

BORATE CHEMISTRY IN THE TRANSFORMATION OF BIOMASS

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Introduction

Agricultural and forestry waste and non-food crops represent enormous resources for the production of energy and chemical feedstocks. In contrast to fossil hydrocarbon resources, plant derived biomass is renewable and can be a carbon neutral source of energy and other useful products. However, development of efficient and economical methods to convert biomass into valuable products requires new chemistries (1).

Important categories of biomass include lignocellulose (40-80% cellulose, 15-30% hemicellulose, 10-25% lignin), triglycerides (fats and oils), sugars, and terpenes. Lignocellulose comprise about 95% of available plant biomass and can be broken down into lignin, hemicellulose and cellulose. The latter are composed of glucose units, the most abundant building block in nature. Each of these components can be transformed into valuable biofuels, chemical feedstocks and agricultural products.

Pathways to convert biomass into useful products can be divided broadly into three categories: hydrolysis, pyrolysis and biochemical processes. Borate chemistry can play useful roles in each of these pathways. They are usefully employed in to catalyze and promote isomerizations and dehydrations, direct reaction pathways, catalyze deoxygenation in pyrolysis reactions, and provide antioxidation effects. This paper briefly reviews some of the recent literature relevant to the use of borates in the transformation of plant biomass.

Interactions of Borate with Biological Substrates

Boron is ubiquitous in both the hydro- and biospheres, where it is mostly present as naturally occurring boric acid. It is found at low levels in all natural waters and soils and is roughly the 10th most abundant element in sea water after hydrogen and oxygen. In recent years an increasing number of roles played by boron in diverse and vital life processes has emerged. These include essential roles in quorum sensing and iron uptake in marine bacteria, regulation of enzymes, nitrogen fixation and plant cell walls. Frogs and fish cannot develop properly without sufficient amounts of boron (2, 3). The many biological roles of boron appear to be based largely on interactions of boron with hydroxyl groups, and especially with diols, which are abundantly present in biomass.

Borate interacts with a wide range of compounds having 1,2- or 1,3-diol functionalities of appropriate conformation to form cyclic esters. These esters are kinetically stabilized and can exert strong structure and reaction directing influences. It can be noted that facile formation of these cyclic esters involves an interplay between three and four coordinate boron and exhibits a direct pH dependence (4).

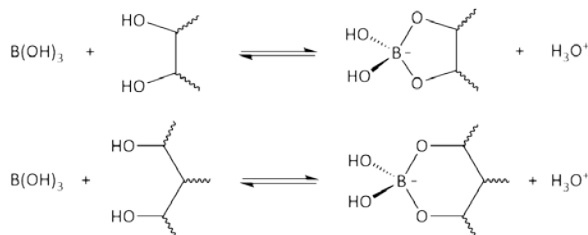


Figure 1. pH dependent borate interactions with 1,2- and 1,3-diols.

Boron and plants. As illustrated in Figure 2, an essential role played by boron in all plants involves ester crosslinking of apiosyl moieties of the complex carbohydrate rhamnogalacturonan-II (RG-II) in plant cell walls, which is critical to plant growth and functioning (5). Boron likely plays other important roles in both plants and animals involving similar interaction with diol functionalities of other biologically active chemical species, such as ribose (6).

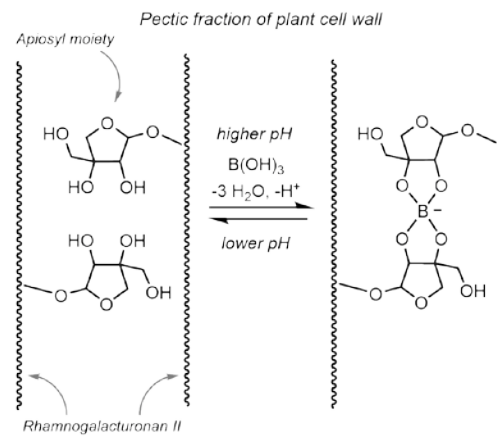


Figure 2. Borate crosslinking of RG-II in the plant cell walls is critical to plant functioning (5).

Inadequate boron in soils is a prevalent micronutrient deficiency problem that constrains agricultural production in many parts of the world (7). Consequently, supplementation of crops with borates is common agricultural practice to boost crop yields and enhance their quality. Borate micronutrients are also applied in forestry. Thus, boron plays a fundamental role in the growth of plant biomass and may be important for efficient production of crops grown specifically for their value as sources of energy and other useful products.

Utilization of Sugars

Borates interact strongly with many carbohydrates and catalyze many reactions including isomerizations and esterifications. They catalyze isomerizations of sugars relevant to biomass utilization and also complex with sugars to shift reaction equilibria in favor of desired product or intermediates.

5-HMF. Hydrolysis of highly bioavailable cellulose leads to glucose. Glucose can be fermented to provide ethanol or converted into other useful products. Important among these products is 5-hydroxyfurfural (5-HMF), which forms in the dehydration of fructose resulting from isomerization of cellulose-derived glucose, shown in Figure 3. 5-HMF is a key intermediate to fuels, solvents, polymer precursors and many other useful compounds (8).

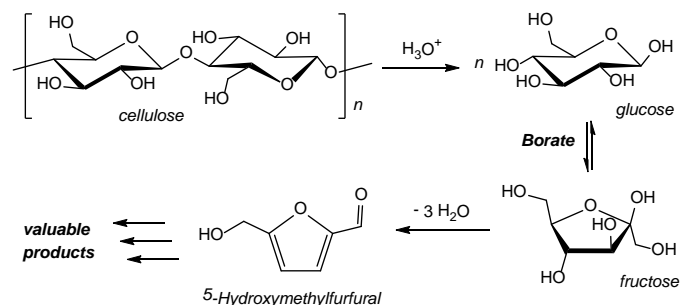


Figure 3. Production of 5-HMF by dehydration of fructose formed by borate catalyzed isomerization of cellulose-derived glucose.

Boric acid synergy with salts in catalytic dehydration of hexoses to 5-HMF. Riisager and co-workers reported that boric acid in the presence of metal salts is an efficient catalyst for the dehydration of fructose to 5-HMF (9). They reported that a 60% yield of 5-HMF at 92% fructose conversion was accomplished using a 30% aqueous fructose solution with 100 g·L⁻¹ B(OH)₃ and 50 g·L⁻¹ NaCl in the aqueous phase and methyl-isobutylketone as the extracting solvent. Dehydration of glucose resulted in a yield of 14% 5-HMF at 41% glucose conversion after 5 h under similar conditions. Catalysis was attributed to the strong complexation between the boron and the hexoses. They described their results as competitive with currently reported aqueous hexose to 5-HMF dehydration systems. Considering the low cost, safety and low corrosivity of boric acid compared to other homogeneous catalysts used for this dehydration process, such as H₂SO₄ and HCl, the boric acid-salt mixture has attractive features for this process.

Boric acid promoted dehydration of glucose to 5-HMF. Dehydration of glucose and other hexoses to 5-HMF in imidazolium-based ionic liquids in the presence of boric acid was also described (10). Conversion of glucose to 5-HMF in 42% yield and of sucrose to 5-HMF in 66% yield was reported. This work provides further evidence that borates promote this reaction by catalyzing the isomerization of glucose to fructose, which then undergoes dehydration. These workers concluded that borate provides an attractive alternative to metal-catalyzed systems for the efficient formation of 5-HMF from biorenewable sources. It is likely that borate may also be usefully employed in combination with other catalyst systems.

A highly selective one-pot conversion of carbohydrates to 5-HMF was reported (11). This work involved optimizing a borate-phosphate buffer system to efficiently match glucose isomerization and dehydration processes with key parameters being pH and borate:glucose mole ratio.

Antioxidation and Lignin Utilization

Lignin, a major component of woody biomass, makes up a large portion of the biomass on earth and contains ca. 40% of the energy. Lignin is a complex high molecular weight substance that presents challenges for processing into useful chemical products. One problem presented by lignin is the ease of oxidation of its phenolic breakdown products, often resulting in intractable oligomeric byproducts (12).

Lignin
from
Biomass

Fuels and solvents
Fossil-fuel-like aromatics (BTX)
Ethyl levulinate
Methyltetrahydrofuran
Valerolactone

Polymer Precursors
Polyurethanes
Thermoplastics

Fine Chemicals
Benzoic acids
Catechols
Cinnamic acids
Substituted phenols
Vanillin, vanillic acid

Additives
Paints/Coatings
Adhesives/Sealants
Surfactants

Borates as antioxidants. Borate has long been known to exhibit antioxidant properties. For example, borate was known since at least the 1920s to protect reducing sugars from oxidation, observed in classical tests using Fehling's or Benedict's reagents (Cu²⁺ → Cu⁰ driven oxidation) (13). Boric acid is also utilized to control the extent of oxidation of cyclohexane in the commercial production of cyclohexanol and cyclohexanone, which are precursors to caprolactam, polyamides and other products.

Catalytic lignin depolymerization with borate. The primary products of base-catalyzed lignin hydrolysis are phenolic monomers. However, unwanted oligomers are generally obtained as secondary products. Oligomerization of the reactive primary phenolic products limits the amount of useful low molecular weight compounds obtained in the hydrolysate product oil. Developing methods to inhibit oligomerization and polymerization reactions that take place during base-catalyzed hydrothermal lignin depolymerization are important to the optimization of useful product yields.

In order to increase oil yields above 20–25 wt% it is necessary to protect the highly reactive substituted phenols from further reaction. It was shown that the presence of borate during base-catalyzed lignin depolymerization greatly enhances the yield of monomeric products and also acts as a catalyst for hydrolysis of acidic ether groups (14). It was reported that the use of borate allowed 85 wt% of the lignin to be utilized in a single reaction step.

Boric acid acts as a protecting agent by forming esters with phenolic hydroxyl groups, thereby reducing oligomerization and polymerization reactions during hydrothermal depolymerization of lignin.

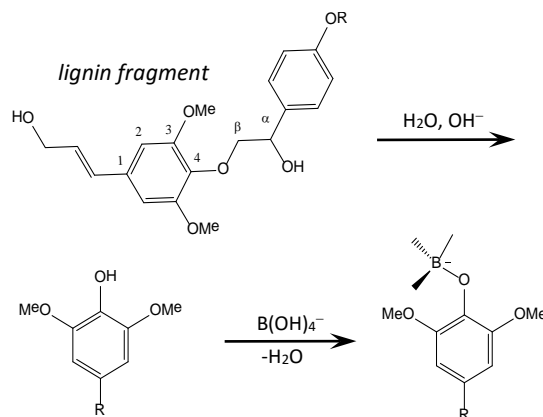
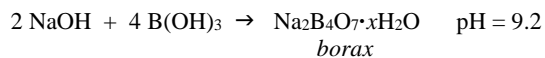
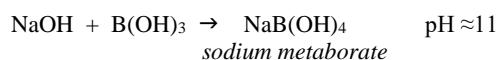


Figure 4. Borate antioxidation of phenolic monomers derived from lignin depolymerization mediated by borate ester complexes (14).

In this study boric acid was added to the base-catalyzed lignin depolymerization reactions, but other borate reagents should be preferable. It can be noted that borax pentahydrate and borax decahydrate, Na₂B₄O₇·xH₂O (x = 5, 10) are equivalent to boric acid that has been half neutralized to B(OH)₄⁻ by sodium hydroxide:



Also, the commercial sodium metaborates, NaB(OH)₄ and NaB(OH)₄·2H₂O (often written as NaBO₂·2H₂O and NaBO₂·4H₂O), are equivalent to boric acid that has been fully neutralized by sodium hydroxide to the conjugate base B(OH)₄⁻:



Borax pentahydrate, borax decahydrate and the sodium metaborate hydrates and all readily available commercial products that are produced on large industrial scale. Since the use of borate in the protection of reactive phenolic compounds involves the use borate in alkaline solution, more alkaline borate reagents should be more practical and economical choices. Borax pentahydrate, in particular, is often the most economical borate reagent since it is produced in industrial quantities exceeding 10⁶ metric tons per year (4).

Pyrolysis

Pyrolysis is an efficient means of utilizing biomass. The pyrolysis process involves heating biomass feedstocks in the absence of air to form volatile and solid products. The condensable volatile products are referred to as bio-oil and a non-condensable syngas fraction is also obtained (15).

When biomass is heated rapidly and gaseous pyrolysis products are removed quickly bio-oils are obtained in up to 80% yield based on dry feed with the remainder being biochar and syngas. Bio-oils can be further refined into high value transportation fuels. Heating biomass feedstock slowly and allowing the volatile pyrolysis products to remain in contact with the solids produces larger amounts of biochar.

Biochar. Biochar is a charcoal-like carbonaceous substance produced as a byproduct of bio-oil production and the primary product of slow lignocellulose pyrolysis. Its utilization dates to the pre-Columbian era where it was applied to crops by Amazonian tribes to amend soils. It is thought to improve soil fertility and boost productivity by improving soil chemistry, facilitating movement of plant-growth promoting bacteria, and influencing water flow through dense or sandy soils (16). Biochar is expected to play an increasingly important role in modern agriculture.

Carbon Sequestration: The carbon richness of soils is critical to agricultural production. Plants absorb CO₂ through photosynthesis and incorporate carbon in biomass. Conventional practice, such as tillage and composting, returns carbon to soils, but biodegradation of agro-waste also results in massive CO₂ generation and loss of carbon to the atmosphere instead of incorporation into soils. Agro-waste is also burnt releasing large amounts of carbon back into the atmosphere. This CO₂ cycling can be greatly moderated when carbon from biomass is stored in soils in the form of biochar (17).

Pollution Mitigation: With their ability to bind heavy metals, biochars are increasingly used to clean up polluted soils and waters. Recent studies demonstrate the benefits of biochar to remediate mine sites and also their value in cleaning fluids used in oil and gas production (18).

Soil boron levels that are suboptimal for important food crops is a serious micronutrient deficiency problem facing global agriculture (7). As a result, application of borates is common agricultural practice in many regions of the world where soil boron levels are inadequate. Street and co-workers described positive effects on bioavailability of micronutrients, including boron, from biochar (19). These considerations suggest that boron-containing biochars resulting as byproducts of borate catalyzed pyrolysis of lignocellulose, described below, could be valuable agricultural products. The potential for excessive boron application must also be considered in the proper use of such products.

Borates in the production of bio-oil. Pyrolysis of biomass leads to solid, liquid and gaseous products: biochar, bio-oil and syngas. A major problem for biomass pyrolysis is oxygen removal, since the energy value of bio-oil is reduced by retention of oxygen-containing chemical species.

Borates have been used for many years as highly effective fire retardants for cellulosic and lignocellulosic materials. Experience with this application teaches that borates exert a strong influence over

pyrolytic processes involving these materials and can dramatically alter the nature of volatile pyrolysis products. In addition to retarding flaming and smoldering combustion, borates act as efficient char promoters and smoke suppressants and greatly influence the composition of gaseous pyrolysis products.

Borate catalyzed production of deoxygenated bio-oil. Palm oil production results in enormous quantities of waste biomass presenting a current environmental problem as well as a huge opportunity for biomass utilization. It was reported that boric oxide is a useful catalyst in the fast pyrolysis of oil palm biomass (20). In this study, oil palm empty fruit bunches and fronds were pyrolyzed at in a fixed-bed reactor operating at 400 °C. Boric oxide was found to selectively reduce 50–80% of hydroxy and methoxy groups in both water soluble and insoluble fractions of the resulting bio-oil. An increase in water and biochar yield was also noted, suggesting that pyrolysis using boric oxide enhances the cleavage of C–O bonds in biomass polymers and also promotes the retention of inherent oxygen in the biochar solid product. This allows organic compounds with less oxygen substitution to volatilize and condense as bio-oil. These findings are consistent with observations pertaining to the extensive use of borates as fire retardants for cellulosic and related materials. Further studies should include combinations of boric oxide and other borates with additional catalyst systems.

It can be noted that boron micronutrients products are extensively used today in oil palm production to improve crop yields. Thus, boron-containing biochar byproducts of borate catalyzed pyrolysis of waste biomass may have value in oil palm cultivation.

Borates in Enzymatic and Microbial Reactions

Borate interacts with enzyme substrates in ways that are useful to provide high selectivity for desired products. In addition, borates can interact directly with enzymes. Borates are extensively used today on large commercial scale to stabilize enzymes; and direct interactions between borates and many enzymes can be used to selectively regulate enzyme activity.

Simultaneous isomerization and fermentation of xylose. Lignocellulose derived glucose is converted to ethanol using fermentation by yeasts, but xylose obtained by hydrolysis of hemicellulose is not fermentable by these yeasts. Xylose fermentation by native yeasts is achievable only after isomerization of xylose to xylulose. However, xylose isomerase isomerizes optimally at pH 7–8, whereas subsequent fermentation of xylulose to ethanol requires pH 4–5. Rao and co-workers reported a method to efficiently isomerize xylose to xylulose under conditions suitable for the fermentation using immobilized enzyme capable of sustaining two different pH microenvironments (21). To help shift the equilibrium in favor of xylulose, sodium tetraborate (borax) was added to isomerization solutions. Borate-xylulose binding effectively reduces xylulose concentration to shift the equilibrium in favor of increase xylose isomerization. This strategy resulted in xylose to xylulose conversion as high as 86%. These results have significant potential for increasing the yield of ethanol from biomass derived xylose.

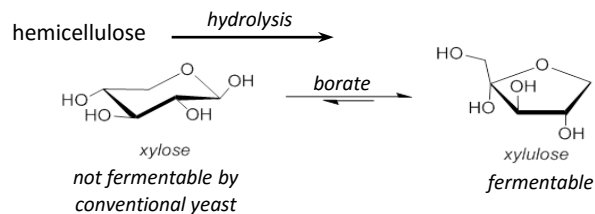


Figure 5. Borate catalyzed equilibrium shift between xylose and xylulose.

Conversion shift of for enzyme-catalyzed epimerization. Improved conversion yields of *d*-psicose from *d*-fructose using *d*-psicose 3-epimerase from *A. tumefaciens* (*Rhizobium radiobacter*) in the presence of borate was reported (22). Formation of psicose-borate complex resulted from a higher borate the binding affinity for psicose vs. fructose. The psicose-borate complex is not thought to participate directly in the conversion reaction, but instead shifts equilibrium resulting in higher fructose to psicose conversion. Maximum yield of psicose with borate was ~2X that obtained without borate and occurred optimally at a 0.6 molar ratio of borate to fructose. Above this ratio the yield decreased because the amount of available fructose was removed through formation of fructose-borate complex.

The presence of borate can dramatically influence enzymatic and microbially mediated reactions in other ways. Although not directly related to biomass transformation, the following example serves to illustrate how borate can be used to direct bio-catalyzed reactions.

Although specifically related to biomass or energy applications, the following example illustrates the dramatic effect that borate can have on reaction selectivity. Certain fungi promote pyridoxine (vitamin B₆) glucosylation to give a mixture of 4' and 5'-glucosides. Pyridoxine 5'- α -D-glucoside has greater nutritional importance and is the preferred product. However, a mixture of the two products is obtained. Wada and co-workers showed that the presence of borate greatly increases the selectivity for glucosylation at the pyridoxine 5' position, as illustrated in Figure 6 (23).

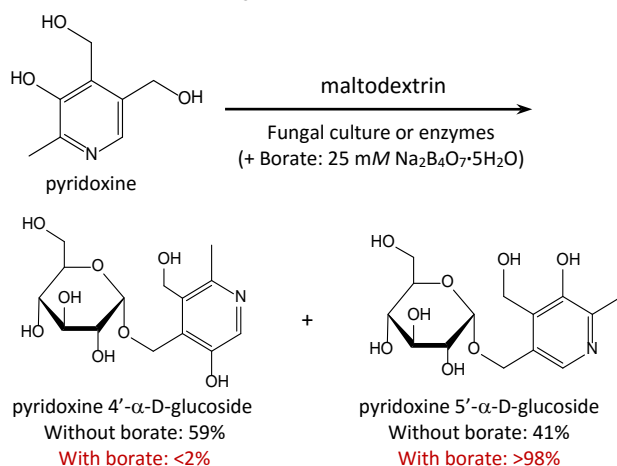


Figure 6. Borate induced selectivity in pyridoxine glucosylation.

Increased selectivity results from formation of cyclic borate ester complexes with pyridoxine. Because of ring strain, borate forms only five- and six-member ring complexes with 1,2- and 1,3-diols, respectively, and does not complex with the 1,4-diol. In this case, borate forms six-membered ring complexes, shown in Figure 7, with the 1,3-diol functionality of pyridoxine, leaving the hydroxymethyl group at the pyridoxine 5' position free to esterify.

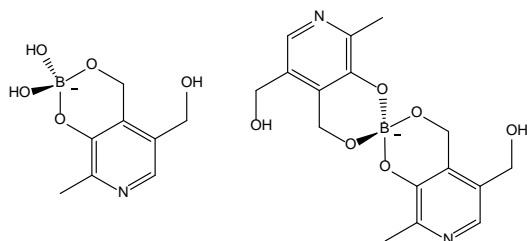


Figure 7. Borate ester complexes involved in reaction directing.

Ionic Liquids and Utilization of Glycerol Byproduct from Biodiesel Production

Production of biodiesel involves transesterification of triglycerides, resulting in substantial quantities of glycerol byproduct. Chiappe and co-workers described the synthesis and characterization of a series of alkali metal bis(glycerol)borate ionic liquids, shown in Figure 8 (24).

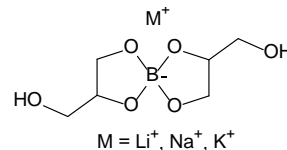


Figure 8. Alkali metal bis(glycerol)borates.

It further demonstrated that these alkali metal bis(glycerol)borate ionic liquids are good reusable solvents to carry out synthetic reactions. In particular, they reported results of carbonyl condensation reactions between 2-aminobenzaldehyde and a range of aldehydes and ketones carried out in these IL solvents (25). These reactions went to completion in short times with good to excellent yields. They also showed that these reaction media could be reused repeatedly without loss of efficiency.

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