen release.
- Can **J** be a liquid at room temperature?
- How much more stable than CBN cyclopentanes? Are the liquids as stable as the solids?

Future Work (6/14 to 3/15) CBN cyclohexanes

II. Compd G (3.5 wt% H₂) *potential for reversibility* – ΔH for release of H₂ is calculated endothermic.

- measure ΔH using calorimetry
- investigate reaction conditions to regenerate with H₂ pressure.



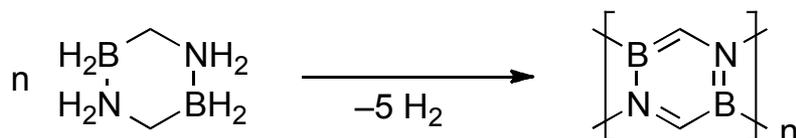
potential **reversible** material

$$\Delta G (298) = +3.9 \text{ kcal/mol}$$

$$\Delta H (298) = +9.5 \text{ kcal/mol H}_2$$

III. Compd H (4.7-5.3 wt% H₂) *super stable*. why so stable? (stability is very attractive for long term storage and portable power applications)

- Use theory understand stability (different mechanism?)
- Develop catalysts to release hydrogen



11.6 wt.%, potential blend material with a liquid carrier, thermally stable, no volatile byproducts

IV. Final Report 3/15

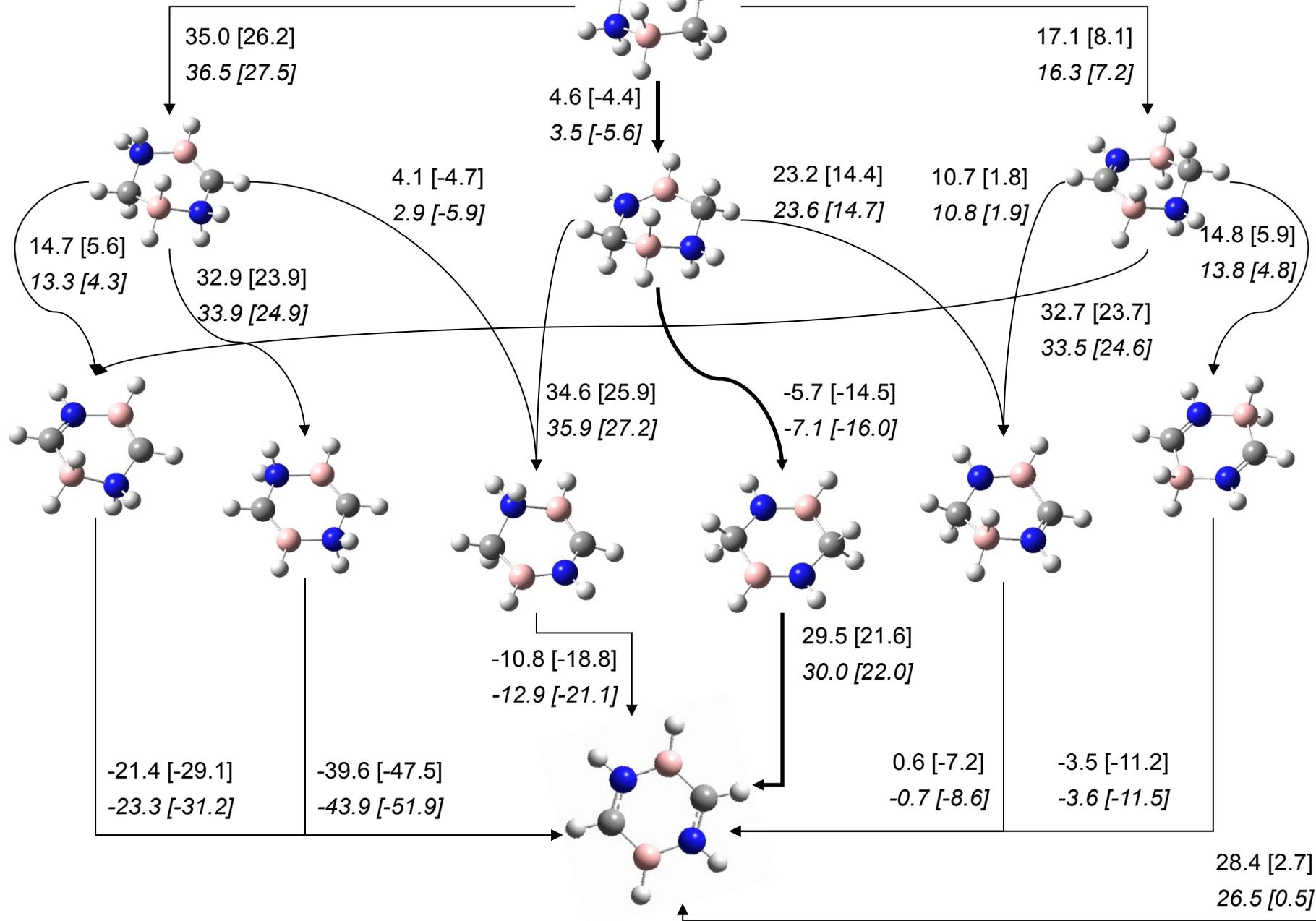
- Compilation of all results, lessons learned, recommendations, etc.

Presentations

- 1) “Development of a Single-Component Liquid-Phase Hydrogen Storage Material”; Singapore, 15th Asian Chemical Congress 2013, Asia America Chemical Symposium on “Advanced Materials, August 2013. (Presentation, Liu)
- 2) “Novel Carbon(C)-Boron(B)-Nitrogen(N)-Containing H₂ Storage Materials ”; Washington DC, DOE Annual Merit Review, May 15, 2013. (Presentation, Liu)
- 3) “Exploring the use of carbon, nitrogen, and boron containing heterocycles in liquid hydrogen storage”; Dalls TX, 247th American Chemical Society National Meeting & Exposition, March 16, 2013 (Presentation, Sean Whitemore, PNNL)

Technical Backup Slides

ΔH [ΔG] G3MP2
 ΔH [ΔG] B3LYP/DZVP2 **Compound H**



Accomplishments: Boiling Point Predictions



$$\begin{aligned}\Delta H_{f, \text{gas}} &= -14.0 \\ \Delta H_{f, \text{liquid}} &= -27.7 \\ \text{BP} &= 549 \text{ K}\end{aligned}$$



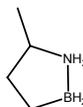
$$\begin{aligned}\Delta H_{f, \text{gas}} &= -19.8 \\ \Delta H_{f, \text{liquid}} &= -27.6 \\ \text{BP} &= 311 \text{ K}\end{aligned}$$



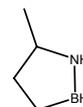
$$\begin{aligned}\Delta H_{f, \text{gas}} &= 3.8 \\ \Delta H_{f, \text{liquid}} &= -4.6 \\ \text{BP} &= 335 \text{ K}\end{aligned}$$



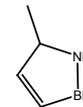
$$\begin{aligned}\Delta H_{f, \text{gas}} &= 4.5 \\ \Delta H_{f, \text{liquid}} &= -3.5 \\ \text{BP} &= 317 \text{ K}\end{aligned}$$



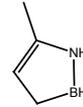
$$\begin{aligned}\Delta H_{f, \text{gas}} &= -22.7 \\ \Delta H_{f, \text{liquid}} &= -31.3 \\ \text{BP} &= 572 \text{ K}\end{aligned}$$



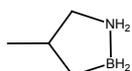
$$\begin{aligned}\Delta H_{f, \text{gas}} &= -28.7 \\ \Delta H_{f, \text{liquid}} &= -37.2 \\ \text{BP} &= 345 \text{ K}\end{aligned}$$



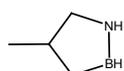
$$\begin{aligned}\Delta H_{f, \text{gas}} &= -5.6 \\ \Delta H_{f, \text{liquid}} &= -14.8 \\ \text{BP} &= 368 \text{ K}\end{aligned}$$



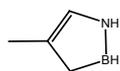
$$\begin{aligned}\Delta H_{f, \text{gas}} &= -4.1 \\ \Delta H_{f, \text{liquid}} &= -13.1 \\ \text{BP} &= 357 \text{ K}\end{aligned}$$



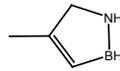
$$\begin{aligned}\Delta H_{f, \text{gas}} &= -21.4 \\ \Delta H_{f, \text{liquid}} &= -30.0 \\ \text{BP} &= 572 \text{ K}\end{aligned}$$



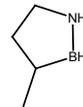
$$\begin{aligned}\Delta H_{f, \text{gas}} &= -27.0 \\ \Delta H_{f, \text{liquid}} &= -35.6 \\ \text{BP} &= 342 \text{ K}\end{aligned}$$



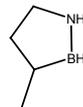
$$\begin{aligned}\Delta H_{f, \text{gas}} &= -5.2 \\ \Delta H_{f, \text{liquid}} &= -14.0 \\ \text{BP} &= 350 \text{ K}\end{aligned}$$



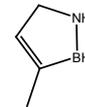
$$\begin{aligned}\Delta H_{f, \text{gas}} &= -3.7 \\ \Delta H_{f, \text{liquid}} &= -13.1 \\ \text{BP} &= 376 \text{ K}\end{aligned}$$



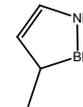
$$\begin{aligned}\Delta H_{f, \text{gas}} &= -19.7 \\ \Delta H_{f, \text{liquid}} &= -28.4 \\ \text{BP} &= 570 \text{ K}\end{aligned}$$



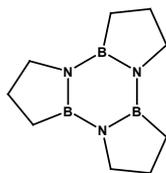
$$\begin{aligned}\Delta H_{f, \text{gas}} &= -24.5 \\ \Delta H_{f, \text{liquid}} &= -33.1 \\ \text{BP} &= 345 \text{ K}\end{aligned}$$



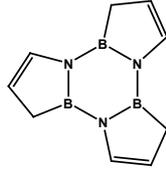
$$\begin{aligned}\Delta H_{f, \text{gas}} &= 0.7 \\ \Delta H_{f, \text{liquid}} &= -12.8 \\ \text{BP} &= 362 \text{ K}\end{aligned}$$



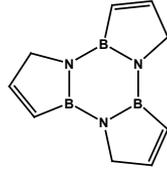
$$\begin{aligned}\Delta H_{f, \text{gas}} &= -3.8 \\ \Delta H_{f, \text{liquid}} &= -8.1 \\ \text{BP} &= 351 \text{ K}\end{aligned}$$



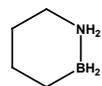
$$\begin{aligned}\Delta H_{f, \text{gas}} &= -120.5 \\ \Delta H_{f, \text{liquid}} &= -137.2 \\ \text{BP} &= 670 \text{ K}\end{aligned}$$



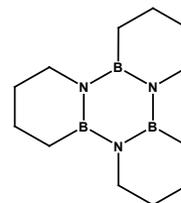
$$\begin{aligned}\Delta H_{f, \text{gas}} &= -47.1 \\ \Delta H_{f, \text{liquid}} &= -63.6 \\ \text{BP} &= 658 \text{ K}\end{aligned}$$



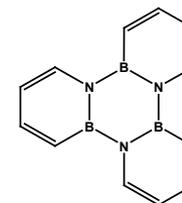
$$\begin{aligned}\Delta H_{f, \text{gas}} &= -48.5 \\ \Delta H_{f, \text{liquid}} &= -65.5 \\ \text{BP} &= 682 \text{ K}\end{aligned}$$



$$\begin{aligned}\Delta H_{f, \text{gas}} &= -23.3 \\ \Delta H_{f, \text{liquid}} &= -37.7 \\ \text{BP} &= 577 \text{ K}\end{aligned}$$



$$\begin{aligned}\Delta H_{f, \text{gas}} &= -146.1 \\ \Delta H_{f, \text{liquid}} &= -165.8 \\ \text{BP} &= 790 \text{ K}\end{aligned}$$

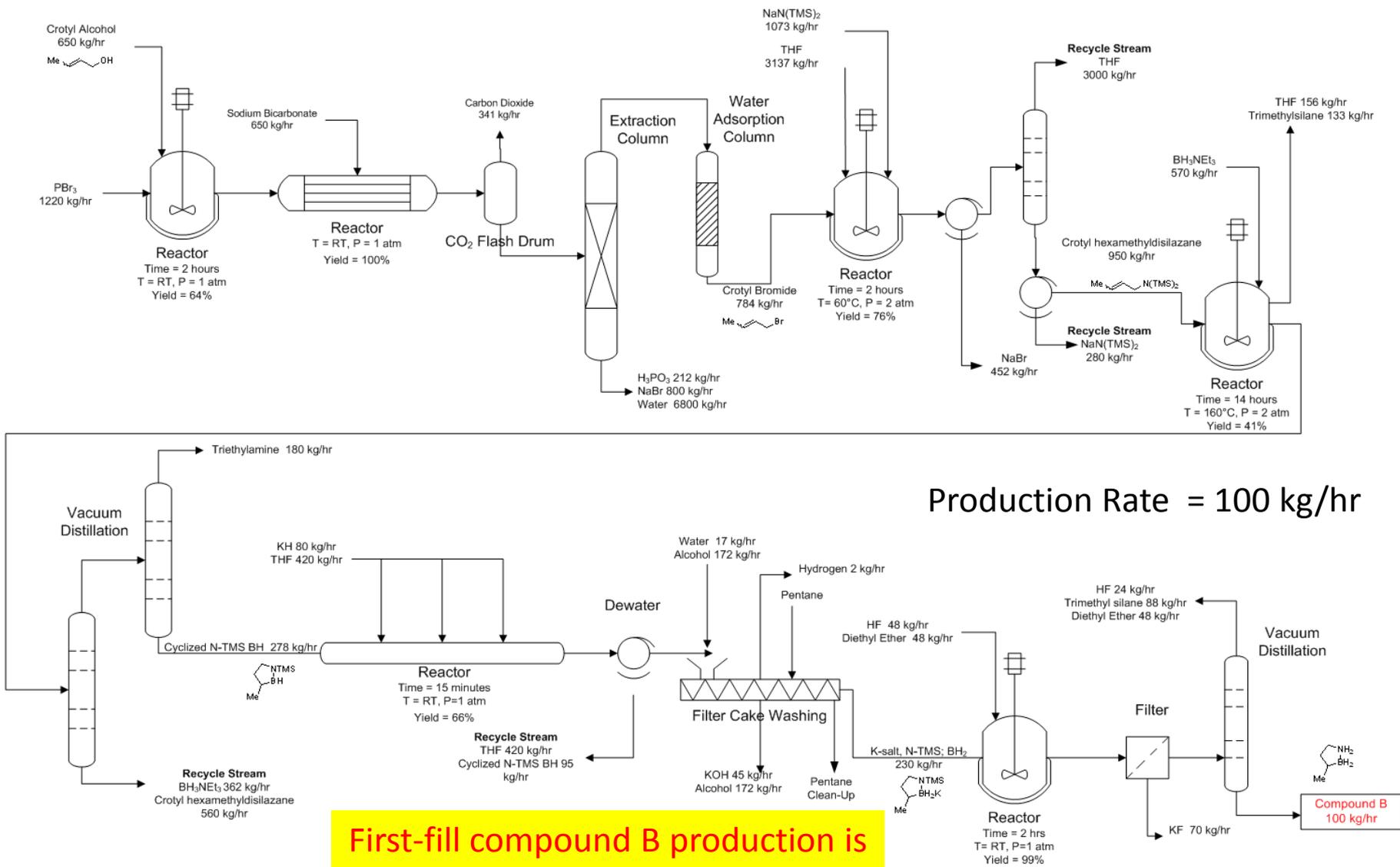


$$\begin{aligned}\Delta H_{f, \text{gas}} &= -49.1 \\ \Delta H_{f, \text{liquid}} &= -68.4 \\ \text{BP} &= 771 \text{ K}\end{aligned}$$

COSMO-RS implementation in ADF.
 ΔH_f obtained at G3MP2 level.

Boiling points for several CBN materials have been predicted. The predicted bp are consistent with experimental observations. Efforts are geared toward predicting melting points of new proposed compounds.

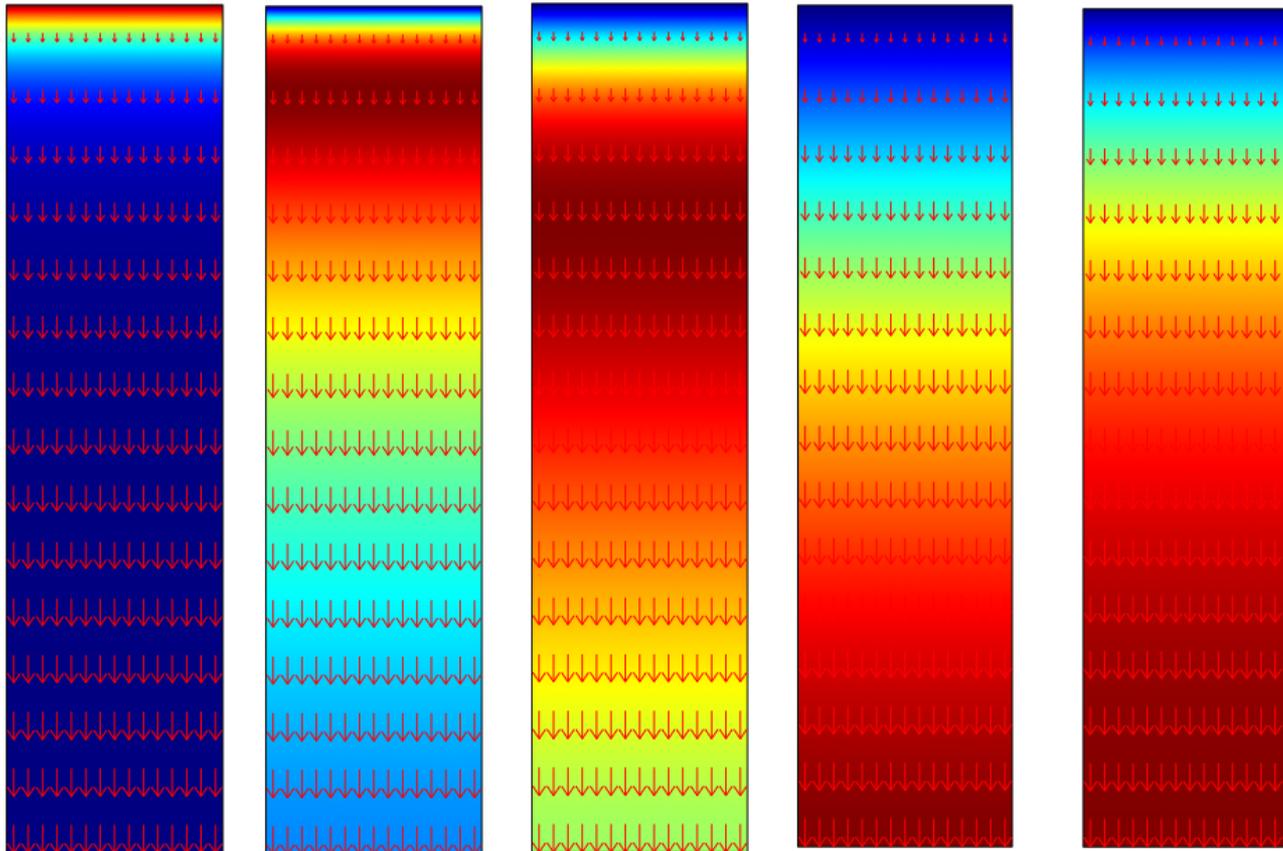
First-Fill Production Scale-up of Compound B



Coupled Exothermic/Endothermic Reactions

Two Dimensional Axisymmetric COMSOL Model Results

Compound B 1st Equivalent 2nd Equivalent 3rd Equivalent H₂ Concentration



Assumptions

- Reaction kinetics from Compound B and cyclohexane dehydrogenation
- Reaction Enthalpy from Compound A and J
- 0.16 m tall, 0.08 m diameter tubular reactor
- 250 W of H₂ produced
- Inlet Temp. = 140°C
- System Press. = 10 bar

Note increase in velocity from H₂ generation

