# Hydrogen Generation from Noncatalytic Hydrothermolysis of Ammonia Borane for Vehicle Applications

**Moiz Diwan, Hyun Tae Hwang, Ahmad Al-Kukhun, and Arvind Varma**
School of Chemical Engineering, Purdue University, West Lafayette, IN 47907

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*Ammonia borane (AB) is a promising hydrogen storage material as it contains 19.6 wt % hydrogen. In this article, our recently developed hydrothermolysis approach to release hydrogen is studied over a wide range of AB concentrations (6–88 wt %), at pressure 14.7 and 200 psia, and temperature 85–135°C. It is shown that with increasing AB concentration up to 77 wt %, the $H_2$ yield increases, and that the role of thermolysis, when compared with hydrolysis, increases. The maximum hydrogen storage capacity, obtained at 77 wt % AB and $T_{reactor} \sim 85°C$ along with rapid kinetics, was 11.6 and 14.3 wt % at pressure 14.7 and 200 psia, respectively. To our knowledge, on a material basis, the AB hydrothermolysis process is the first one to provide such high hydrogen yield values at near PEM fuel cell operating temperatures without use of catalyst, and thus is promising for use in fuel cell-based vehicle applications.* © 2010 American Institute of Chemical Engineers *AIChE J*, 57: 259–264, 2011

*Keywords: hydrogen storage, ammonia borane, hydrothermolysis, hydrolysis, thermolysis*

## Introduction

The inherent higher specific energy (Wh/g) of fuel cells, when compared with batteries, can serve the power demand of next generation vehicle applications. Hydrogen fuel cells can provide higher specific energy, power density (W/L), and double conversion efficiency when compared with batteries,[1,2] provided that a practical, high density hydrogen storage method is available.[3,4] Current on-board hydrogen storage approaches involve compressed hydrogen gas, cryogenic and liquid hydrogen, adsorbents, metal hydrides, and chemical hydrides. Compressed and cryogenic hydrogen, adsorbents, and some metal hydrides can be reversibly recharged with gaseous hydrogen, whereas chemical hydride materials require regeneration of spent fuels.[5–9]

Among various alternatives, chemical methods of hydrogen storage provide high specific energy at relatively simple storage conditions. Ammonia borane (AB) is a promising hydrogen storage material as it contains 19.6 wt % hydrogen.[10] To release hydrogen from AB, thermolysis[11] and catalytic hydrolysis[12,13] have been proposed. Because of limited AB solubility in water, catalytic hydrolysis provides low theoretical $H_2$ yield (~5.6 wt %), and it also requires expensive catalysts such as ruthenium.[14,15] Thermolysis, on the other hand, requires an external heating source to provide relatively high temperature to release 2 moles of hydrogen per mol of AB, whereas the third $H_2$ mole requires even higher temperature.[10,16]

$$\text{Hydrolysis:}\quad NH_3BH_3 + 4H_2O \rightarrow NH_4B(OH)_4 + 3H_2 \quad (1)$$

Thermolysis:

$$NH_3BH_3 \rightarrow \frac{1}{x}(NH_2BH_2)_x + H_2; \quad (90\text{–}117^{\circ}C) \quad (2)$$

$$\frac{1}{x}(NH_2BH_2)_x \rightarrow \frac{1}{x}(NHBH)_x + H_2; \quad (150\text{–}170^{\circ}C) \quad (3)$$

$$\frac{1}{x}(NHBH)_x \rightarrow \frac{1}{x}(NB)_x + H_2; \quad (>500^{\circ}C) \quad (4)$$

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Correspondence concerning this article should be addressed to A. Varma at avarma@purdue.edu.

Recently, new methods have been proposed to generate hydrogen from AB at lower temperatures. Thermolysis of AB within mesoporous silica scaffolds releases $H_2$ even at 80°C, with a 6 wt % material capacity, including the scaffold.[17] The same effect was found when ammonia borane was impregnated inside nanoporous carbon.[18,19] Catalytic dehydrogenation of AB using transition metal catalysts occurs at 60°C.[20] Bluhm et al.[21] showed that thermolysis of AB in ionic liquids at 85°C, 90°C, and 95°C releases 1.2, 1.4, and 1.6 equivalent of $H_2$, respectively. Heldebrant et al.[22] found that addition of trace quantities of diamoniate of diborane ($[NH_3BH_2NH_3][BH_4]$, DADB), a product of AB isomerization, to neat AB significantly reduces the induction time and onset temperature at which hydrogen is released. Nanophase boron nitride (nano-BN) additives to AB play a similar role as DADB and also serve as a scaffold, both decreasing the onset temperature of $H_2$ release.[23] Unfortunately, these methods involve expensive materials which also increase the overall system weight.

In this context, we have recently proposed and demonstrated a novel noncatalytic AB hydrothermolysis based method,[24] where heating solutions of lean AB (~10 wt %) in $D_2O$, deuterated water, at ~135°C under moderate argon pressure (~10 atm) generates 1 equivalent of $H_2$ (thermolysis) and 2 equivalent of HD, deuterium hydride, (hydrolysis). Note that owing to exchange between excess $D_2O$ and acidic NH moieties of AB, the role of thermolysis is likely underestimated particularly at low AB concentrations. While our previous results confirmed the feasibility and potential of this approach, it is important to extend it to higher AB concentrations, which potentially can provide higher hydrogen yield values.

The solubility of AB in water at room temperature (22°C) is about 26 wt %,[25] which means that for catalytic hydrolysis, maximum 26 wt % AB could be dissolved without phase separation. The noncatalytic hydrothermolysis, however, does not require AB/water mixture to be in a solution form, allowing the use of AB concentrations above its solubility limit (i.e., AB/water slurries). The use of higher temperature is further expected to increase the AB solubility. For these reasons, AB solubility in water is studied over a wide temperature range.

In this work, the hydrothermolysis approach to generate hydrogen is investigated over a wide range of AB concentrations, pressure, and temperature. The use of $D_2O$, instead of $H_2O$, was continued to clarify the reaction mechanism, and the equation of AB hydrolysis corresponding to Eq. 1 is as follows:

$$NH_3BH_3 + 4D_2O \rightarrow NH_3DB(OD)_4 + 3HD \qquad (5)$$

Since the release of hydrogen from AB via both thermolysis (1 equivalent of $H_2$) and hydrolysis is exothermic,[10–12,26] it was expected that hydrogen could be released from rich-AB/water mixtures at temperatures lower than required for pure AB thermolysis. This hypothesis is verified in this article by conducting hydrothermolysis experiments at reactor temperature ($T_{reactor}$) near PEM fuel cell temperatures (~85°C). This study also includes the effect of AB concentration and pressure on hydrogen ($H_2$ + HD) yield, measurement of transient pressure and temperature to understand the heat effects during hydrogen release, characterization of products using $^{11}B$ NMR spectroscopy, and gaseous product analysis using mass spectrometry.

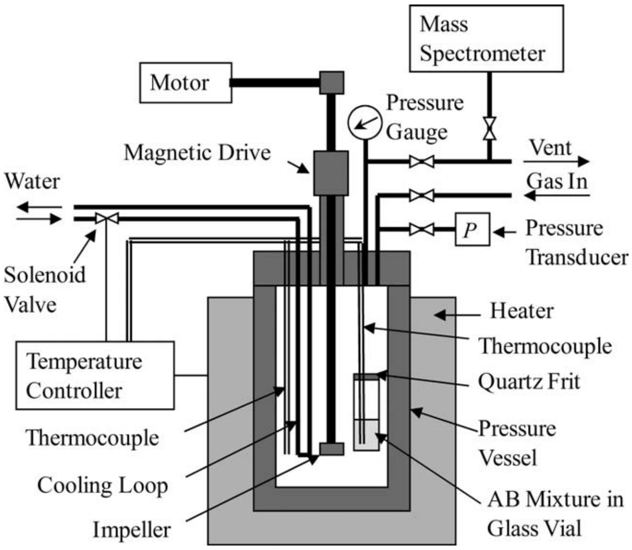

**Figure 1. Schematic diagram of the experimental setup used for AB hydrothermolysis experiments.**

## Experimental

The hydrothermolysis experiments were conducted in a stainless steel reactor (Parr Instrument Company, Model 4561) with external heating and water-flow cooling coil for temperature stabilization (Figure 1). The reactor volume, including added fittings and tubing, was determined to be 360 mL. The samples (0.5–1 g) were prepared by mixing AB (97% pure, Sigma Aldrich) with $D_2O$ (99.8% D, Sigma Aldrich) in varying weight ratios. Note that while $D_2O$ was used in the experiments, the weight of the equivalent $H_2O$ was applied to report the AB concentration in the mixture. The mixture was placed in a small glass vial (3 mL) inside the reactor, under argon (99.99% pure) environment (15–200 psia). The top of the vial was covered with a porous quartz frit (pore size ~100 $\mu$m) to minimize water loss by vaporization. Starting at room temperature, with heating rate programmed at 7°C/min, the reaction vessel was maintained for 30-min hold at a specific temperature in the range 85–135°C ($T_{reactor}$; Omega Engineering, type J thermocouple) with continuous gas stirring. The reactor pressure was monitored using a transducer (Omega Engineering PX35D1-1000AV). Apart from the reactor temperature, the sample temperature ($T_{sample}$) was also recorded by inserting a thermocouple (Omega Engineering, type J) inside the sample. To measure AB solubility, the glass vial with known amount of water was used. It was submerged in a water bath for temperature control and AB was added gradually until its precipitation was observed.

The product gas composition was analyzed by mass-spectrometry (Hiden Analytical HPR-20) after cooling the reactor to room temperature at the end of the experiment. Deuterium hydride (HD, 99.8% pure, Sigma Aldrich), 10% $H_2$/90% Ar gas mixture (Mittler) and mixture of $H_2$ (99.999% pure, Matheson Tri Gas) and Ar (99.997% pure, Matheson Tri Gas) were used for mass-spectrometer calibration. The hydrogen generation was calculated using the gas composition analysis, along with pressure increase during the experiment.

The solid products were characterized by solid-state $^{11}B$ NMR, where the spectra were recorded using a Chemagnetics CMX400 spectrometer and were referenced to $NaBH_4$ (−42.06 ppm). The samples were run with magic angle spinning (MAS), whereas the spectra were obtained without $^1H$ decoupling.

## Results and Discussion

The AB solubility in water from 22°C (room temperature) to 70°C was investigated (Figure 2). For $T > 70°C$, hydrogen bubble formation from the aq. AB solution was observed, indicating initiation of the AB/$H_2O$ reaction. At room temperature (22°C), the AB solubility was found to be 27.5 wt %; it increased linearly with temperature and was ~50 wt % at 70°C. This study helped to determine the maximum amount of AB that could be dissolved in water, and the temperature to store AB in solution form without hydrogen evolution.

To investigate the effect of AB concentration on hydrogen yield via noncatalytic hydrothermolysis process, experiments were initially conducted for AB < 43 wt % at $T_{reactor} \sim 135°C$ and $P \sim 200$ psia, where the temperature and pressure values are the same as used in our prior work.[24] Further experiments with higher concentrations of AB in water, above the solubility limit, were also conducted. Figure 3 shows the typical reactor pressure and temperature profiles for AB hydrothermolysis and AB thermolysis. The increase in pressure is due to heating the argon gas and hydrogen generation. The pressure profile for hydrothermolysis experiment is shown for 68 wt % AB in $D_2O$. It was found that for AB concentration ≥43 wt %, the pressure increased sharply at $T_{reactor}$ in the range 75–85°C (depending on AB concentration). This pressure rise was not observed for AB thermolysis. The detailed pressure rise for AB hydrothermolysis (see inset of Figure 3) shows that within a few seconds all the gases were generated and further pressure increase was due to the combined effect of reaction exothermicity and reactor temperature rise to the set point value. These results suggest that all the gas generation occurred at $T_{reactor} \sim 80°C$ and for AB concentration ≥43 wt %, $T_{reactor} \sim 85°C$ was sufficient to release the same amount of hydrogen as at 135°C (Figure 4). For this reason, all experiments for AB ≥ 43 wt % were conducted at $T_{reactor} \sim 85°C$. The sharp pressure rise, however, was not seen for AB ≤ 32 wt %, where $T_{reactor} \sim 135°C$ was required to release the gas.

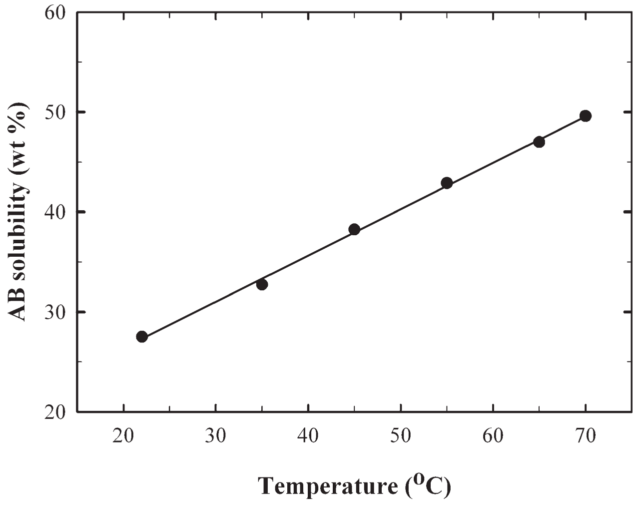

**Figure 2. AB solubility as a function of temperature.**

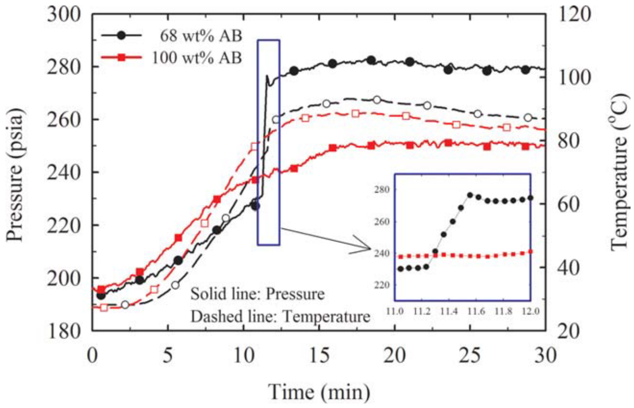

**Figure 3. Typical reactor pressure and temperature profiles obtained during AB hydrothermolysis (68 wt % AB in $D_2O$) and AB thermolysis. The detailed pressure–time profiles for the rectangular region are shown in the inset.**

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

As noted above, in experiments where $D_2O$ is used instead of $H_2O$, $H_2$ results from AB thermolysis, whereas HD from its hydrolysis. The $H_2$ and HD equivalents were calculated by taking the molar ratio of the specific gas and AB. As the AB concentration increased from 6 to 77 wt %, the $H_2$ molar equivalent increased from 0.8 to 2.5, whereas HD molar equivalent decreased from 2.2 to 0.35 (Figure 5). The total hydrogen molar equivalent ($H_2$ + HD), however, remained in the relatively narrow range of 2.8–3.0. Thus, the role of thermolysis, when compared with hydrolysis, increases with AB concentration. For further increase in AB concentration from 77–88 wt %, the $H_2$ equivalent decreased from 2.5 to 2.0, whereas HD equivalent decreased from 0.35 to 0.16.

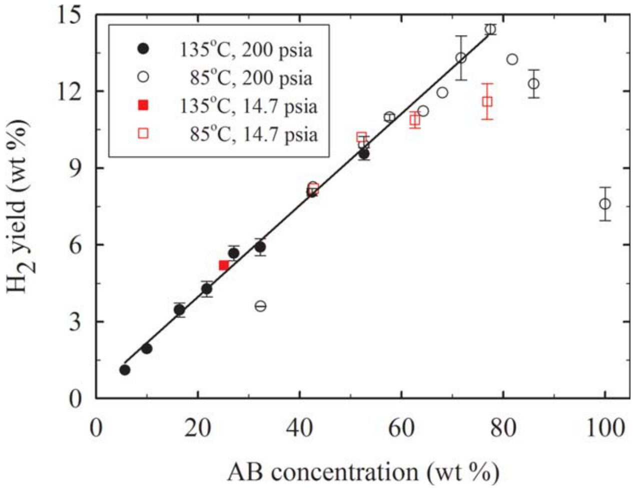

**Figure 4. Hydrogen yield as a function of AB concentration, at different operating conditions.**

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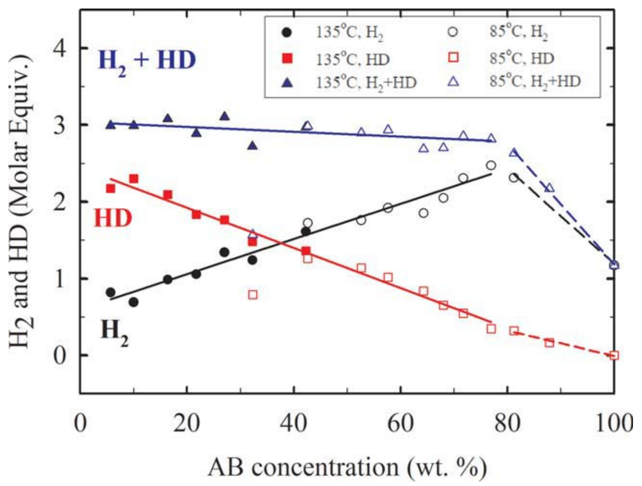

**Figure 5. The $H_2$ and HD molar equivalents as a function of AB concentration; $P$ = 200 psia.**

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The total hydrogen molar equivalent ($H_2$ + HD) also decreased from 2.8 to 2.2.

Figure 4 shows the overall hydrogen yield as a function of AB concentration, calculated as follows:

$$H_2\text{Yield}(\text{wt}\,\%) = \frac{\text{wt}(H_2) + \text{wt}(\overline{HD})}{\text{wt}(AB) + \text{wt}(\overline{D_2O})} \times 100 \qquad (6)$$

where wt($\overline{HD}$) and wt($\overline{D_2O}$) are the weights of $H_2$ and $H_2O$, respectively, corresponding to the measured HD and $D_2O$ values, with D replaced by H. Each data point for AB concentration ≤88 wt % is an average of two to four experiments, and the standard deviation is indicated by the error bars. The results for AB > 88 wt % are not presented due to poor reproducibility, caused by nonuniform mixing of AB in limited $D_2O$. At 85°C and 200 psia, from 43 to 77 wt % AB, hydrogen yields increased from 8.1 to 14.3 wt %. Further increase in AB concentration decreased the hydrogen yield. The reason for this decrease could be related to the lower heat release from hydrolysis reaction to drive the AB thermolysis, caused by lower $H_2O$ availability. The $H_2$ yield for pure AB thermolysis conducted at 200 psia and $T_{\text{reactor}} \sim 85°\text{C}$ was only 7.6 wt % (1.17 $H_2$ molar equivalent), consistent with previous findings.[11] Because of the exothermic release of the first mole of hydrogen, the maximum $T_{\text{sample}}$ for thermolysis was found to be 105°C.

Figure 4 also shows the effect of initial argon pressure on hydrogen yield, where experiments were conducted at 14.7 and 200 psia. For AB concentration up to 60 wt %, the results show no significant effect of pressure on hydrogen yield (Figure 6) as also demonstrated for pure thermolysis at 600 bar by Baitalow et al.[27] Particularly for lower AB concentrations, however, the sample product was found to be dry for 14.7 psia, whereas it was in solution form at 200 psia initial pressure. This is likely due to evaporation of water from the sample during the long cooling period following reaction. For 77 wt % AB, the hydrogen yield (Figure 4) and total hydrogen molar equivalent (Figure 6) for 14.7 psia were lower (11.6 wt %, 2.3 molar equivalent) when compared with 200 psia (14.3 wt %, 2.9 molar equivalent). Since the water content in high AB concentration mixtures is small, its evaporation has a strong impact and raises the effective mixture AB concentration beyond 77 wt %. In this range, as discussed above, the hydrogen yield decreases with increasing AB concentration.

Figure 7a, b shows transient mass-spectrometry analysis for 43 and 68 wt % AB concentration at $T_{\text{reactor}} \sim 85°\text{C}$, where Ar continuously flowed through the Parr reactor at 200 psia and gas composition was measured with time. It was found that at $T_{\text{reactor}} \sim 80°\text{C}$, $T_{\text{sample}}$ increased sharply up to ~180°C (sufficient to release the second $H_2$ mole from AB), with simultaneous evolution of $H_2$ and HD. The sharp increase in sample temperature is due to heat evolution during hydrothermolysis reaction (as noted above, both AB hydrolysis and the first step of AB thermolysis are exothermic). The $H_2$ and HD evolution began simultaneously at $T_{\text{sample}} \sim 105°\text{C}$ and reached maximum value within a few seconds, which suggests rapid reaction kinetics. For 43 wt % AB, the maximum $H_2$ and HD mole fractions were close, whereas for 68 wt %, the HD value was lower than $H_2$ owing to decreased hydrolysis when compared with thermolysis (Figure 5).

The effective recycling of spent fuel to AB remains a challenge for AB dehydrogenation processes to become practical. In general, it is known that AB hydrolysis results in the formation of B—O bonds, which are thermodynamically more stable than B—N bonds formed by thermolysis.[28] The regeneration method is different depending on the composition of the spent fuel generated.[28,29] For this reason, AB hydrothermolysis products were characterized by solid-state $^{11}$B NMR. As shown in Figure 8a, b, two features are observed in the product spectra obtained from 40 wt % AB for both 200 psia and 14.7 psia. The main peak near 0 ppm is likely corresponding to boric acid, produced by hydrolysis of AB.[30,31] A broad shoulder in the area of tricoordinated boron atoms, i.e., (poly)-borazine, (poly)-iminoborane, etc., is also found over 20 to 0 ppm, and these species result from release of ~2 hydrogen equivalent by AB thermolysis.[22,32] The spectrum of the 80 wt % AB product (200 psia) is similar to that obtained for the 40 wt % AB product

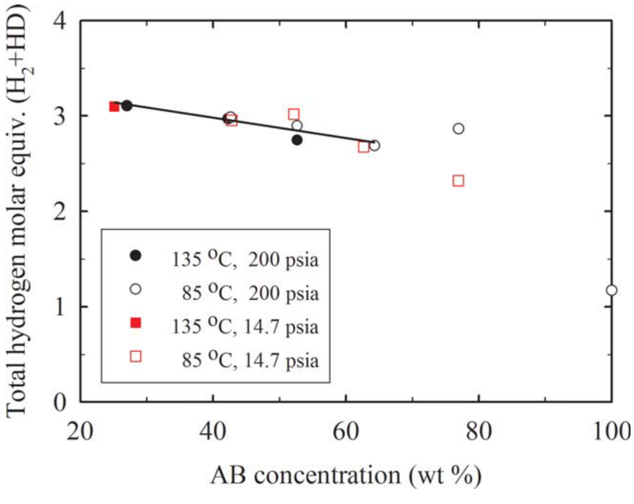

**Figure 6. The effect of initial Ar pressure on the total hydrogen molar equivalent for varying AB concentrations.**

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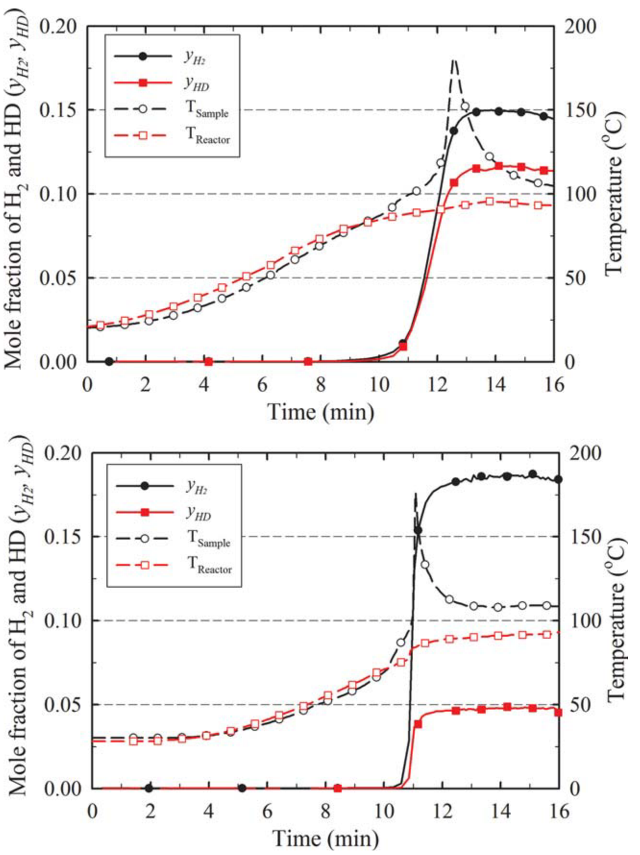

**Figure 7. Transient analysis during hydrothermolysis process for (a) 43 wt % (b) 68 wt % AB in $D_2O$; $T_{reactor}$ = 85°C, $P$ = 200 psia.**

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(Figure 8c). However, the spectrum of the product obtained from 80 wt % AB for 14.7 psia clearly shows additional peaks over 0 to 40 ppm (Figure 8d). These peaks can be attributed to tetracoordinated boron atoms, i.e., (poly)-aminoborane, cyclotriborazane, etc., which result from AB thermolysis to ~1 hydrogen equivalent.[22,32] The product characterization results are in good agreement with the $H_2$ yield values presented in Figure 4. It is worth noting that methods for AB regeneration from the products described above have been published recently.[28,29,33]

## Conclusions

The noncatalytic AB hydrothermolysis method to release hydrogen was studied over a wide range of AB concentrations, pressures, and temperatures. In the experiments, instead of $H_2O$, $D_2O$ was used to clarify the reaction mechanism. It was shown that with increasing AB concentration up to 77 wt %, the $H_2$ molar equivalent increased, whereas the HD molar equivalent decreased. Thus, the role of thermolysis ($H_2$ yield), when compared with hydrolysis (HD yield), increases with AB concentration. The effect of pressure on hydrogen yield was found to be insignificant up to 60 wt % AB. An important finding is that for AB concentration >43 wt %, $T_{reactor}$ ~ 85°C is sufficient to release the same amount of hydrogen as at $T_{reactor}$ ~ 135°C. This, however, does not hold for lower AB concentrations (≤32 wt %). The maximum observed hydrogen storage capacity, obtained at 77 wt % AB concentration and $T_{reactor}$ ~ 85°C, was 11.6 and 14.3 wt % at pressure 14.7 and 200 psia, respectively. Transient experiments showed that during the hydrothermolysis process, the sample temperature increased sharply due to heat evolution by reaction (both AB hydrolysis and the first step of AB thermolysis are exothermic). The $H_2$ and HD evolution began simultaneously at $T_{sample}$ ~ 105°C and reached maximum value within a few seconds, which suggests rapid reaction kinetics.

The spent product from hydrothermolysis was characterized using $^{11}$B NMR. The spectra show that the product contains boric acid, produced by AB hydrolysis and also tricoordinated boron atoms, i.e., (poly)-borazine, (poly)-iminoborane, etc., resulting from release of ~2 hydrogen equivalent by AB thermolysis. For high AB concentrations (~80 wt %) at lower pressure (14.7 psia), there are additional peaks corresponding to tetracoordinated boron atoms, i.e., (poly)-aminoborane, cyclotriborazane, etc., which result from AB thermolysis to ~1 hydrogen equivalent. Methods for regenerating AB from these products have been published

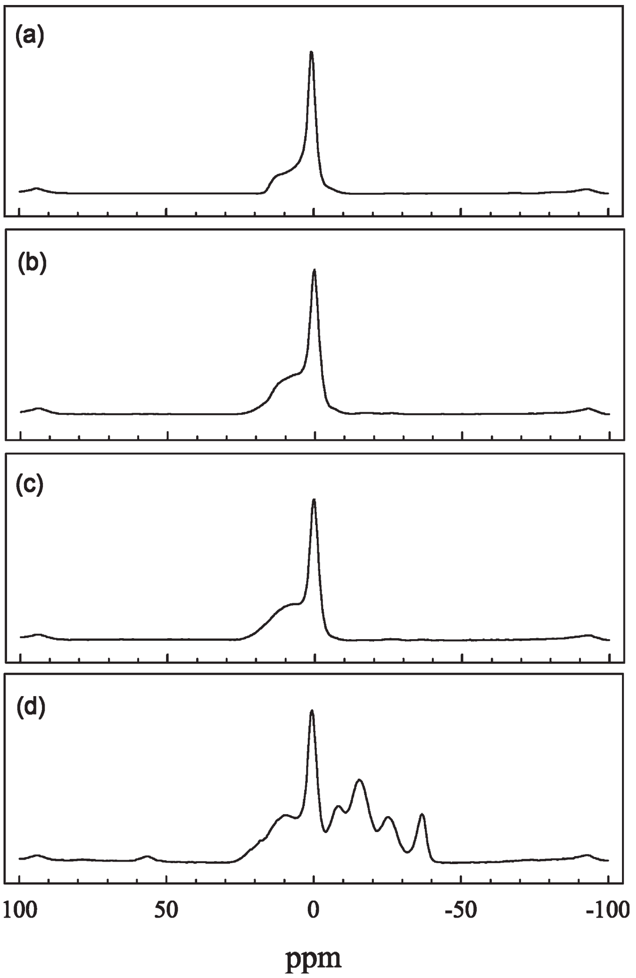

**Figure 8. $^{11}$B NMR spectrum of the AB hydrothermolysis product at $T_{reactor}$ 85°C (a) 40 wt % AB, 200 psia; (b) 40 wt % AB, 14.7 psia; (c) 80 wt % AB, 200 psia; and (d) 80 wt % AB, 14.7 psia.**

recently.[28,29,33] As noted above, from the $H_2$ yield viewpoint, 77 wt % AB is found to be optimal, but it could well be that even higher AB concentrations provide a better balance between sufficiently high $H_2$ yield along with low B—O bond spent fuel product.

To our knowledge, on a material basis, the AB hydrothermolysis process is the first one to provide such high hydrogen yield values at near PEM fuel cell operating temperatures without use of catalyst. Further, for the same temperature range, these yield values are higher than previously reported in the literature by either AB hydrolysis or thermolysis alone. It is worth noting that DOE system targets for $H_2$ yield are 4.5 and 5.5 wt % for the years 2010 and 2015, respectively.[34] The material-based $H_2$ yield (~14.3 wt %) achieved in this work is sufficiently higher than the target values, suggesting that the noncatalytic AB hydrothermolysis method is promising for hydrogen storage in fuel cell-based vehicle applications.

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