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## Blending materials composed of Boron, Nitrogen and Carbon to transform approaches to Liquid Hydrogen Stores

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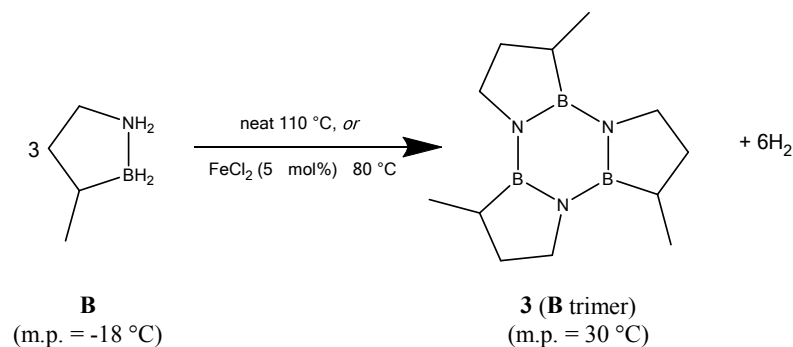
**Abstract.** Mixtures of hydrogen storage materials containing the elements of boron, nitrogen, carbon, i.e., isomers of BN cyclopentanes are examined to find a ‘fuel blend’ that remains a liquid phase throughout hydrogen release, maximizes hydrogen storage density, minimizes impurities and remains thermally stable at ambient temperatures. We find that the mixture of ammonia borane dissolved in 3-methyl-1,2-dihydro-1,2-azaborolidine (compound B) provide a balance of these properties and provides ca. 5.6 wt% hydrogen. The two hydrogen storage materials decompose at a faster rate than either individually and products formed are a mixture of molecular trimers. Digestion of the product mixture formed from the decomposition of the AB + B fuel blend with methanol leads to the two corresponding methanol adducts of the starting material and not a complex mixture of adducts. The work shows the utility of using blends of materials to reduce volatile impurities and preserve liquid phase.

### Introduction

Energy storage remains a key challenge for the advancement of fuel cell applications. Because of this, hydrogen has garnered much research attention for its potential as an energy carrier. This can be attributed to its abundance from non-petroleum sources, and its energy conversion efficiency.<sup>1-5</sup> Our group, among others, has been studying the use of ammonia borane as a chemical hydrogen storage material for the past several years.<sup>6-24</sup> Ammonia borane (**AB**,  $\text{NH}_3\text{BH}_3$ ), a solid complex that includes the light weight main group elements nitrogen and boron, is isoelectronic with ethane and as such is an attractive hydrogen storage

material with a high gravimetric capacity of H<sub>2</sub> (19.6 wt%).<sup>25</sup> However, the widespread use of **AB** as a chemical hydrogen storage material has been stalled by some undesirable properties and reactivity. Most notably, **AB** is a solid, which presents compatibility issues with the existing liquid fuel infrastructure. The thermal release of H<sub>2</sub> from **AB** also results in the formation of volatile impurities (borazine and ammonia) that are detrimental to operation of the fuel cell. Additionally, the major products in the spent fuel are polyborazylene and amine borane oligomers that present challenges in regenerating **AB**.<sup>26-30</sup>

In recent years, the Liu group has sought to use carbon, boron, and nitrogen (CBN)-containing heterocycles to combat some of these issues.<sup>31-37</sup> The cyclic amine boranes 1,2-dihydro-1,2-azaborolidine (compound **A**, see Figure 1) and 3-methyl-1,2-dihydro-1,2-azaborolidine (compound **B**) show great potential as materials for liquid hydrogen storage. Liu and coworkers have shown that **B** is a liquid at room temperature (m.p. -18 °C), and that the resulting trimer that forms after release of H<sub>2</sub> (Scheme 1) is a low-melting solid (m.p. 30 °C).<sup>33, 35</sup> The carbon backbone of **B** not only acts to keep the material in the liquid phase, but also helps prevent the formation of volatile side products, such as ammonia and borazine. Additionally, only the trimer **3** is observed as a dehydrogenation product, making the regeneration of **B** from the spent fuel much more practical.<sup>31</sup>



**Scheme 1.** Desorption of H<sub>2</sub> from Compound **B**.

Fluid storage materials offer clear materials handling advantages over solids while also having the potential for high gravimetric and volumetric capacity. A comprehensive analysis<sup>38,39</sup> of different fluid storage strategies recently described *materials* property guidelines which are likely to meet the US DOE vehicular *system* targets. This work showed that liquid carriers should have a gravimetric H<sub>2</sub> capacity of at least 7.8 wt.% for an idealized system design, and that solutions or slurries required correspondingly higher materials

capacities. The gravimetric capacity of **B** (4.7 wt.% for the hydrogens bonded to boron and nitrogen) is somewhat less than this, so different materials or strategies are required to meet vehicular targets.

Fuel blends of **AB** with alkylamine and alkoxyamine boranes have been examined before<sup>40-42</sup> in an effort to dissolve **AB** in the lower melting substituted boranes. Blends with methylamine borane produced volatile N,N',N''-trimethylborazine dehydrogenation products and were unstable at room temperature. Blends of **AB** with *sec*-butylamineborane were more promising, but precipitated solid polyiminoborane. This could be eliminated by use of an ionic liquid co-solvent, but at the expense of capacity (3.6 wt % H<sub>2</sub>).

In this work, we explore the use of fuel blends based on compound **B** as a strategy to optimize materials properties. We combined **B** with other BN compounds, hypothesizing that the two would interact to provide an outcome different from a simple combination of their properties. In particular we were motivated by the possibility of keeping the spent fuel in a liquid phase and to avoid polymeric reaction products from the dehydrogenation of **AB**. These outcomes will assist with transfer of the spent fuel from a vehicle as well as offering a more facile route to regeneration. In addition, the higher gravimetric H<sub>2</sub> content of **AB** is expected to increase the capacity of the blend compared to **B**.

## Experimental

All manipulations were carried out under inert (N<sub>2</sub>) atmosphere using standard Schlenk or glovebox techniques unless otherwise stated. Samples of compound **B**<sup>34</sup>, and ethane 1,2-di-amineborane (**EDAB**)<sup>10</sup> were synthesized according to published procedures. Synthesis of compounds **A** and **D** is detailed in the Supplemental Information. Ammonia borane was purchased from Sigma-Aldrich and used as-received. Borazine was prepared according to the reported literature procedure.<sup>43</sup> Dichloromethane was passed through a neutral alumina column under argon prior to use.

NMR spectra were recorded on a 500 MHz or 300 MHz Varian INOVA spectrometer equipped with a boron-free 5-mm dual broadband gradient probe. Gas chromatography-mass spectrometry (GC/MS) data were recorded on a 5977A Series GC/MSD system from Agilent Technologies. Hydrogen release was measured using an automated gas burette system.<sup>44</sup>

Mixture of **A** and **B**: To 83.5 mg of **B** in a vial was added slowly (in portions) 72.3 mg of purified compound **A**. The vial was shaken intermittently to ensure complete dissolution of **A** into **B**, as portions of **A** were added. A clear solution was obtained at the end. The solution was transferred to a quartz NMR tube and  $^{11}\text{B}$  NMR spectra recorded which revealed 2 broad peaks in almost equimolar ratio ( $-9$  ppm = compound **B**;  $-12$  ppm = compound **A**).

Mixture of **B** and **D**: Liquid compound **B**, 89 mg was added to solid compound **D**, 2-methyl-1,2-dihydro-1,2-azaborolidine, 86 mg in a vial and the suspension was allowed to sit for at room temperature for about 15 min. Solid **D** completely dissolved in **B** over the course of 15 min to form a clear colorless liquid.  $^{11}\text{B}$  NMR of the mixture shows 2 distinct set of peaks one each for **B** and **D** respectively. Thermolysis: A 1:1 mixture of **B**:**D** (51.9 mg) was charged in a round bottom flask and immersed in an oil bath pre-heated to  $110$  °C for 3 h. The dehydrogenation product was observed to be a liquid (determined by letting the post-burette mixture stand in the glove box for 18h).

Mixture of **B** and **AB**: In a typical experiment a 25 mL round bottom flask was charged with compound **B** (35 mg, 0.388 mmol), ammonia borane (6.3 mg, 0.194 mmol), and the reaction initiated by submerging the reaction vessel into a heated oil bath. The quantity of borazine in the  $\text{H}_2$  gas was determined in separate reactions using a residual gas analyzer (SRS RGA 200). Reactions (ca. 0.4 mmol **B**, 0.2 mmol **AB**) were carried out in a stainless steel tube immersed in a heated oil bath with a capillary line leading to the RGA. A mass spectrum was recorded from 0 – 200 amu at 2 minute intervals. The response factor for borazine was determined by sampling the headspace in the same stainless steel reactor at temperatures between  $-10$  and  $+20$  °C. The vapor pressure of borazine was calculated from the known<sup>45</sup> temperature relationship and a response factor ( $3.53 \pm 0.15$ ) referenced to  $\text{N}_2$  gas which filled the headspace prior to the calibration and all other reactions.

## Results

The thermolysis of neat compound **B** in the presence of catalysts has been previously reported.<sup>46</sup> Neat compound **B** is a low melting solid but the dehydrogenated product, trimer **3** (Scheme 1), is a solid at  $20$  °C.

To address this challenge of a phase change from a liquid to a solid hydrogen carrier we examined four different mixtures of BN materials with a goal to lower the melting point of the starting material *and products* and preserve a liquid or flow-able liquid phase through the full dehydrogenation or hydrogen release reaction. The four blends examined were: (i) a mixture of **A** and **B**; (ii) a mixture of **D** and **B**; (iii) a mixture of **EDAB** and **B**; and (iv) a mixture of **AB** and **B**. These compounds are shown in Figure 1.

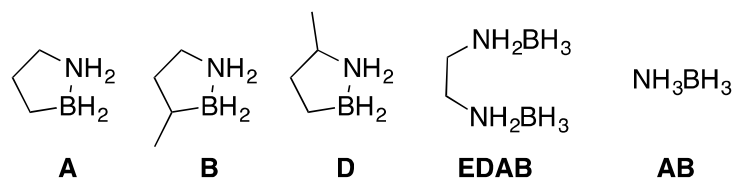


Figure 1. Compounds used for fuel blends in the present study.

A mixture of the structurally related methyl BN cyclopentane compounds **A** and **B** was the first blended hydrogen storage carrier evaluated. Compound **A** is a solid but readily dissolves in liquid **B**. We hypothesized that these two BN cyclopentane compounds would release  $H_2$  by similar reaction pathways and make similar products; either the independent formation of individual trimers or the formation of mixed trimers. In either case the products after release of  $H_2$  would comprise a mixture and reduce the observed melting point of dehydrogenated state of the BN hydrogen carrier. To our surprise we discovered that compound **A**, stable as a neat solid for days, was not stable at room temperature when dissolved in a liquid and slowly decomposed to release hydrogen.

Figure 2 shows the results of storing the mixture in an NMR tube for 3 days in a glove box at ambient temperature. It was observed that solids had precipitated out in the NMR tube and the  $^{11}B$  NMR spectrum of the **A** + **B** mixture reveals slight decomposition of **A** as evidenced by a broad peak at 0.4 ppm and a decrease in the intensity of the peak for compound **A** (Figure 2).

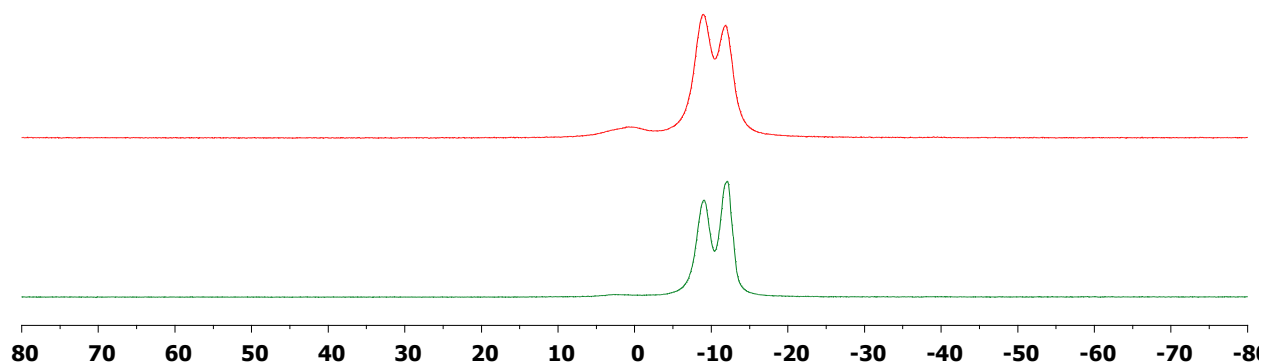


Figure 2. Overlay of  $^{11}\text{B}$  NMR of isolated compound **A** + **B** Neat (Bottom Trace Day 1, Top Trace Day 3)

The second mixture we evaluated was a blend of **D** in **B**. Compound **D** is also a solid, but it is readily soluble in liquid **B**. This fuel blend proved to be more stable, so further study of the decomposition products was undertaken. Figure 3 shows the  $^{11}\text{B}$  NMR spectra of an equal molar mixture of **D** and **B** before and after heating to 110 °C. As compound **D** and compound **B** are structural isomers with the same molecular weight the amount of hydrogen released is equal to the hydrogen from either independently. However, as opposed to neat compound **B** that becomes a solid upon hydrogen release, the blend remains a liquid throughout the release of hydrogen. Thus, the blending of **D** in **B** lowers the melting point of the starting material **D** and the melting point of the product trimer of neat **B**.

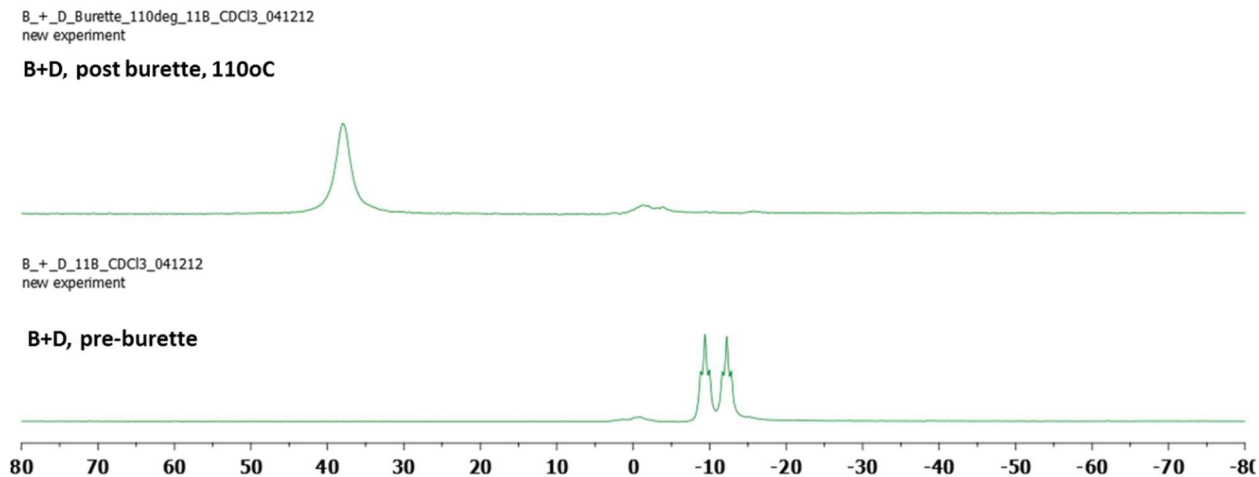


Figure 3. Liquid phase  $^{11}\text{B}$  NMR spectra of a ca. 1:1 mixture of compounds **B** and **D** before (bottom panel) and after (top) release of hydrogen upon heating to 110 °C.

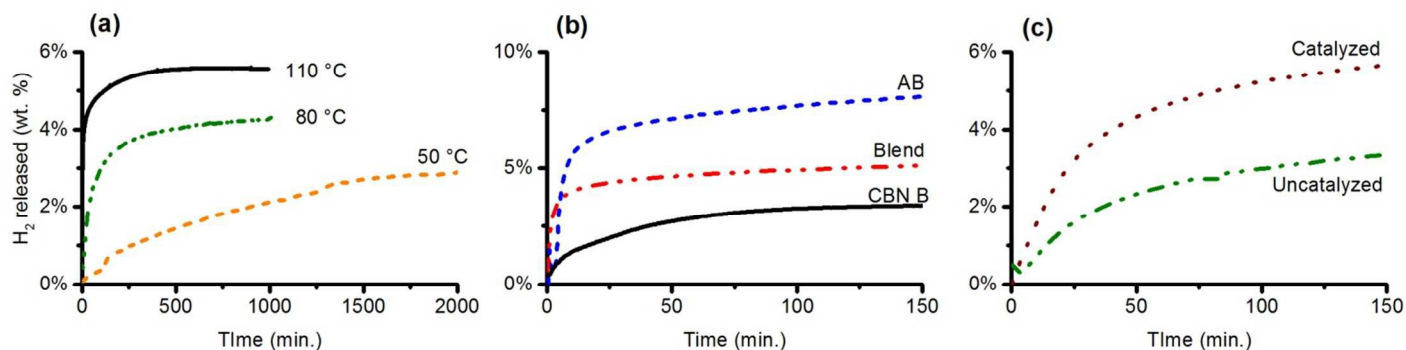
The third mixture evaluated was a blend of **EDAB** in **B**. Both of these compounds are thermally stable at room temperature and we hypothesized that the two were sufficiently similar that **EDAB** would be highly soluble in compound **B**. However, a comparison of the intensities of the  $^{11}\text{B}$  NMR peaks of the respective compounds showed that less than 1% **EDAB** could be dissolved into **B** at room temperature. No further work on this mixture was undertaken given the limited solubility of **EDAB** in **B**. However, we found **AB** to have increased solubility in **B** as well as providing for a greater hydrogen storage density; thus our focus shifted to **AB**.

A 1:1 molar mixture of **B:AB** was placed in an NMR tube and left to equilibrate at room temperature with occasional agitation. Solid **AB** was observed at the bottom of the tube, and integration of  $^{11}\text{B}$  spectra indicated that the clear solution above contained **B** and **AB** in a 5:1 molar ratio, suggesting this is the room temperature solubility limit. However, during the course of our experiments we observed that the spent fuel produced from the thermal release of  $\text{H}_2$  remained as a clear liquid at room temperature up to a 2:1 **B:AB** molar ratio (see Figure S1). Furthermore, this blended material was a fluid slurry at room temperature before dehydrogenation, and remained liquid at the temperatures investigated for  $\text{H}_2$  release, up to 110 °C.

Thermal release of hydrogen from this 2:1 blend was measured by gas burette at various temperatures (Fig. 4a). Dehydrogenation was slow at 50 °C, taking approximately 40 hours to release 1 equivalent  $\text{H}_2$  (3 wt. %). At 110 °C, the quantity of  $\text{H}_2$  reached a plateau of 5.6 wt. % after ca. 500 minutes, close to the theoretical yield expected for this blend (6.0 wt. %) assuming 2 equivalents of  $\text{H}_2$  from each of **B** and **AB**. To our surprise, the initial rate at which hydrogen was released was enhanced compared to either **B** or **AB** alone under the same conditions (Fig. 4b). Presumably this is in part due to the elimination of the induction period which precedes  $\text{H}_2$  release in solid **AB**.<sup>47</sup> The increase of hydrogen release rate provided the first evidence that the two compounds were in fact reacting together, rather than each component reacting by independent mechanisms. These measurements also confirmed that the hydrogen capacity of the blend was a combination of the capacity of the components.



Thermal hydrogen release from both  $\mathbf{B}^{33}$  and  $\mathbf{AB}^{48, 49}$  is accelerated by the use of metal catalysts. Dehydrogenation of the blend is similarly enhanced, shown in Fig. 4c at 80 °C with a Pt/Ni catalyst. The rate of dehydrogenation is clearly faster with the catalyst, but the total amount of hydrogen released is also improved. Without the catalyst, only 4.3 wt.%  $\text{H}_2$  was observed after 1000 minutes; with the catalyst, 5.8 wt.% was released after 150 minutes.



**Figure 4.** Gas burette measurements of (a)  $\text{H}_2$  release from a 2:1  $\mathbf{B}/\mathbf{AB}$  fuel blend at different temperatures; (b)  $\text{H}_2$  release at 110 °C from this blend compared to the individual components; (c) comparison of release at 80 °C with and without a Pt/Ni catalyst supported on carbon.

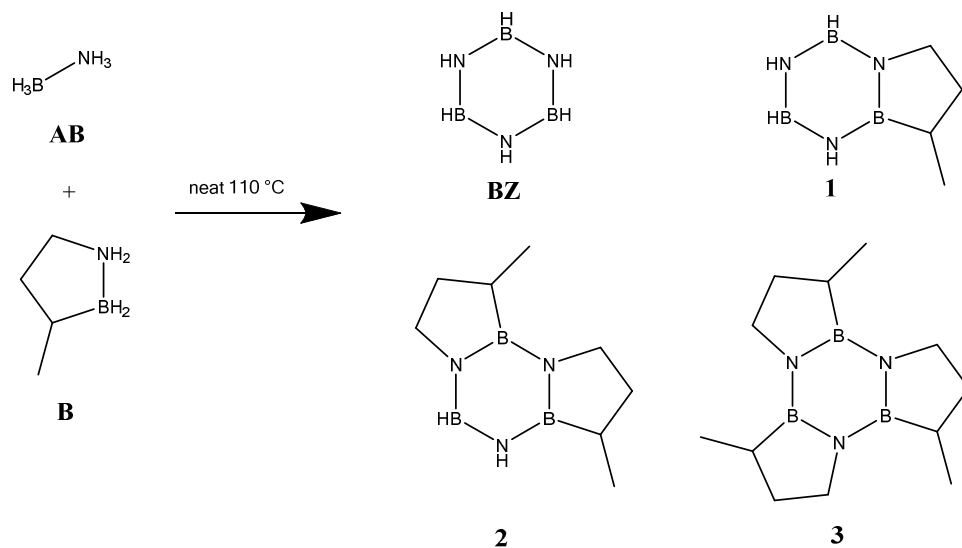
If  $\mathbf{AB}$  and  $\mathbf{B}$  react together, it is likely this will have a significant effect on the formation of borazine, which is an unwanted contaminant from the thermal release of  $\text{H}_2$  from  $\mathbf{AB}$ .<sup>50</sup> To investigate this, blends with different molar ratios of  $\mathbf{B}:\mathbf{AB}$  ranging from 1:1 to 4:1 were sealed under  $\text{N}_2$  in a stainless steel tube, connected to a residual gas analyzer (RGA), and heated to 110 °C. The concentration of borazine in the gas was determined from the ratio of  $m/z$  80 and  $m/z$  28 signals, calibrated with known borazine concentrations. Since  $\mathbf{AB}$  remains a solid at this temperature and our study is focused on liquid carriers, the results were compared to a tetraglyme solution of  $\mathbf{AB}$  under the same conditions. The results (Table 2) showed a substantial reduction in borazine, beyond what would be expected from mere dilution of  $\mathbf{AB}$ . The effect became even greater for catalytic release of  $\text{H}_2$  at 80 °C where only 0.01% borazine was detected in the gas released compared to 7.3% for the  $\mathbf{AB}$  reference.

**Table 1.** Analysis of Borazine ( $\mathbf{BZ}$ ) in the  $\text{H}_2$  released from fuel blends. \*Reaction was performed at 80 °C in the presence of 1% PtNi/C as a catalyst.

Mole Ratio $\mathbf{B}:\mathbf{AB}$	% $\mathbf{BZ}$ in $\text{H}_2$ Gas	n-Fold Reduction in $\mathbf{BZ}$
0:1 ( $\mathbf{AB}$ )	7.32%	-
1:1	1.26%	6

2:1	0.48%	15
3:1	0.35%	21
4:1	0.16%	46
2:1*	0.01%	676

We attribute the reduction in borazine to a reaction between **B** and **AB**, or their decomposition intermediates, so that B–N moieties that are not part of pentacyclic rings become incorporated into the dehydrogenation products. Instead of the single trimer formed by **B** (Scheme 1), we suspected that a range of products intermediate between this compound and borazine formed (Scheme 2).  $^{11}\text{B}$  NMR spectroscopy showed resonances at ca. +40 and +31 ppm, consistent with borazine and the trimer **3** respectively. However, first principles calculations (see Figure S2) indicated that the  $^{11}\text{B}$  chemical shifts of the mixed trimers **1** and **2** will overlap with the end members, making this technique unsuitable for distinguishing these compounds. Essentially, the chemical shift of boron atoms in the central aromatic ring is strongly dependent on whether it is also part of a 5-membered CBN ring and not on whether other boron atoms in the central ring are.



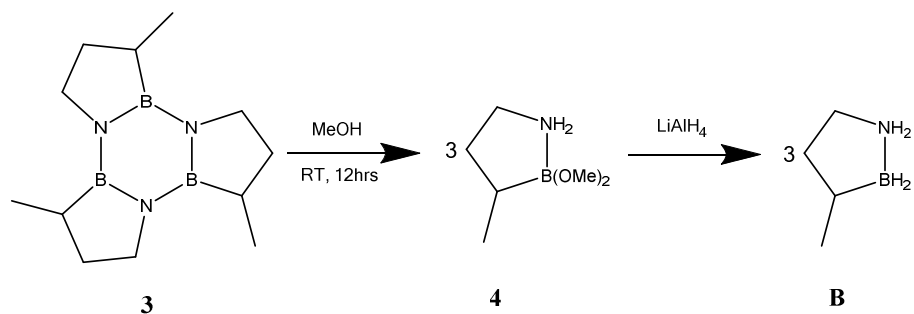
**Scheme 2.** Potential products formed during thermal desorption of H<sub>2</sub> from fuel **B/AB** blends.

The formation of mixed trimers (**1** and **2**) was confirmed by analysis of spent fuel mixtures with gas chromatography-mass spectrometry (GC-MS, see Figure S3), along with trimer **3**. The distribution of these trimers for the blends investigated is summarized in Table 2. At the 1**B**:1**AB** stoichiometry ratio all four products were observed, with trimer **2** as the most dominant. As expected, increasing the amount of **B** shifted

the product distribution toward trimers with a larger number of CBN rings, i.e. less of **1** and more of **2** and **3**. It is likely that the mixture of products formed after dehydrogenation of the **B:AB** blends is responsible for keeping the spent fuel liquid at room temperature through freezing point depression. This situation has parallels with the hydrolysis of  $\text{NaB}_3\text{H}_8$ <sup>51</sup> which was also found to have a mixture of spent fuel components that contributed to the retention of a liquid state. In that case, the distribution of hydrolysis products led to an increased solubility of the spent fuel compared to the single hydrolysis product found from  $\text{NaBH}_4$ .

**Table 2.** Product distribution (see Scheme 2 for identification) of spent fuel samples.

Mole Ratio <b>B:AB</b>	% Composition			
	<b>BZ</b>	<b>1</b>	<b>2</b>	<b>3</b>
1:1	7.3	12	73	7.3
2:1	3	2.5	56	38
3:1	0.9	1.5	45	53
4:1	0.9	-	18	81



**Scheme 3.** Regeneration of **B** from spent fuel (ref. Liu *et al.*<sup>33</sup>).

The observation of these products suggests that the regeneration path reported for **B** may also be suitable for the blends. Regeneration of **B** can be accomplished in 92% overall yield (Scheme 3<sup>33</sup>) by digestion in methanol to form the dimethyl borate **4**, and subsequent reaction with lithium aluminum hydride. The methanol digestion product of the spent fuel from the 2:1 **B:AB** blend was investigated here by <sup>11</sup>B NMR spectroscopy (see Figure S4), which did not show any of the spent fuel signals from +30 to +40 ppm. Instead, the major product was the dimethyl borate **4**, identified by the strong resonance at +9.5 ppm. The broad resonance at +13 ppm was identified as the ammonia adduct of  $\text{B}(\text{OMe})_3$ , identified from the NMR of an authentic sample (Figure S5). Earlier work has shown that borazine<sup>52</sup> and **AB** spent fuel<sup>53</sup> can be digested

by methanol, and the present results confirm that the mixed trimers can be easily digested to simpler borates. Hydrogenation of these borates using metal hydrides has been previously reported, and so regeneration of the fuel blend can be accomplished.

## Discussion

Over the past 10 years there has been significant progress into understanding the advantages and disadvantages of BN complexes (e.g. **AB**, the diammoniate of diborane<sup>54</sup>, and ammonium borohydride<sup>55</sup>) as hydrogen storage materials for vehicular fuel cell applications. The advantages include high material gravimetric and volumetric hydrogen densities, thermal stability of **AB** at 60 °C, and low temperatures for release of H<sub>2</sub>, i.e., temperatures approaching the waste heat provided by the PEM fuel cell (85 °C). However, there are significant challenges to the implementation of these materials in practical applications:

- (i) maintaining the thermal stability at 60 °C. **AB** is stable as a neat pristine solid, however, any dopant or catalyst added to the neat material renders **AB** thermally unstable. While there has been a great level of research directed at increase in the rates of H<sub>2</sub> release at lower temperature, consideration of the material at a scale for practical fuel cell applications teaches us that once the reaction is initiated it will be self-propagating due to the heat releases from the exothermic reaction. To this end it is critical to examine approaches that stabilize **AB**, not destabilize it. The rates of H<sub>2</sub> release will be more than sufficient after the reaction is initiated, particularly at the scale required for vehicular applications. The challenge here is to minimize dopants to maintain thermal stability.
- (ii) solid phase transfers and transformations. The challenge for vehicular applications is to the loading and unloading of the hydrogen carrier on and off a vehicle. The infrastructure for liquid transfers is mature and at a high technical readiness level.
- (iii) maintaining a liquid phase from beginning to end of H<sub>2</sub> release. Having a liquid starting material is important but it is also important that the products are liquids to take full advantage of a liquid transfer infrastructure.
- (iv) minimizing volatile impurities that are generated in competition with H<sub>2</sub>. For example, the purity of H<sub>2</sub> released from **AB** depends on the carrier media as well as the heating rate.
- (iv) economical and efficient regeneration of the starting material from the spent fuel material. H<sub>2</sub> release from **AB**, ammonium borohydride, or the diammoniate of diborane results in the formation of

polyiminoboranes (PIB) that consist of mixture of unidentified oligomers that are difficult to regenerate.

To address these technical challenges a number of creative solutions have been proposed. For example, Sneddon's group<sup>15, 56</sup> prepared high concentrations of **AB** in ionic liquids to maintain the carrier as a liquid phase carrier. Although this approach showed good release kinetics and substantially reduced formation of borazine, the polymeric products pose the same difficulties with regeneration as **AB**. Similar difficulties were encountered with blends of **AB** with substituted amine boranes.<sup>41, 42</sup> The early computational work of Gutowski<sup>57</sup> was an effort to demonstrate the use of theory to guide experiment towards materials that are predicted to have more favorable properties. This work was pioneering in that it provided a rationale for the investigation of cyclic CBN compounds that were predicted to provide more favorable thermodynamics, potentially reversible but definitively less exothermic to minimize heat management. Liu and Dixon<sup>31</sup> followed up on these predictions to look in more detail and the cyclic CBN materials demonstrated a number of benefits. Some of the starting materials are liquids, e.g., the BN-methylcyclopentanes such as compound **B**, and decomposition or H<sub>2</sub> release leads to far fewer volatile impurities.

The work described here was undertaken to expand upon the prior computational and experimental work. Our goal was to experiment with a fuel blend that would remain liquid throughout the cycle, fully hydrogenated to fully reduced. The concept was simple melting point depression approach by mixing two hydrogen storage materials to reduce the melting point of both. We looked at mixtures of **A + B**, **D + B**, **B + AB**, and **B + EDAB**. In the first three cases, we observed significant depression of the melting point to achieve our goal of remaining liquid before and after H<sub>2</sub> release. In the fourth case, we found that **EDAB** has little measurable solubility and did not pursue this approach further. In the first case, **A + B**, we found that compound **A** was not thermally stable at room temperature. This was somewhat surprising given the structural similarity of compounds **A** and **B**, and we did not pursue this approach further. In the second case, **D + B**, we found that both the starting blend and the products remained liquid but were limited to xca. 4.7 wt% hydrogen. Our focus was then placed on mixtures of **B** and **AB**, ca. 6 wt% hydrogen expected for release of 2 equivalents of hydrogen from both **AB** and **B**. The addition of **AB** to **B** had the benefits of decreasing the melting point of the products, forming a mixture of trimers that do not crystalize, as well as providing greater gravimetric capacity as a blend compared to neat **B**. Conversely, addition of **B** to **AB** reduced the amount of volatile impurities as the intermediates formed upon loss of H<sub>2</sub> from the parallel

reactions react together to form higher molecular weight compounds with decreased volatility providing 5.6 wt% hydrogen observed.

Note that the blend provides a combination of properties in some cases (capacity, purity) but an improvement over the “weighted average” in other cases (rate, regeneration, liquid phase). In particular, the formation of relatively simple molecular dehydrogenation products, which is a feature of **B**, was also observed from the blend. This means that the simpler regeneration scheme for **B** compared to **AB** has been retained for the blend, shown by methanol digestion to break down the trimeric products to form borates of the two blend components. A new property that the blend offered was a liquid dehydrogenated product. Neither **B** (spent fuel melts at 30 °C) or **AB** (spent fuel is a polymeric product that does not melt) have this property and so this is an important new outcome of combining materials in the present example.

The solutions and slurries examined as part of an engineering analysis<sup>38,39</sup> took the approach that the solvent or suspending fluid did not release any hydrogen itself. This was reasonable since the systems under consideration included solutions of **AB** in ionic liquids, or suspensions of **AB** in silicone oil. The approach suggested here is different in that both components have an appreciable H<sub>2</sub> capacity and react together to form new products. A significant solubility or miscibility is desirable for efficient reaction, although complete dissolution may not be required. In the example studied here, the solubility of **AB** in **B** at room temperature was only 16 mol%, but this was sufficient for complete reaction of the two compounds at relatively low temperature (80 °C with a catalyst). Creating a fuel blend where the solvent or suspending fluid also contributes to the overall H<sub>2</sub> capacity means that the blend can be considered as a liquid in terms of the engineering studies with a capacity equivalent to the weighted average of the two components.

## Conclusion

Combining chemical hydrides into a fuel blend offers a path for developing new hydrogen carriers with tunable properties. In the case of blend of a BN-methylcyclopentane and ammonia borane, we have shown that the blend: (i) releases hydrogen at a faster rate than either of the components, (ii) forms mixed trimer products which are liquid at room temperature, and (iii) produces a spent fuel which may be digested for regeneration. In addition, the concentration of borazine is reduced compared to ammonia borane because the two components react together during dehydrogenation. The hydrogen capacity of the blend is intermediate

between its components; future work includes investigating catalysts that will remove hydrogen from the carbon backbone of **CBN compounds**, thus further increasing the available capacity of the blend.

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