Final Report

DOE award number: DE-FG36-08GO18140

Recipient: U.S. Borax Inc.

Project title: Collaborative research on amine borane regeneration and market analysis of hydrogen storage materials

Project PI: David Schubert, Ph.D.

Consortium Partners: Center of Excellence for Chemical Hydrogen Storage led by Los Alamos and Pacific Northwest National Laboratories

Report Date: 12/06/10; **Project performance period:** 10/01/08 – 09/30/10

This report has no distribution limitations

Executive Summary

Amine borane (AB) is a very high capacity hydrogen storage material that meets DOE gravimetric and volumetric targets for on-board delivery of hydrogen for fuel cell vehicles (FCVs). This research helped make process toward the ultimate goal of practical generation of spent AB and added to the understanding of materials and processes required to utilize AB in practical applications. In addition, this work helped to enhance our fundamental understanding of the properties of boron materials now being pursued for new frustrated Lewis pair catalyst systems for activation of hydrogen and carbon dioxide, of interest for carbon capture and fuels production.

This project included four primary areas of investigation: (1) synthesis of borate esters for use as amine borane regeneration intermediates, (2) spent ammonia borane fuel generation and analysis, (3) spent fuel digestion for production of borate esters, and (4) worldwide borate resource analysis. Significant progress was made in each of these areas during the two-year course of this project, which involved extensive collaborations with partners in the Center of Excellence for Chemical Hydrogen Storage, and particularly with partners at the Pacific Northwest National Laboratory.

Results of the boron resource analysis studies indicate that sufficient boron reserves exist within the United States to meet forecast requirements for a U.S. fleet of hydrogen FCVs and sufficient resources are available worldwide for a global fleet of FCVs.

Comparison of Accomplishments with Project Goals: This project was in support of a larger project of the DOE-sponsored Virtual Center of Excellence for Chemical Hydrogen Storage (CoE CHS). This work was directed at development of technologies for the practical use of boron-based materials for hydrogen storage, and particularly for ammonia borane. Substantial progress, in accordance with project plans, were made in each of the primary project activity areas: (1) synthesis of borate esters for use as amine borane regeneration intermediates, (2) spent ammonia borane fuel generation and analysis, (3) spent fuel digestion for production of borate esters, and (4) worldwide borate resource analysis. In addition, this project contributed to exciting new developments in materials for activation of hydrogen for fuels production now being investigated.

Summary of Project Activities

Activity 1: Borate Esters Synthesis Related to Amine Borane (AB) Regeneration Intermediates

Background: Borate esters can be reduced to borane as part of a practical regeneration cycle, returning BNH_x (spent fuel) to AB fuel. This requires esters that have enhanced hydride affinities – a property closely related to Lewis acidity. Calculations done at the Pacific Northwest National Laboratory (PNNL) and elsewhere indicate that phenolic esters possessing electrophilic substituents may have suitable hydride affinities. In order to validate these calculations, we have prepared and characterized a series of 27 orthoborate esters. The Lewis acidity was determined by measuring the acceptor number for each ester. In addition to this analysis, we have provided PNNL with samples of these esters for further experimental investigation, such as hydride transfer studies.

Triphenyl borate and its halogenated derivatives can be synthesized from a number of reagents as shown in the following general reaction:

$$BR_3 + 3\,ArOH \longrightarrow B(OAr)_3 + 3\,HR \qquad (1)$$

In Equation 1, R may be H, Cl, OH, or OCH_3, while Ph is a phenyl or halogenated phenyl group. This type of reaction may be carried out in ethers, toluene, or alkanes with or without drying agents such as CaH_2. The boric acid reagent (R = OH) was preferred for the high purity synthesis of aryl borate esters due to its relative stability and purity. The purity of the phenol reagent is also critical. Impurities of the phenol reagents were often extremely difficult or impossible to remove from the product $B(OPh)_3$. The $B(OPh)_3$ product is moisture sensitive as it reacts with water in the reverse of Equation (2). Therefore, the product must be isolated and stored under strict anhydrous conditions.

$$B(OH)_3 + 3\,ArOH \rightleftarrows B(OAr)_3 + 3\,H_2O \qquad (2)$$

Accomplishments: A list of the borate esters prepared and supplied to PNNL as part of this project are listed in Table 1. Additional experimental details are provided in the Appendix.

The borate esters were characterized by IR and NMR spectroscopy to verify the high purity of these materials. Common impurities of the product were $B(OH)_3$ (absence verified by ^{11}B NMR – single boron peak), phenol (absence verified by ^{1}H NMR–absent alcoholic H), and residual solvent (absence verified by ^{1}H NMR and IR – absent sp^3 C-H bonds).

Lewis acidity measurements were determined by acceptor number (AN) measurements. The AN is determined by forming a Lewis acid/acceptor adduct with triethlyphosphine oxide (Et_3PO) and measuring the $\delta\ ^{31}P$ NMR signal of the adduct.

$$Et_3PO + B(OPh)_3 \rightleftarrows Et_3PO\text{-}B(OPh)_3 \qquad (3)$$

The difference between the $\delta\ ^{31}P$ of the "free" Et_3PO (more accurately, the Et_3PO-hexane adduct, 42.47 ppm) and the $\delta\ ^{31}P$ of the ester adduct is the $\Delta\delta\ ^{31}P$ value. These $\Delta\delta\ ^{31}P$ values can be rescaled on an arbitrary axis were $\Delta\delta$ ^{31}P Et_3PO in hexane is zero and $\Delta\delta$ ^{31}P of $Et_3PO\text{-}SbCl_5$ in $C_2H_4Cl_2$ (42.98 ppm) is set to 100. The resulting dimensionless units are AN.

Table 1. Borate ester compounds prepared and supplied to PNNL as part of this project.

Fluorophenylborate esters	
Tris(*2*-fluorophenyl)orthoborate	$(2\text{-}FC_6H_4O)_3B$
Tris(*3*-fluorophenyl)orthoborate	$(3\text{-}FC_6H_4O)_3B$
Tris(*4*-fluorophenyl)orthoborate	$(4\text{-}FC_6H_4O)_3B$
Tris(*2,3*-difluorophenyl)orthoborate	$(2,3\text{-}F_2C_6H_3O)_3B$
Tris(*2,4*-difluorophenyl)orthoborate	$(2,4\text{-}F_2C_6H_3O)_3B$
Tris(*2,6*-difluorophenyl)orthoborate	$(2,6\text{-}F_2C_6H_3O)_3B$
Tris(*3,4*-difluorophenyl)orthoborate	$(3,4\text{-}F_2C_6H_3O)_3B$
Tris(*3,5*-difluorophenyl)orthoborate	$(3,5\text{-}F_2C_6H_3O)_3B$
Tris(*3,4,5*-trifluorophenyl)orthoborate	$(3,4,5\text{-}F_3C_6H_2O)_3B$
Chlorophenylborate esters	
Tris(*2*-chlorophenyl)orthoborate	$(2\text{-}ClC_6H_4O)_3B$
Tris(*3*-chlorophenyl)orthoborate	$(3\text{-}ClC_6H_4O)_3B$
Tris(*4*-chlorophenyl)orthoborate	$(4\text{-}ClC_6H_4O)_3B$
Tris(*2,3*-dicloorophenyl)orthoborate	$(2,3\text{-}Cl_2C_6H_3O)_3B$
Tris(*2,4*-dichlorophenyl)orthoborate	$(2,4\text{-}Cl_2C_6H_3O)_3B$
Tris(*2,6*-dichlorophenyl)orthoborate	$(2,6\text{-}Cl_2C_6H_3O)_3B$
Tris(*3,4*-dichlorophenyl)orthoborate	$(3,4\text{-}Cl_2C_6H_3O)_3B$
Tris(*3,5*-dichlorophenyl)orthoborate	$(3,5\text{-}Cl_2C_6H_3O)_3B$
Tris(*2,4,5*-trichlorophenyl)orthoborate	$(2,4,5\text{-}Cl_3C_6H_2O)_3B$
Tris(*2,4,6*-trichlorophenyl)orthoborate	$(2,4,6\text{-}Cl_3C_6H_2O)_3B$
Tris(pentachlorophenyl)orthoborate	$(Cl_5C_6O)_3B$
Bromophenylborate esters	
Tris(*4*-bromophenyl)orthoborate	$(4\text{-}BrC_6H_4O)_3B$
Iodophenylborate esters	
Tris(*4*-iodophenyl)orthoborate	$(4\text{-}IC_6H_4O)_3B$
Mixed halophenylborate esters	
Tris(*2*-fluoro-*4*-chlorophenyl)orthoborate	$(2\text{-}F,4\text{-}ClC_6H_3O)_3B$
Tris(*2*-fluoro-*6*-chlorophenyl)orthoborate	$(2\text{-}F,6\text{-}ClC_6H_3O)_3B$
Tris(*2*-fluoro-*4*-bromophenyl)orthoborate	$(2\text{-}F,4\text{-}BrC_6H_3O)_3B$
Tris(*3*-fluoro-*4*-chlorophenyl)orthoborate	$(3\text{-}F,4\text{-}ClC_6H_3O)_3B$
Chelate Borate Esters	
Non-halogenated chelate ester	$(C_{13}H_{11}NO_2)BH$
Dichlorinated chelate ester	$(C_{13}H_9Cl_2NO_2)BH$

The δ ^{31}P measurement of the $Et_3PO\text{-}B(OAr)_3$ adduct requires a few precautions and corrections. Equation 3 is reversible. In a 1:1 mixture of reagents, the measured δ ^{31}P will be some intermediate value (dependent on the equilibrium) of free Et_3PO and the adduct. Therefore, extrapolation to infinite concentration of $B(OAr)_3$ (or infinite dilution of Et_3PO) will give a more accurate δ ^{31}P value for the adduct.

Like Et_3PO, most of the esters studied are solids and a solvent is required for this analysis. The solvent can compete with adduct formation as shown in Equation 4. Extrapolation to infinite dilution of solvent is necessary for correction of solvent effects.

$$Et_3PO\text{-Solvent} + \text{Solvent-}B(OPh)_3 \rightleftharpoons Et_3PO\text{-}B(OPh)_3 \qquad (4)$$

The δ ^{31}P measurement of the Et_3PO-hexane adduct is more straightforward requiring only extrapolation to infinite dilution of Et_3PO in hexane. Additional details regarding experimental conditions, δ ^{31}P corrections, and AN calculations are provided in the Appendix.

In Figure 1, the AN determined for each ester have been plotted with gas phase calculated hydride affinities for comparison. The plot shows that the Lewis acidity measurements generally agree with the hydride affinity calculations with only a few exceptions.

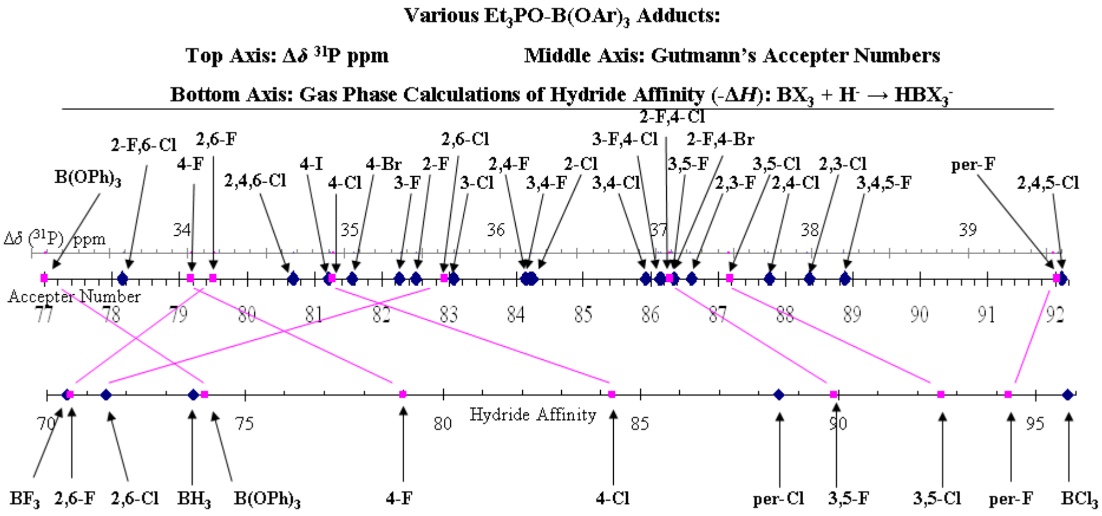


Figure 1: Plot of borate ester acceptor numbers and calculated hydride affinity.

Three effects of halogen substitution on the Lewis acidity of $B(OAr)_3$ were elucidated. Lewis acidity is most increased according to the following halogen identity trend:

$$Br > Cl \geq I > F > H$$

This ordering could be rationalized by two competing factors: electro negativity – the ability to remove electron density via σ interaction (F > Cl > Br > I > H) – increases Lewis acidity; and orbital overlap – the ability to back-donate electron density via π interaction (F > Cl > Br > I >> H) – decreases Lewis acidity. Lewis acidity is most increased according to the following halogen quantity trend:

$$5 > 3 > 2 > 1 > 0$$

The more halogens present the more electron density is removed to increase the Lewis acidy. Lewis acidity is most increased according to the following halogen position trend:

$$2/6 > 3/5 > 4$$

An additional effect considered is the steric effect. Substituents at both 2 and 6 positions sterically hinder intermolecular boron interactions. While these types of esters had higher Lewis acidities than expected by the calculated hydride affinities, they are not likely candidates for use in hydride transfer with bulky transition metal complexes. It should be noted that substitution at only one ortho position (at the 2 but not at the 6 position) did not result in a noticeable steric effect.

Activity 2: Spent Ammonia Borane Fuel Generation and Analysis.

Background: To study digestion of spent fuel, a large, well characterized lot of spent fuel is desirable. About 0.5-1 gram of the spent fuel is used for characterization, specifically, elemental analysis. Spent fuel generation has been limited to batch sizes of about 1-2 grams of ammonia borane, which typically yield less than a gram of spent fuel. Larger batch sizes result in safety issues due to the rapid, exothermic release of the second equivalent of hydrogen.

Accomplishments: We developed a safe method for larger scale production of spent fuel. This has been accomplished by utilizing a screw feeder to dispense ammonia borane into the reactor at a controlled rate rather than heating the entire lot of ammonia borane at once. In a typical trial, 10 grams of ammonia borane results in 5-6 grams of spent fuel. Two types of spent fuel were produced: hydrated and anhydrous spent fuel. The hydrated spent fuel was produced without restricting water vapor from entering the reactor, while the anhydrous spent fuel was produced under a moisture free atmosphere.

We successfully preformed elemental analyses of spent fuel made in our lab, spent fuel produced at PNNL, and commercially available polyborazylene:

US Borax hydrated spent fuel:	$N_{0.97}H_{1.20}BH_{0.56}O_{0.23}$
	$N_{1.07}H_{0.84}BH_{0.43}O_{0.19}$
US Borax anhydrous spent fuel:	$N_{1.09}H_{0.87}BH_{0.41}O_{0.10}$
	$N_{1.12}H_{0.84}BH_{0.46}O_{0.092}$
PNNL anhydrous spent fuel:	$N_{1.02}H_{1.01}BH_{0.43}O_{0.077}$
PNNL closed system spent fuel:	$N_{1.03}H_{0.76}BH_{0.37}O_{0.087}$
Boron Technologies Polyborazylene:	$N_{1.08}H_{0.74}BH_{0.40}$

Due to the formation of boron nitride in the presence of boron, the combustion method failed to determine nitrogen content. A modified Kjeldahl method was used for the nitrogen analysis of ammonia borane, spent fuel, and polyborazylene. Additional experimental details for the production and analysis of spent fuel are provided in the appendix.

Activity 3: Spent Fuel Digestion for Production of Borate Esters

The goal of this activity is two part: 1) digest the spent fuel, which requires complete dissolution of the spent fuel and liberation of all nitrogen as ammonia; 2) convert the boron species to aryl borate esters [$B(OPh)_3$].

Using 2,4-difluorophenol (2,4-F-PhOH) to make tris(2,4-difluorophenyl)borate ester [$(2,4\text{-F-PhO})_3B$] provides the most desirable combinations of physical properties (Table 2) in addition to providing a borate ester of relatively high Lewis acidity. These properties allow for low distillation temperatures and for reactants and products to be processed as liquids. Such attributes have economic and logistic advantages on an industrial scale.

Table 2. Properties of selected borate esters

	Melting Point °C	**Boiling Point °C**
2,4-FPhOH	22.4	52-53 (@19 mmHg)
$(2,4\text{-FPhO})_3B$	Liquid	120 (under vacuum)

Simultaneous release of nitrogen as ammonia and borate ester formation is not possible for 2,4-FPhOH. This is due to formation of stable ammonia and/or ammonium complexes.

$$N_aH_bB_cH_dO_e + 2,4\text{-FPhOH} \longrightarrow (2,4\text{-FPhO})_3B\text{-}NH_{3(s)} + [NH_4]^+[(2,4\text{-FPhO})_4B]^-_{(s)} \quad (5)$$

Alkyl alcohols (ROH) do not form these types of stable compounds with ammonia or ammonium and could allow ammonia liberation.

$$N_aH_bB_cH_dO_e + ROH \longrightarrow NH_{3(g)} + B(OR)_3 + H_{2(g)} + H_2O \quad (6)$$

Such a route would be acceptable because the alkyl borate ester is easily converted to the desired aryl borate ester by transesterification:

$$B(OR)_3 + 3\,(2,4\text{-F-PhOH}) \longrightarrow (2,4\text{-F-PhO})_3B + 3\,ROH \quad (7)$$

The ROH is collected for recycling by distillation and the $(2,4\text{-FPhO})_3B$ is collected by vacuum distillation. To avoid forming products of Equation 5, Equation 6 must be driven to completion prior to transesterification (Equation 7). Therefore all nitrogen must be liberated as ammonia prior to the introduction of the phenol.

We monitored digestion experiments by following nitrogen release as ammonia. A number of reaction conditions were explored to maximize nitrogen recovery/removal, as listed in Table 3.

Table 3. Hydrated spent fuel (~0.1 g)

Solvent	**mL**	**Post Reaction Appearance**	**Nitrogen Recovered as NH_3**
1.2 M HCl	10	Clear colorless solution	0 %; 100% as NH_4 (theory)
Isopropanol	~15	White solid	85 %
Isopropanol:water	9:1	White solid	83 %
Isopropanol:2,4-FPhOH	9:1	White suspension	≥ 87 %
Isopropanol:2,4-FPhOH	18:2	White suspension	83 %
1,4-dioxane:isopropanol	18:2	Clear solution*	65 %
Water	20	Clear colorless solution*	91 % (final pH ~5.5)
Steam		White solid	93 %

*Small amounts of very fine white solid could be detected upon close inspection

Our results indicate that under all tested conditions quantitative release of ammonia was not achieved. Only with excess acid was the spent fuel completely dissolved. Hydrolysis of generic spent fuel, NHBH, to NH_3 and $B(OH)_3$ is expected to be acid catalyzed. At a low pH, spent fuel digestion should proceed; however, the ammonia generated will not be liberated from the solution. Instead, ammonium hydroxide will form and build up as the reaction proceeds, increasing the pH and inhibiting the acid catalyzed digestion process.

Digestion could be achieved by adding more than quantitative amounts of acid to neutralize all ammonium hydroxide that forms. Then complete liberation of nitrogen as ammonia could be achieved by adding quantitative amounts of base. Unfortunately, this type of process would not likely be economically feasible on larger scales.

Activity 4: Borate Resource Analysis

4-A. Overview. Boron-based materials, such as ammonia borane and alkali-metal borohydrides, are central to several strategies for storing and releasing hydrogen on board fuel cell vehicles (FCVs). In addition to solving technical challenges it is also important to understand the impacts on boron resources associated with the initial fill requirements of a boron-based fuel for a large automotive fleet. This requires assessments of both world boron resources in terms of known relevant borate minerals deposits and the boron requirements for hydrogen storage in FCVs. This involves analysis and reconciliation of publicly available information on borate resources in various parts of the world. To date, we have compiled and analyzed key public sources of information and refined the combined borate resource estimates. These estimates were projected out to 2050 using estimates of boron demands from other competing industrial applications, to produce an adjusted assessment of boron resources over the period relevant to hydrogen fuel cell vehicle (FCV) deployment. These data were then compared with calculated demand due to FCVs.

4-B. Borate Demand Model. Boron demand associated with automotive use of ammonia borane hydrogen storage material was based on known chemistry of the ammonia borane storage system and the number and specifications of FCVs deployed as projected in the Department of Energy publication, *Analysis of the Transition to Hydrogen Fuel Cell Vehicles & Potential Hydrogen Energy Infrastructure Requirements* (ORNL/TM-2008/30), and the VISION model (2). The total number of FCVs in operation is set at 360 million in the United States. A figure of 2 billion vehicles is used as an estimate for the global number of fuel cell vehicles (3). This is based on projections of the global number of light vehicles in 2050 and does not refer to any specific fuel cell deployment scenario or time frame. The model for boron demand resulting from FCV deployment includes the assumptions listed in Table 4.

Table 4. Assumptions used in boron demand base model

Number FCVs deployed in USA by 2050	360
Number FCVs deployed worldwide by 2050	2000
Miles per kg H_2	57.5*
Miles range per tank	400
Miles per year per FCV	12,000*
Months supply in infrastructure	1
% H_2 stored in ammonia borane	15
% Yield of single pass in regeneration	100
% Recycle	100 (insignificant losses)

* from the H2A model

cumulative boron demand associated with 360 million FCVs deployed in the United States by 2050 is calculated to be 60 million metric tonnes of B_2O_3. There is a corresponding demand of 360 million B_2O_3 tonnes for global fleet of 2 billion vehicles.

4-C. Borate Resources. The most widely used system for categorizing resources and resources is that of the U.S. Geological Survey (4). A resource is an identified or a probable physical presence of a mineral, which may or may not be exploitable with currently available technology. Reserves are the portion of the identified resources that have been more precisely measured and are, or might soon be, available for production. One of the main principles of this system is that "resources must be continuously reassessed in the light of new geological knowledge, of progress in science and technology, and of shifts in economic and political conditions" to define reserves. A consequence of this dependence on an array of ever-changing factors is that mineral reserve estimates tend to vary widely between different reports; and borate reserves are no exception to this situation.

For the purpose of assessing how much boron would be available to supply the requirements of fuel cell vehicles it is also desirable not to be too restrictive. The economics associated with high demand are likely to cause more of the identified resources to be included as reserves than are currently so. For this reason, the numbers collected by Garrett (5) are preferred over those reported by the U.S. Geological Survey (6). The review provides reasonable details on the extent, chemistry, and grade of the various borates deposits it includes and is therefore preferable to some other reports that provide large borate reserve numbers with little justification; however, these estimates are still perhaps best referred as identified resources rather than actual reserves.

The assessment of global borate resources, summarized in Figure 2, indicates that more than 1 billion B_2O_3 tonnes are available from known borate reserves. Figure 1 also shows the cumulative amounts of B_2O_3 estimated to be required for both a US and a global fleet of FCVs fueled with ammonia borane.

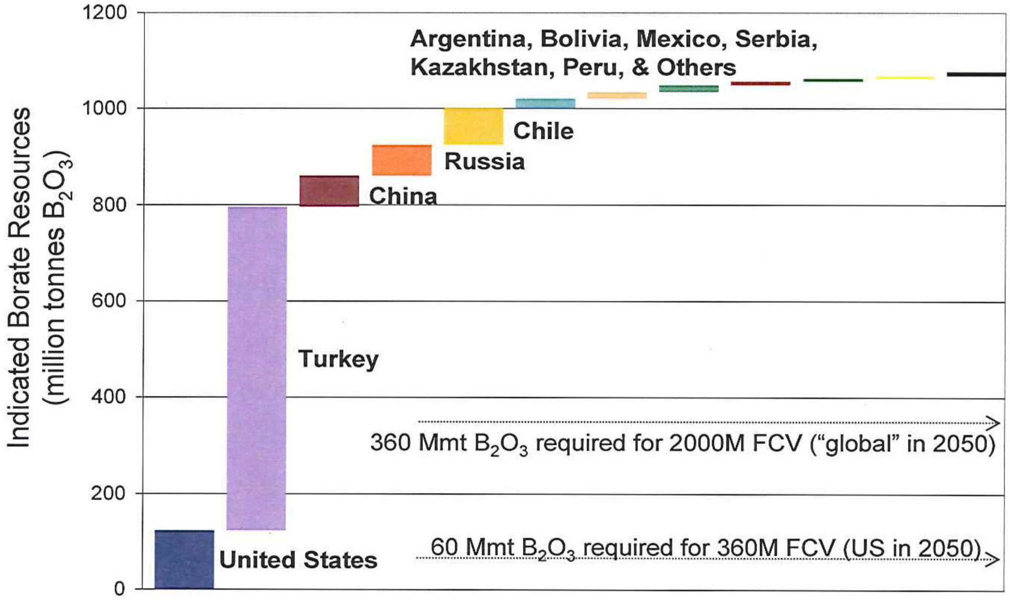


Figure 2. Estimated global borate resources showing the cumulative amounts of B_2O_3 estimated to be required for both a US and a global fleet of FCVs fueled with ammonia borane.

The conclusions drawn from these data are that:

(1) *There are sufficient borate reserves within the United States to satisfy the B_2O_3 requirements for initial fill of a US FCV fleet*.

(2) *There are sufficient borate reserves in the world to satisfy the B_2O_3 requirements for initial fill of a global FCV fleet*.

4-D. Sensitivities of the Boron Demand Model. The sensitivity of the calculated boron demand to the assumptions in the base model should be examined. Figure 3 is a tornado diagram that plots the ranges of the calculated boron demand for minimum and maximum values of the variables in the model. An additional variable representing the single-pass yield of the regeneration process that had been implicitly included in the base model was also introduced for the sensitivity analysis. Although all the ammonia borane is assumed to be regenerated eventually, that which isn't regenerated on the first pass must be recycled and adds to the material in the infrastructure. That boron demand is calculated with each variable independently at an extreme while the others are assumed to be their base values. Reasonable estimates for these extremes are used. For example, the %H_2 stored in ammonia borane is varied between the maximum amount that could be stored and released (3 moles of H_2 per mole of ammonia borane) and the case where only 2 moles are released.

The sensitivity analysis shows that the number of days supply in the structure can profoundly affect the boron demand. The lowest estimate of 15 days is half of that used in the base model and is approaching the limit of 11 days supply which would correspond to a case where a tank of new fuel is waiting to be dispensed and there is no other fuel in the infrastructure. In contrast a 90-day supply in the infrastructure almost triples the boron requirement. It should be noted that a similar tripling of the global boron demand would bring it in line with all the available resources. These extremes may be a little unrealistic but highlight the need to design an efficient infrastructure for delivering and regenerating the fuel to avoid pushing demand to unmanageable levels.

The chemistry of the ammonia borane storage and regeneration are the next two most important factors. Since 100% yield was assumed in the base model, anything less creates higher demand than initially predicted and could potentially increase it by 50% if the yield were as low as 70%.

Vehicle characteristics and the number of FCVs deployed have a smaller impact on the boron demand.

Losses of boron from the system were assumed to be zero or insignificant. These were not included in the sensitivity analysis as they would be expected to recur whereas the other factors contribute to a fixed boron demand that is required to "fill" a functioning FCV fleet and the infrastructure required to support it. Another reason losses were excluded is that they simply have to be engineered to be insignificant. Consider that 1% loss of boron from a full fleet of 360 million vehicles would represent approximately 0.6 million tonnes of B_2O_3. This is roughly equivalent to current production levels in the United States.

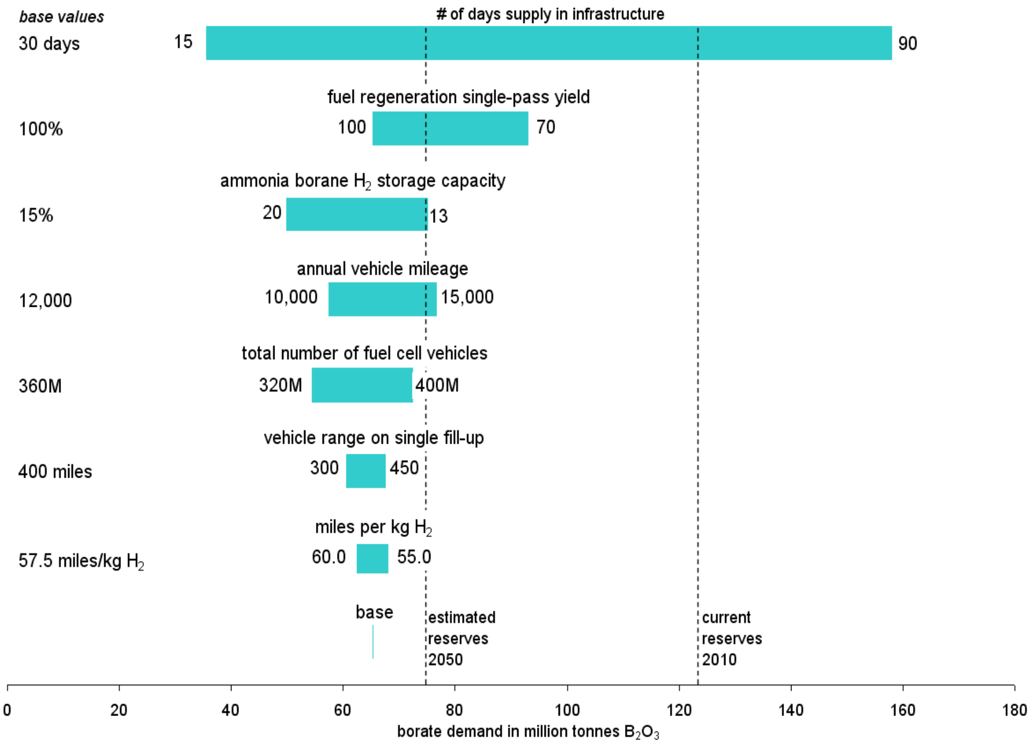


Figure 3: The sensitivity of boron demand estimates to assumptions in the base model.

4-E. Production Capacity Issues. Companies in the United States mined the equivalent of 0.61 million tonnes of B_2O_3 in 2005 (6, 7). This is the last year that U.S. production was widely reported. These data were withheld after that to protect proprietary company information. Nonetheless, the figure is a reasonable estimate for the years following that and is used without change to forecast the annual production in the years 2010 through 2050. If this production was maintained to supply existing applications, by 2050 the resources in the United States would be reduced to just over 100 million tonnes of B_2O_3. This leads to the following conclusion:

(3) *There are sufficient borate resources within the United States to satisfy the B_2O_3 requirements for both an initial fill of a US FCV fleet and demand from existing industrial applications during the maturation of the FCV market.*

The additional annual demand for boron calculated using the most aggressive scenario from the *Analysis of the Transition to Hydrogen Fuel Cell Vehicles & Potential Hydrogen Energy Infrastructure Requirement* (2). The demand is shown in Figure 4.

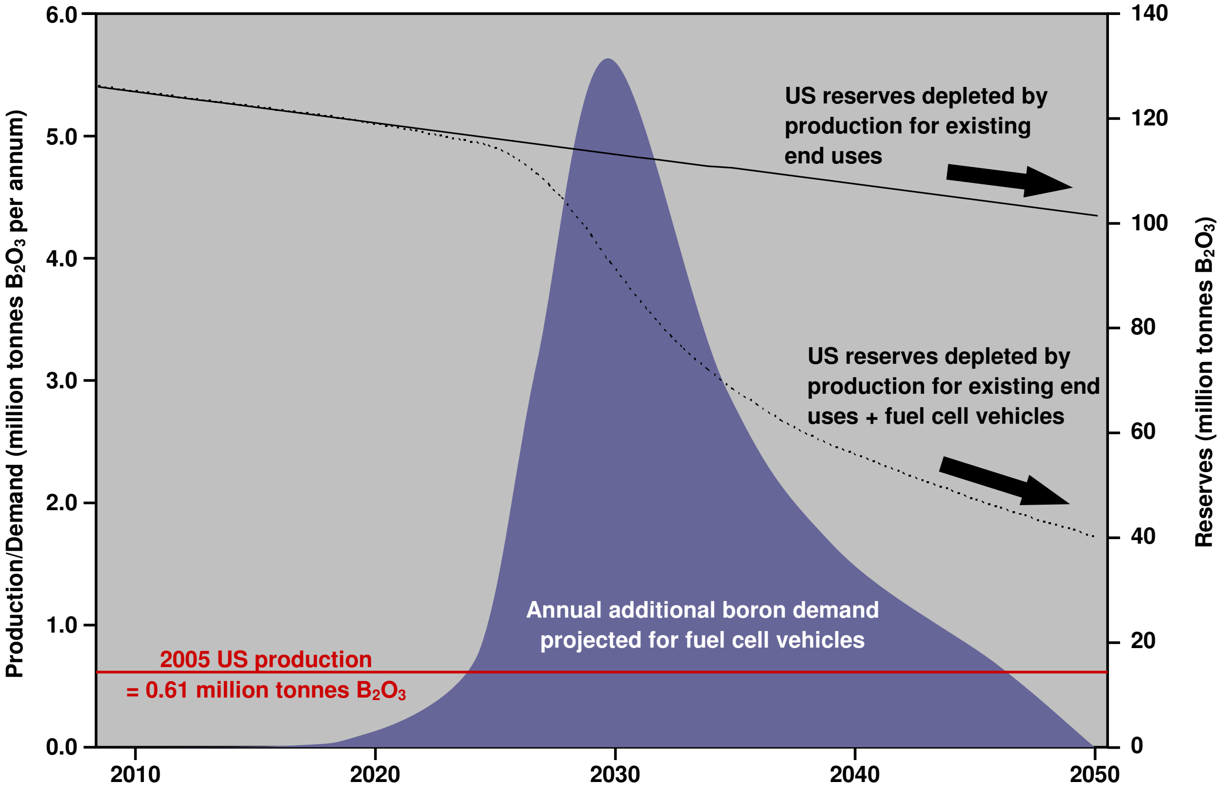


Figure 4: The effects of fuel cell vehicles on United States boron reserves and annual demand in comparison to current usage levels.

The demand peaks around 2030 as annual deployment of new fuel cell vehicles peaks in the deployment of new vehicles reaches its peak. At this peak an additional 5.5 million tonnes of boron (as B_2O_3) would be required to meet the demand from the fuel cell vehicles deployed in the U.S. that year. This additional demand would be 9 times the U.S. production level of 0.6 million tonnes supplying all other end uses. Global consumption of boron in these other end uses was 1.8 million tonnes B_2O_3 in 2005 (7).

The rise and duration of the additional demand are of concern. In the model, the demand from fuel cells in the United States becomes equal to that of all other end uses by 2025 rapidly growing from just 20% over all other end uses in 2020. The period of strong demand is also relatively brief, exceeding 50% of the maximum for approximately one decade.

While there appears to be sufficient boron in the ground, should the forecast growth follow this scenario, borate suppliers in the United States and rest of the world will face difficult decisions on how to manage a total U.S. annual demand that sharply rises by a factor of ten over a decade and then declines almost as rapidly.

As a point reference, in 2002 Turkey widely publicized a 100,000 tonnes per annum expansion to boric acid production capacity (7). The cost of this expansion was quoted as being $80 million. The projected capacity expansion required to meet the peak boric acid demand from fuel cell vehicles in just the United States would be 100 times this size.

References

(1) Acceptor numbers were determined by the method set forth in: a) Gutmann, V. *Coord. Chem. Rev.* **1976**, *18*, 225. b) Mayer, U.; Gutmann, V.; Gerger, W. *Monat. Chem.* **1975**, *106*, 1235.
(2) Greene, D.L.; Leiby, P.N.; Bowman, D. "Integrated Analysis of market Transformation Scenarios with HyTrans"; ORNL/TM-2007/094; Oak Ridge National Laboratory, Oak Ridge, TN, 2007.
(3) *Energy Technology Perspectives 2008 – Scenarios and Strategies to 2050*; International Energy Agency, Paris, France, 2008; Chap 15.
(4) *Principles of a Reserve/Resource Classification for Minerals*; U.S. Geological Survey Circular 831; U.S. Bureau of Mines and Geological Survey: Arlington, VA., 1980.
(5) Garret, D.E *Borates: Handbook of Deposits, Processing, Properties, and Use*; Academic Press: San Diego, CA, 1998; p 442.
(6) *The Economics of Boron*, 11th ed.; Roskill Information Services: London, England, 2006; Chap 1 & 2.
(7) *Mineral Commodities Summaries*; U.S. Geological Survey; U.S. Government Printing Office: Washington DC, 2003.

Publications:

1) This work resulted in a DOE record on boron resources published at the DOE website.

2) A paper summarizing results of Lewis acidity measurement for borate ester, to be published jointly by U.S. Borax Inc. and PNNL, is currently in preparation.

Networks/Collaborations Fostered: This project was highly collaborative and fostered continuing ties between U.S. Borax Inc. and the National Laboratories leading the CoE CHS, as well as the wider scientific community involved in hydrogen storage. As part of this project one member of the U.S. Borax R&D staff, Dr. Duane Wilson, worked as a visiting scientist at PNNL and performed project experiments together with PNNL partners.

Project personnel: Dr. Duane Wilson, hired in Q109, was committed full time to this project. Other project personnel included, Dr. David Schubert, who was project PI and also participated in hands-on laboratory work, Jonathan Owen, who did the borate resource analysis work, and Daniel Natan and Larry Harrower, who provided analytical and general laboratory support to the project.

Appendix

Experimental Borate Ester Synthesis:

General Procedures. All manipulations were performed in an inert atmosphere dry box under dry N_2 or under argon utilizing a standard Schlenk line unless otherwise stated. Halogenated phenols were obtained from Sigma-Aldrich and purified by vacuum sublimation and/or vacuum distillation. *Optibor*® boric acid manufactured by U.S. Borax Inc was used. All other reagents were purchased from commercial sources and used as received. Borate esters were synthesized by azeotropic distillation of a mixture of boric acid and the respective phenol in toluene.

tris(2-fluorophenyl)borate ester, 2-F: A three-necked, 250 mL round bottom flask was charged with boric acid (1.802 g, 29.15 mmol), 2-fluorophenol (10.082 g, 89.936 mmol, 3.086 equivalents) and toluene (60 mL) and fitted with a thermal couple and a Dean-Stark trap with a water cooled condenser. The mixture was warmed and held at reflux over night with stirring (magnetic) to collect 1.5 mL of water for removal in the trap (expected 1.6 mL). Toluene was distilled from the reaction mixture at room pressure. Excess phenol and the product were isolated from the reaction mixture by short path, vacuum distillation. The product, (2-$FC_6H_4O)_3B$, (5.657 g, 16.44 mmol, 56.4% yield) was collected at 165 ℃ as a clear colorless viscous liquid that solidified upon standing. The product was further purified by redistillation and hermetically sealed under vacuum in a flame-dried glass ampule.

All other borate esters were synthesized in a similar manor at 40-60% yields. The temperature of product collection by vacuum distillation varied: **3-F**, 128 °C; **4-F**, 131 °C; **2,3-F**, ~120 °C; **2,4-F**, 120 °C; **2,6-F**, ~150 °C; **3,4-F**, ~165 °C; **3,5-F**, ~155 °C; **3,4,5-F**, 130 °C; **2-Cl**, 172 °C; **3-Cl**, 174 °C; **4-Cl**, 185 °C; **2,3-Cl**, 210 °C; **2,4-Cl**, 225 °C; **2,6-Cl**, >285 °C; **3,4-Cl**, 225 °C; **3,5-Cl**, 246 °C; **2,4,6-Cl**, 240 °C; **4-Br**, 220 °C; **4-I**, 290 °C; **2-F,4-Br**, 230 °C; **2-F,4-Cl**, 170 °C; **2-F,6-Cl**, 180 °C; **3-F,4-Cl**, 193 °C.

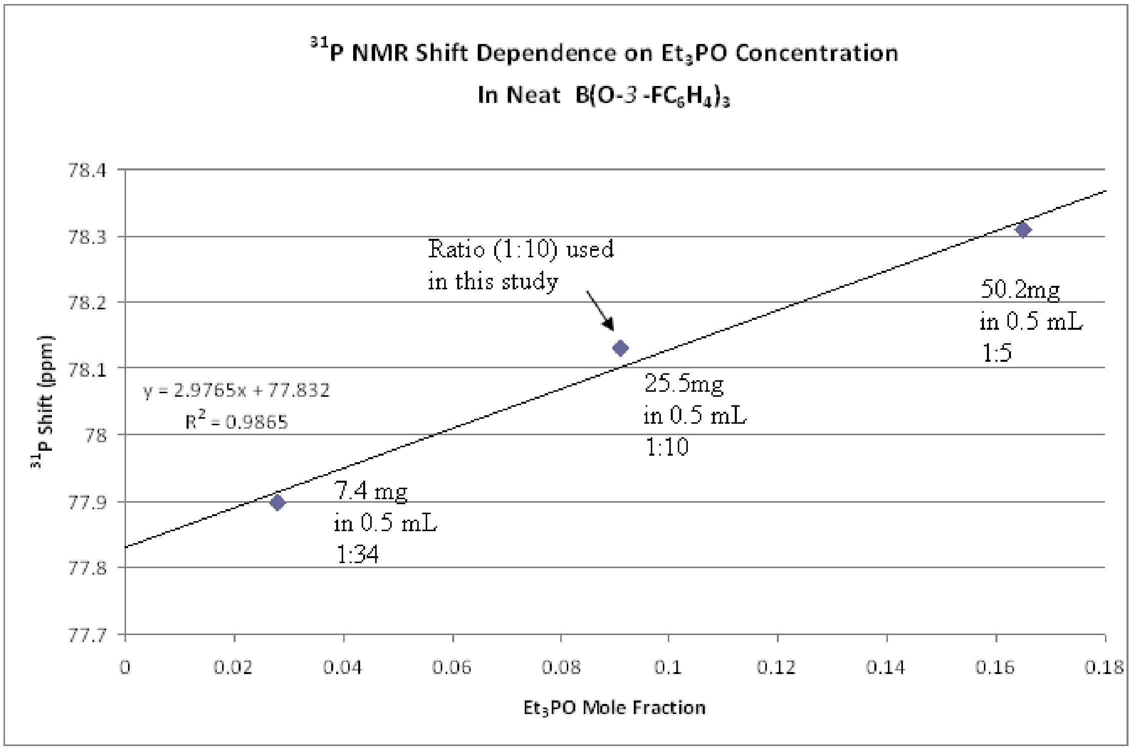
Triethyl phosphine oxide-borate ester adducts: Et_3PO-$B(OAr)_3$ for IR analysis and single crystal X-ray diffraction were prepared by dissolving 1:1 (0.05 mmol) mixtures in minimum $CHCl_3$ followed by slow evaporation of solvent at ~65 °C under dry N_2.

Acceptor Number Determinations:

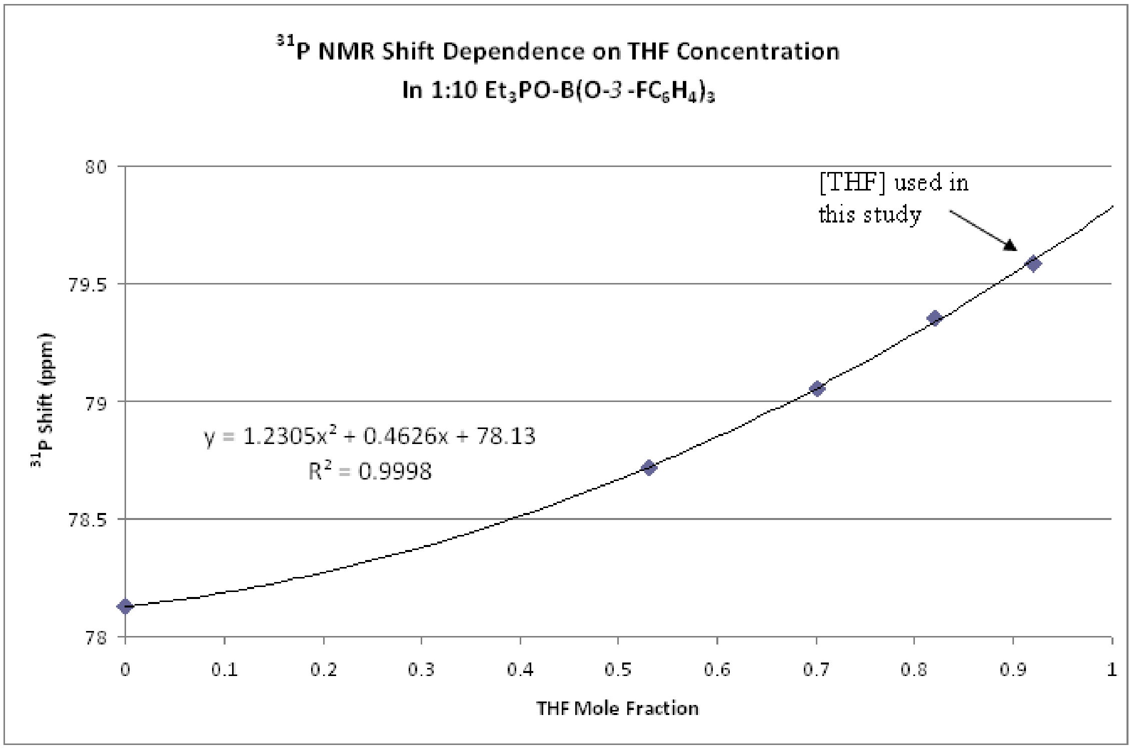
Experimental conditions: The raw δ ^{31}P shift of each Et_3PO-$B(OPh)_3$ adduct was measured from a solution of Et_3PO and $B(OPh)_3$ in THF (1.0:10.0:135 mole ratio) prepared by adding $B(OAr)_3$ (0.500 mmol), Et_3PO (6.7 mg, 0.050 mmol: via 50 µL solution of 0.671 g Et_3PO in 5.00 mL THF), and THF (0.500 mL, 0.443 g, 6.14 mmol, dried and degassed) to a J. Young NMR tube under dry nitrogen. The sealed tube was repeatedly inverted until all solids had dissolved. The ^{31}P NMR spectra were recorded within an hour.

δ ^{31}P corrections: Pure 3-F ester is a liquid at room temperature allowing for the preparation of a solution containing Et_3PO in neat ester. These solutions are ideal for determining solvent effects. Correction factors were determined for the Et_3PO–$B(O$-3-$FC_6H_4)_3$ ester adduct and applied to all other ester adducts under the assumption that they are similar.

Three solutions of Et_3PO in neat $B(O$-3-$FC_6H_4)_3$ ester (1:34, 1:10, and 1:5) were prepared for ^{31}P NMR analysis. The following plot shows the extrapolation to infinite dilution of Et_3PO, which represents the corrected δ ^{31}P value (77.83 ppm) for the $Et_3PO–B(O\text{-}3\text{-}FC_6H_4)_3$ ester adduct. The difference between this value and the value observed for the 1:10 ratio of Et_3PO: $B(O\text{-}3\text{-}FC_6H_4)_3$ ester (78.13 ppm) is the infinite dilution correction factor (-0.30).



Solvent effects were also analyzed. Solutions with Et_3PO and $B(O\text{-}3\text{-}FC_6H_4)_3$ ester in a 1:10 ratio were prepared with varying amounts of THF. A polynomial function fits the δ ^{31}P data nicely, as shown in the figure below. The difference in the δ ^{31}P value (79.59 ppm) for the THF concentration (0.92 THF mole fraction) typically used in this study and the δ ^{31}P value (78.13 ppm) without THF is the THF solvent correction factor (-1.46 ppm). For low solubility esters (such as 2,6-Cl), more THF was need to dissolve all solids. In this case, the polynomial function determined by this method was used to calculate a more accurate solvent correction factor.



Raw δ ^{31}P value obtained for each Et_3PO-$B(OAr)_3$ adduct was corrected with the infinite dilution correction factor and the THF solvent correction factor to obtain the corrected δ ^{31}P value, which was used to calculate acceptor numbers (AN).

Acceptor Number (AN) calculations: The raw δ ^{31}P value for Et_3PO-hexane was measured. The fit of δ ^{31}P data vs. Et_3PO concentration in hexane reported by Gutmann et al. (*Monatshefte fur Chemie* **1975**, 1235.) was used for the infinite dilution correction to obtain a corrected δ ^{31}P value of 42.47 ppm. All Et_3PO-$B(OAr)_3$ $\Delta\delta$ ^{31}P values were calculated from the difference of the corrected δ ^{31}P value for Et_3PO-$B(OAr)_3$ and the corrected δ ^{31}P value of Et_3PO-hexane (42.47 ppm). These $\Delta\delta$ ^{31}P values are plotted in Figure 1.

The δ ^{31}P value (85.45 ppm) for Et_3PO-$SbCl_5$ in dichloroethane reported by Gutmann et al. (*Monatshefte fur Chemie* **1975**, 1235.) was used to calculate the $\Delta\delta$ ^{31}P value (42.98 ppm) for Et_3PO-$SbCl_5$ in dichloroethane. With this value the AN for each ester can be calculated as follows:

$$AN = \Delta\delta\ ^{31}P \cdot (100/42.98)$$

The following table contains raw δ ^{31}P values, correction factors used, corrected δ ^{31}P values, $\Delta\delta$ ^{31}P values, and AN for each ester analyzed.

TABLE	δ ^{31}P ppm	Correction[a]	δ ^{31}P ppm	$\Delta\delta$ ^{31}P ppm	AN[b]
2,4,5-Cl	83.81	-1.76	82.05	39.58	92.1
per-F	83.78	-1.76	82.02	39.55	92.0
3,4,5-F	82.43	-1.76	80.67	38.20	88.9
2,3-Cl	82.20	-1.76	80.44	37.97	88.3
2,4-Cl	81.95	-1.76	80.19	37.72	87.8
3,5-Cl	81.7	-1.76	79.94	37.47	87.2
2,3-F	81.45	-1.76	79.69	37.22	86.6
2-F, 4-Br	81.34	-1.76	79.58	37.11	86.3
3,5-F	81.32	-1.76	79.56	37.09	86.3
2-F,4-Cl	81.26	-1.76	79.50	37.03	86.2
3-F, 4-Cl	81.25	-1.76	79.49	37.02	86.1
3,4-Cl	81.16	-1.76	79.40	36.93	85.9
2-Cl	80.44	-1.76	78.68	36.21	84.2
3,4-F	80.42	-1.76	78.66	36.19	84.2
2,4-F	80.39	-1.76	78.63	36.16	84.1
3-Cl	79.93	-1.76	78.17	35.70	83.1
2,6-Cl	79.95	-1.84	78.11	35.64	82.9
2-F	79.69	-1.76	77.93	35.46	82.5
3-F	79.59	-1.76	77.83	35.36	82.3
4-Br	79.29	-1.76	77.53	35.06	81.6
4-Cl	79.16	-1.76	77.40	34.93	81.3
4-I[c]	79.145	-1.76	77.38	34.91	81.2
2,4,6-Cl	78.91	-1.76	77.15	34.68	80.7
2,6-F	78.402	-1.76	76.64	34.17	79.5
4-F	78.26	-1.76	76.50	34.03	79.2
2-F, 6-Cl	77.82	-1.76	76.06	33.59	78.2
B(OPh)$_3$[c]	77.32	-1.76	75.56	33.09	77.0

[a] Correction factors determined for the 3-F ester were applied to the other esters under the assumption that they are similar.

[b] AN = (δ^{31}*P(corrected)* – 42.47)·{100/(85.45-42.47)}

[c] Multiple determinations were averaged.

Spent Ammonia Borane Fuel production and analysis

Spent Fuel Synthesis. Spent fuel samples were generated by thermo dehydrogenation of ammonia borane (Aviabor) at 150-160 °C under inert atmospheres (Ar or He) in the absence of oxygen. Three classes of spent fuel were produced by varying the atmospheric conditions for comparison with commercial polyborazylene (Boron Technologies). These classes are referred to as hydrated, anhydrous, and closed system spent fuel.

Hydrated Spent Fuel: The apparatus used for the production of hydrated spent fuel was a four-necked 500 mL round bottom flask fitted with a screw feeder, blowout tube, mechanical stirrer, and thermal couple. The screw feeder was fitted with a ramrod and a valve. Any material falling from the screw feeder that became stuck was force into the flask with the ramrod. The valve was opened to purge the setup with Ar prior to the experiment and closed during the reaction. The blowout tube was fabricated from 22 mm Pyrex tubing into an "S"-shape with a male 24/40 ground glass joint. The open end of the blowout tube was submerged into water to permit the collection and measurement of total evolved gas. No check valve was implemented to prevent the back flow of water vapor. The blowout tube was toggled between two inverted 2 L volumetric flasks each fitted with a large funnel. One of the 2 L volumetric flasks collected the evolved gasses while the other was measured and refilled with water. The mechanical stirrer effectively works the gas out of the reacting material and smears the spent fuel to the bottom of the flask to make room for more material. The initial and final reaction temperatures are determined with the retractable thermal couple, which also is used to occasionally knock spent fuel that tends to buildup on top of the stirring paddle.

In a typical trial, the screw feeder was charged with ammonia borane and the reaction apparatus was purged with Ar for 3-12 h. After closing the purge valve, the reaction flask was submerged in a silicon oil bath warmed at the appropriate temperature to produce the desired reaction temperature within the flask. The blowout tube was toggled into position for gas measurement after the flask reached the reaction temperature. Ammonia borane was screw feed into the reaction flask with stirring (mechanical). After complete addition of ammonia borane, the resulting spent fuel was kept at the reaction temperature for 3-12 h. The flask was then cooled to room temperature under a slow Ar purge. The spent fuel was measured and collected in air.

Anhydrous Spent Fuel: Two lots of anhydrous spent fuel were produced using modified versions of the apparatus used for the production of hydrated spent fuel. The modifications implemented for each are described below.

For one experiment, the blowout tube was replaced with a water cooled condenser (20 mm inner diameter) connected to a mineral oil bubbler to prevent the back flow of water vapor. The oil bubbler exhausted into the inverted water burette gas measuring setup as described for the hydrated spent fuel production. The anhydrous spent fuel was measured and collected under dry Ar.

In a second experiment, the valve attached to the screw feeder was replaced with a liquid N_2 trap attached to a mineral oil bubbler to prevent the back flow of water vapor. The oil bubbler exhausted into the inverted water burette gas measuring setup. The original blowout tube was replaced with a valve for He purge. While a helium atmosphere was used for this experiment, the spent fuel was measured and collected under dry Ar.

Elemental Analysis. Detailed elemental analyses are presented in the table below.
Boron analyses were preformed on samples (0.1 g, measured to 0.001 g under dry argon) dissolved in 10% $HCl_{(aq.)}$ with an ICP. Each solution was measured in triplicate. A set of three solutions were made for each sample resulting in nine determinations per sample. The average and standard deviation are reported.

Nitrogen analyses were preformed on the same solutions as prepared for boron analyses described above. A 250 mL round bottom flask was charged with the sample solution (100g), phenolphthalein, and a stir bar. The flask was fitted with a rubber septum and a 70 degree elbow connected to a water-cooled condenser. The condenser was fitted with an 8 mm glass tube with the tip submerged in a collection flask containing 20 mL of aqueous 4 % boric acid cooled via ice bath. Sodium hydroxide (6 M) was added to the sample solution via syringe until the phenolphthalein (red) color change, plus an additional 1 mL. The sample solution was distilled until the collection flask contained 75 mL, which was then titrated with standardized 0.05 N $H_2SO_{4(aq)}$ solution to the equivalence point at a pH of 4.8.

Total hydrogen analyses were determined externally by Prevalere Life Sciences, Inc. (Whitesboro, NY) via combustion analysis method. Hydride analyses were determined for each sample by adding 30 mL of 10% $HCl_{(aq.)}$ to the samples (0.1 g, measured to 0.001 g under dry argon) and measuring gas formation with an inverted burette. Protonic hydrogen content was calculated by the difference of the total hydrogen and hydridic hydrogen values.

A few key findings to note: The wet atmosphere increases the overall nitrogen (and boron) recovery even though it provides an additional pathway for nitrogen loss. The percent nitrogen in polyborazylene is higher than that found for any spent fuel sample.

Nitrogen:Boron ratios in the spent fuel from the screw feed trials are typically higher than those from the single pot trials. The lost material in the screw feed trials is likely more rich in boranes than that from the single pot trials, which are likely more rich in borazine. This difference is possibly due to initial reaction temperature/heating rate of AB.

Spent Fuel Production Conditions with Spent Fuel, Polyborazylene, and Ammonia Borane Analyses and Elemental Recovery

Atmosphere	AB Delivery Method	Initial (°C)	Final (°C)	Analysis								
					AB (g)	SF (g)	N (%)	H^+ (%)[a]	B (%)	H^- (%)	O (%)[b]	Formula
Wet Ar	Screw Feeder	150	150	SF Composition			45.5(239)	4.07	36.29(34)	1.88(5)	12.26	$N_{0.97}H_{1.20}BH_{0.56}O_{0.23}$
				Recovery	2.05	1.30	63.6	26.3	65.7	12.2		
Wet Ar	Screw Feeder	160	160	SF Composition			49.78(28)	2.82	36.03(48)	1.45(2)	9.92	$N_{1.07}H_{0.84}BH_{0.43}O_{0.19}$
				Recovery	10.17	6.14	66.2	17.4	62.1	8.9		
Anhydrous Ar	Screw Feeder	160	160	SF Composition			52.53(36)	3.03	37.30(26)	1.43(2)	5.72	$N_{1.09}H_{0.87}BH_{0.41}O_{0.10}$
				Recovery	10.20	5.11	58.0	15.5	53.3	7.3		
Anhydrous He	Screw Feeder	160	160	SF Composition			53.52(94)	2.90	36.96(79)	1.58(14)	5.04	$N_{1.12}H_{0.84}BH_{0.46}O_{0.092}$
				Recovery	9.77	5.30	64.0	16.1	57.2	8.7		
Anhydrous N_2	Single Pot	20	150	SF Composition			51.35(45)	3.67	39.00(64)	1.55	4.43	$N_{1.02}H_{1.01}BH_{0.43}O_{0.077}$
				Recovery	2.034	0.815	45.3	15.0	44.6	6.3		
Anhydrous N_2	Single Pot	20	150	SF Composition			51.94(67)	2.77	38.94(129)	1.36	5.00	$N_{1.03}H_{0.76}BH_{0.37}O_{0.087}$
Closed System				Recovery	2.031	0.776	43.7	10.8	42.5	5.3		
				PB Theory			53.54	2.57	41.32	2.57	0.00	$NH_{0.67}BH_{0.67}$
				PB[c] Found			56.06(65)	2.77	39.90(60)	1.471(1)	-0.20	$N_{1.08}H_{0.74}BH_{0.40}$
				AB Theory			45.38	9.80	35.03	9.80	0.00	NBH_6
				AB[d] Found			45.23		35.12	19.85(24)[e]	-0.20	$N_{0.99}BH_{6.11}$

a Total Hydrogen Less Hydride

b Remaining Percentage

c Boron Technologies Inc.

d Aviabor

e Total Hydrogen Value