

Chapter 19

Opportunities with Wood Dissolved in Ionic Liquids

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Biomass represents an abundant carbon-neutral renewable resource for the production of bioenergy and biomaterials. Shifting society's dependence away from petroleum to renewable biomass resources is generally regarded as an important contributor to building up a sustainable society and effective management of greenhouse gas emissions. An ionic liquids-based processing platform for the efficient transformation of lignocellulosic materials into new materials and value-added chemicals has been developed. We have demonstrated that woody lignocellulosic materials are soluble in certain ionic liquids. The first preparation of homogenous wood solutions not only extends the utilization of lignocellulosic materials from heterogenous to homogenous processing conditions, but also creates a variety of new strategies for converting our abundant lignocellulosic biomass to novel value-added bioproducts. This chapter describes some applications under development, aimed at converting woody lignocellulose into new materials, chemicals and energy using ionic liquids as a processing platform.

1. Introduction

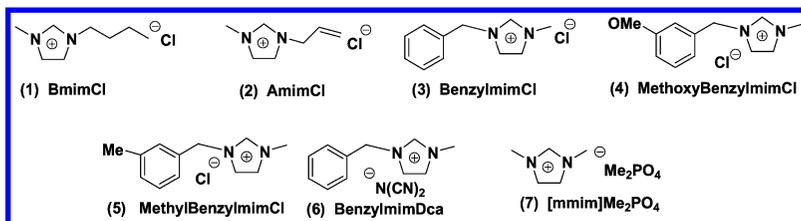
Over the past several decades the contributions of the modern fossil-based energy and chemical industries, while they have enriched our way of life, have placed our environment under immense stress. One of those most noticeable issues is global warming, caused by our over dependence on non-renewable fossil-based resources. From a sustainability point of view, the renewable carbon inherent in biomass is vast, making biomass an attractive alternative as a new carbon source. Shifting society's dependence away from fossil-based energy resources to renewable alternatives, such as biomass, can be regarded as an important contribution towards the establishment of favorable conditions for environmentally sustainable economic solutions (1–3).

It is estimated that by 2025, up to 30% of raw materials for the chemical industry will be produced from renewable sources. To achieve this goal, partially or completely, will require a major re-adjustment of the overall techno-economic approach. This will require entirely new concepts and approaches to be developed if these novel process technologies are to emerge. B. Kamm has provided an overview of these new technologies. As the author points out, the production of value added chemicals from lignocellulosic materials based on environmentally friendlier effective biorefinery platforms will be a step in the right direction (4).

Desirable biorefinery operations will first extract high-value chemicals already present in biomass, and then the biorefinery will focus on processing plant polysaccharides and lignin into feedstocks for bio-derived materials and value-added chemicals (5). This requires the development of innovative process technologies, separation and depolymerization processes, as well as catalytic systems. Supercritical CO₂, near critical water, gas-expanded liquids and ionic liquids (ILs) are well suited to meet these challenges (6–8). These tunable solvents offer distinct green chemistry processing advantages that could be exploited toward the processing of renewable bioresources (9). Among these new technologies, IL-based platforms involve relatively new technology concepts. Research into this field is currently rather extensive as ILs show extremely low vapor pressures, effectively eliminating a major pathway for environmental releases and contamination. Furthermore, some ILs have been shown to possess a strong hydrogen bond-destroying ability, thus imparting good solubility to biopolymers, such as cellulose (10), silk fibroin (11), wool keratin (12), chitin and chitosan (13), etc. Thorough chemical modification of biopolymers can thus be carried out, and after reconstitution, biodegradable composites and advanced materials have been reported (14, 23, 30).

The ultimate goal in our laboratories is to develop new strategies for the transformation of the a variety of lignocellulosic resources into value-added materials and chemicals based on environmentally sustainable and economically viable processing platforms, with ILs' playing a central role in these considerations. A thorough understanding of the way complete wood dissolution occurring in ILs provides a variety of options for the development of novel homogenous processing platforms aiming at the efficient utilization of lignocellulosic resources.

Scheme 1. Structures and Abbreviations of the Examined Ionic Liquids



2. Dissolution of Wood in Ionic liquids

Wood is among the most abundant lignocellulosic resources on the planet. The main components of wood are cellulose (~30% to 50%), lignin (~15% to 30%), hemicellulose (~25% to 30%), and extractives. In general, it is thought that it is practically impossible to dissolve wood in its native form, because the three-dimensional cross-linked lignin network binds the whole wood architecture together. The insolubility of wood in common solvents has severely hampered the development of new processes for its efficient utilization. Therefore, the development of new homogenous processing technologies aiming at wood utilization offer tremendous potential (15–18, 22, 24, 56).

2.1. Solubility-Structure Relationships of Ionic Liquids & Lignocellulosic Materials

In 2007 (18), we reported the details of the dissolution of wood-based lignocellulosic materials and defined the various variables that determine its solubilization efficiency in ILs. A series of imidazolium-based ILs were used in this study, to investigate the relationship between wood solubility and ILs structure (Scheme 1).

Complete wood dissolution [up to 8% (w/w)] can be carried out by simple mixing of dried wood sawdust samples with the ILs (AmimCl or BmimCl) and stirring the mixtures mechanically at 80–120 °C. We found that the solubility of wood-based lignocellulosic material is related to several key factors, such as ILs' structure, size of lignocellulosic materials, water content of both the ILs and lignocellulosic materials, etc. In ILs, both the cation and anion of the salt play a crucial role in the dissolution of wood. During our work we found that AmimCl, and BmimCl showed good ability to dissolve wood. Although the appearance of BmimCl and AmimCl wood solutions were not fully clear, the introduction of a phenyl group into ionic liquids ([Bzylmim]Cl) can result in a completely transparent, amber colored but viscous solution. We conjectured that although ILs have a more complex solvent behavior compared with traditional solvents, such as dispersion, π - π , n- π , hydrogen bonding, dipolar and ionic/charge-charge, In our case, conceivably the active chloride ions in the BmimCl would disrupt the hydrogen bonding interactions present in wood, allowing it to diffuse into the

interior of the wood resulting in a viscous but cloudy solution. However, both BmimCl and AmimCl still can not effectively and fully interact and solvate the aromatic character of lignin imparting a cloudy characteristic to such solutions. Based on the Abraham salvation equation, a cationic moiety with an electro-rich aromatic π -system may create stronger interactions for polymers capable of undergoing π - π and n - π interactions (19), which resulted in a more desirable wood solution in ILs.

The solubility of wood in ILs varies with the particle size of the used lignocellulosic materials. During our work we discovered that the solubilization efficiency of the lignocellulosic materials in ILs was found to be of the order: ball milled wood powder > sawdust \geq TMP fibers \gg Wood chips. The dissolution of fine sawdust (Norway spruce, particle size 0.1–2 mm) in ILs takes place within a few hours, even under ambient conditions. Furthermore, thermomechanical pulp (TMP) samples readily dissolved in BmimCl and/or AmimCl. The water content of a wood sample plays a key role in determining its solubility in ILs. Besides the aforementioned factors, we have determined that the applied temperature and water content play a key role in determining their solubility, usually, the desirable temperature is around 100 °C, but it varies with the lignocellulosic materials, as well as ILs' species. Water was found to significantly reduce the solubility of wood in ILs.

2.2. Rheological Properties of Cellulose and Wood/Ionic Liquids Solutions

In an effort to follow on a more quantitative basis, the process of wood dissolution in ILs, the rheological behavior of cellulose/ionic liquid systems and wood/ILs systems was evaluated. This approach has provided important fundamental information for the development of large-scale bio-materials and biorefinery processes (20, 21). Microcrystalline cellulose (MCC, Molecular weight \sim 60,000 g/mol), was used as a model compound, and it was dissolved in two different ILs (AmimCl) and ([mmim]Me₂PO₄) and the solution's viscosities were measured at different temperatures and concentrations. The effect of concentration on the viscosity is shown for both systems, MCC-AmimCl and MCC-[mmim]Me₂PO₄ in Figure 1. The viscosity behavior of MCC-ILs solutions as a function of shear rate is dependent on the concentration of the solution and temperature. At low concentrations, i.e. 0.5-2.63 m% of MCC in ILs, the solutions behave as Newtonian liquids and the viscosity is not dependent on the shear rate in the temperature range 40-80 °C. However, at 20 °C they are shear thinning. At high concentrations and over the whole temperature range, these solutions are non-Newtonian and shear thinning. The concentration of MCC dissolved in ILs affects the solution properties significantly. When the concentration of MCC is fairly low, 0.5-2.33 m% and 0.5-2.63 m% for MCC-AmimCl and MCC-[mmim]Me₂PO₄, respectively, one may infer that there are no interactions between the polymer coils. However, when the concentration is increased above the critical concentration (M_c), 2.33 m% and 2.63 m% for MCC-AmimCl and MCC-[mmim]Me₂PO₄, respectively, the coils start to interact and form transient entanglements, which manifest to the samples a more viscoelastic behavior.

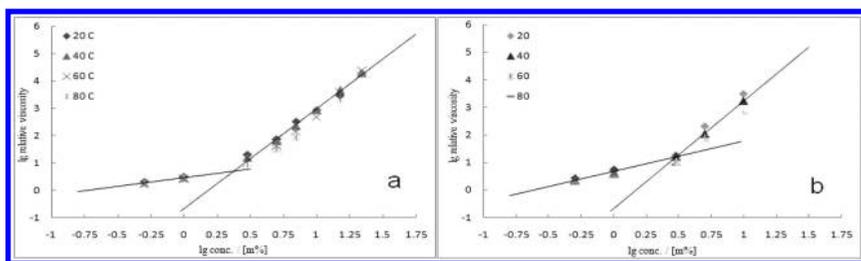


Figure 1. The relative viscosity of (a) MCC-AmimCl- and (b) MCC-[mmim]Me₂PO₄-solutions as function of concentration.

The viscosity of the wood ILs mixtures progressively altered as a function of time is also obtained in the two ILs (Figure 2). As anticipated, the dissolving process of spruce TMP in BmimCl and BenzylmimCl is accompanied by a progressive reduction in the overall viscosity of the mixture. The shapes of these curves can be rationalized on the basis of the resistance to flow of the undissolved wood and the lack of resistance to flow in the case of the dissolved wood. At longer contact times with the solvent the size of the wood fibers become progressively smaller resulting in the decrease viscosity observed. Once complete dissolution has been obtained, the viscosity of the solution remains constant. Furthermore, these measurements allowed for a more detailed description of the actual dissolution kinetics to emerge.

3. Opportunities with Wood Dissolved in Ionic Liquids

3.1. Glucose Production from Pretreated Lignocellulosic Materials with Ionic Liquids

Currently, the production of bioethanol mainly utilizes sugar cane, starch, etc., however, most of them are important food and animal feedstocks, the lignocellulosic materials may be a more ideal source for production biofuels. No commercial wood-based process are available to date possible due to the technological problem and/or economic goals (2). During our work (18, 22), after dissolution of the lignocellulosic material into ILs, it is possible to recover the sample by simply adding a nonsolvent, such as water, into the solution. The X-ray spectra of the regenerated material showed that the X-ray diffraction signals from the crystalline regions of spruce sawdust have disappeared after the dissolution–regeneration process and a fully amorphous material is obtained. Such a transformation is anticipated to allow a greater accessibility for the hydrolytic enzymes to rapidly penetrate and hydrolyze the wood. The pretreated lignocellulosic material in the ILs was then submitted to an enzymatic hydrolysis (18).

Our initial, and completely unoptimized experiments, showed that about 60% of the theoretical amount of glucose was enzymatically released from the wood when predissolved in AmimCl and regenerated by precipitation in water. This

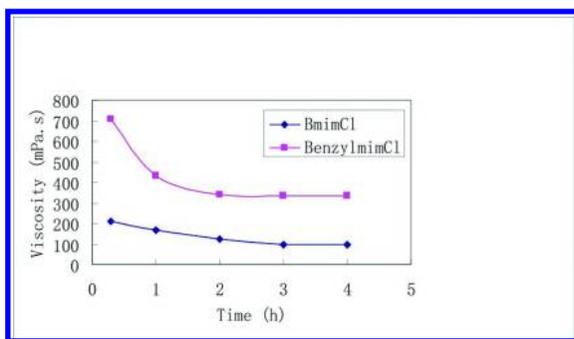


Figure 2. The relationship between the 2% wt spruce TMP in BmimCl, BenzylmimCl and dissolving time at 130 °C

compared to only 12% of glucose units being released from the untreated control wood sample. Similar pretreatments in BmimCl were also found to improve the release of glucose unit but to a significantly lower degree compared to AmimCl. The effective recyclability of ILs within this process provides a promising route for the production of bioethanol directly from lignocellulosic materials, but a number of energy and chemically efficient recycle technologies are still in need of development (18).

3.2. Chemical Modification of Wood in Ionic Liquids

Our research interests in this respect have been focused at how to use wood as a polymeric material by creating completely miscible composites with synthetic commodity plastics. Biodegradable plastics and bio-based composites produced from biorenewable biomass feedstocks are regarded as promising materials that could replace synthetic polymers and reduce global dependence on fossil sources (1). In 2007 (23, 24), Xie et al. reported the effective homogenous chemical modification of wood-based lignocellulosic materials in ILs.

During our efforts to improve the compatibility of lignocellulosic materials with nonpolar thermoplastics, a variety of active chemical reagents were applied to modified lignocellulosic materials in ILs as described in Scheme 2, such as carboxylic acid anhydrides, acid chlorides, and isocyanates, due to their high reactivity toward the hydroxyl groups of lignocellulosic materials. Initially, we investigated the acetylation and benzylation reactions of wood dissolved in ILs using acetyl chloride (AcCl), acetic anhydride (Ac₂O), and benzoyl chloride as acylation reagents. Surprisingly, although acetic anhydride is a desirable acylation reagent for chemical modification of cellulose in ILs, in the absence of pyridine (25), a low Weight Percent Gain (WPG= -30) was obtained for the modification of wood under similar conditions. A significant degradation occurred, possible due to the presence of lignin in the wood compared to pure cellulose. The addition of equivalent amounts of pyridine as an acid acceptor was found to increase the WPG values (WPG=50) significantly under identical conditions, which is close to the theoretically calculated value of 66% (based on 13.3 mmol/g of hydroxyl

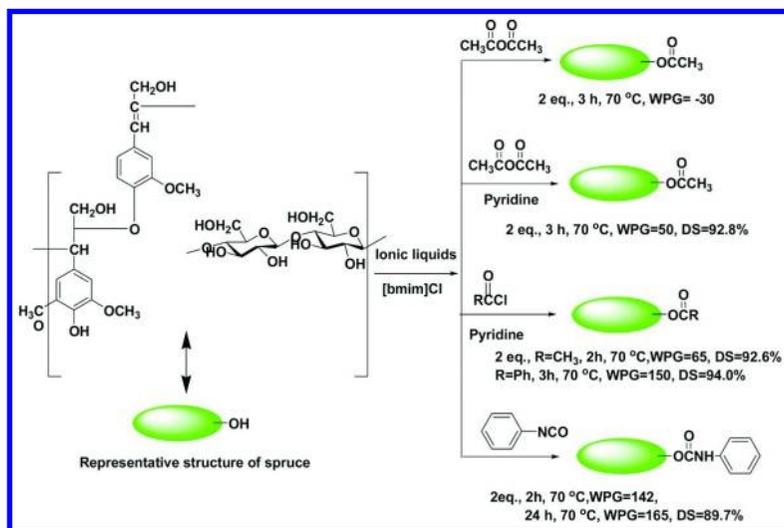
groups present in wood as determined by quantitative ^{31}P NMR) (26, 27, 40–43). As anticipated, acid chlorides, such as acetyl chloride and benzoyl chloride, were found to be more reactive acylation reagents than acetic anhydride, which is evidenced by the higher WPG values of 65%, 150% respectively under similar conditions. An examination of the effect of reaction temperature, time and the required excess of derivatizing reagent was also carried out. On the basis of WPG values obtained, we concluded that increasing the reaction time and temperature did not lead to higher WPG, possible due to partial degradation caused by the presence of the acidic pyridinium acetate formed, while increasing the molar ratio of reagent/substrate beyond 2 did not show any additional significant increase in WPG value. In addition, phenyl isocyanate was commonly used as a “neutral” reagent, for the purpose of wood modification, and a middle WPG value of 142 % was obtained (Theoretical value=187%) under similar reaction conditions. Even after prolonged reaction times (24h), the WPG value only increased to 165%, which is somewhat further from its theoretical value, which demonstrates that the uncatalyzed phenyl isocyanate reaction on lignocellulosic materials is less efficient, as compared to its acylation.

The efficient modification of the lignocellulosic materials in ILs was also evident via the use of infrared spectroscopy, NMR, and quantitative ^{31}P NMR (26, 27, 40–43). For example, a significant decrease in the broad region responsible for the OH stretching vibrations, centered at 3416 cm^{-1} , was apparent in all derivatives, while this decrease was accompanied by a significant increase in the absorption at around $1726\text{--}1752\text{ cm}^{-1}$ characteristic of the carbonyl stretching bands for all derivatives; The appearance of a large acetate $-\text{CH}_3$ signal is apparent in the ^1H NMR spectra of acetylated lignocellulosic material. Similarly, the appearance of strong phenyl proton resonances compared to the anhydroglucose units in the ^1H NMR of benzoylated and carbonylated spruce demonstrates that highly substituted lignocellulosic materials have been obtained; The use of quantitative ^{31}P NMR has been proven to be a useful tool to qualitatively and quantitatively evaluate the various hydroxyl groups present in lignin (26, 27, 40–43). Despite that fact that the wood derivatives, obtained during this work, were only partially soluble in traditional solvents, they were completely soluble in ILs such as AmimCl and BmimCl. Quantitative ^{31}P NMR spectra of spruce and spruce derivatives were therefore obtained using ILs as co-solvents, on which the degree of substitution values (DS) for all wood derivatives were obtained. The DS value of acetylated spruce, benzoylated spruce and carbonylated spruce prepared under optimized conditions were 92.6%, 94.0% and 89.7%, respectively, which demonstrated that highly substituted lignocellulosic materials were obtained (23, 24).

3.3. Highly Compatible Wood Thermoplastic Composites from Lignocellulosic Material Modified in Ionic Liquids

Besides its building and energy applications, wood has been considered to be a pivotal component for the production of bio-composites, also referred to as “wood-thermoplastic composites” or simply “wood-plastic composites” (28). The effective dissolution and modification of wood in ILs are anticipated to result in

Scheme 2. Homogenous functionalization of spruce in *BmimCl*



a significant change in their material properties, such as interfacial compatibility between wood and synthetic polymers, thermal properties and morphological characteristics (29). The thermal properties of the obtained derivatives are of significance as far the eventual utilization of such materials is concerned. We found that the thermal stability of spruce derivatives varies with the structure of the modifying reagent. For example, acetylated (DS=92.6%) and lauroylated spruce (WPG=229%) showed similar thermal stabilities to the original spruce TMP that starts to decompose at around 190 °C. As anticipated, benzoylated spruce (DS=94.0%) showed a higher thermal stability and decomposition temperature (around 220 °C) due to the presence of an aromatic group within the wood structure. However, the carbonylated spruce (DS=89.7%) was found to start decomposing at near 190 °C, and it is seen to be much steeper than either the acetylated or benzoylated spruce. Additional differential scanning calorimetric (DSC) measurements showed that the efficient, homogeneous derivatization of wood in ionic liquids provided an ideal environment for the production of uniformly substituted new materials that showed distinct thermal transitions occurring below their decomposition temperatures (23, 24).

To better understand the effects of the thorough chemical modification of the wood-based lignocellulosic material in ILs and couple the thermal properties of these derivatives to product performance and other characteristics, the morphology of the derivatives was examined using scanning electron microscopy (SEM). These data showed a highly porous and considerably more uniform and isotropic structure throughout. Such morphological properties, when coupled with the chemical and thermal characteristics of the new materials could offer significant benefits as far as increased compatibility and improved processing ability of wood with synthetic polymers are concerned (23, 24). In 2008, Xie, Argyropoulos et al. reported the preparation of WPCs with poly(styrene) and poly(propylene) using completely benzoylated and lauroylated spruce wood.

This work was done on a MiniLab, counter-rotating twin-screw extruder, with the aim to examine the validity of our earlier observations related to the thermal and morphological properties of the prepared wood derivative materials (30).

The analysis of the torque curves, as obtained for the melted wood derivatives with a synthetic polymer, is an excellent method for monitoring the interfacial adhesion and compatibility of the two components. This information was found to be rather useful in probing the effects of the chemical modification of the wood on its melt flow and melt mixing characteristics, with the synthetic polymers examined (30).

A comparison of the final stabilized torque values for the chemically modified and unmodified pairs was also indicative of melt stability and compatibility between the polymers. The stabilized torque value for the benzoylated wood-poly(styrene) pair was about 80 Ncm as opposed to a value of about 60 Ncm, obtained for the TMP/poly(styrene) pair. We conjectured that polymer melts between two miscible polymers are anticipated to give rise to higher torque values, in the mini extruder, as opposed to polymer melts that contain particles or fibers that create voids within the melt structure (30).

Further examination of fractured surfaces of the composites by SEM gave a direct indication about how modification affects the morphology of the composites and interaction between the synthetic polymeric matrix and wood derivatives. A series of comparative SEM pictures for the cross sections of fractured surfaces of benzoylated wood with poly(styrene) composites, and lauroylated spruce with poly(propylene) are obtained (30). We found that pure poly(styrene) and poly(propylene) show a homogeneous fractured surface. With the addition of 10% of unmodified spruce TMP, both of these polymers showed signs of extreme inhomogeneity with large amounts of fiber pullout being apparent. As anticipated, both findings indicate that there is poor adhesion between the two phases, which is possible due to the poor dispersion of the hydrophilic spruce TMP in nonpolar synthetic polymers. We also conjectured that the absorbed water by spruce TMP was evaporated during the blending process leaving cavities within the composites. However, with the addition of modified wood derivatives, and despite some apparent residual fiber-like regions observable within the composite fractions, the interfacial miscibility was obviously increased as evidenced by the excellent and even dispersion of the fibrous structures throughout the fractured surfaces. It is likely that the reduced hydrophilicity and increased Van der Waals interactions between the aromatic or alkyl functionalities both within the wood derivatives and the poly(styrene) and poly(propylene) are responsible for the observed compatibility. The thermal behavior of the as prepared thermoplastic composites were also investigated by DSC, TGA and DTA confirming the miscible blend behavior. The resultant thermoplastic wood composites exhibited good melting characteristics and they were readily extruded into filaments or sheets (30).

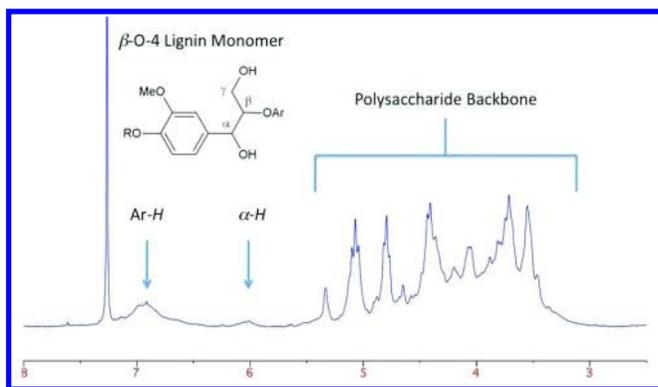


Figure 3. ^1H NMR spectra (CDCl_3) of pulverized Norway spruce wood

3.4. *In-Situ* NMR Analysis of Wood and Its Components based upon Ionic Liquid Pre-Dissolution

In 2003, Lu and Ralph reported the complete dissolution of pulverized wood into a N,N,N,N -tetrabutylammonium fluoride/ d_6 -dimethylsulfoxide (TBAF/ d_6 -DMSO) mixture, followed by a combination of mild chemical modification and ^1H & ^{13}C NMR analysis techniques (31). This has paved the way for the analysis of wood components, such as lignin, without its prior isolation from the wood fiber. More recent accounts have since been published (32, 33), in the form of conference abstracts demonstrating the dissolution and homogeneous solution phase analysis of finely pulverized wood powder in DMSO- d_6 .

The discovery by Swatloski and Rogers et al. (10) that cellulose may be efficiently dissolved into non-derivatizing ILs such as BmimCl has allowed for the dissolution (potential derivatization) and analysis of this biopolymer in solution. As cellulose is generally regarded as the most dissolution resistant purified fraction of wood, using non-destructive solvents, it was later reported by Kilpeläinen, Argyropoulos et al. (18) that imidazolium chloride ILs, such as AmimCl, were able to dissolve pulverized wood. This has further expanded the potential for the analysis of wood biopolymer functionalities based upon pre-dissolution of lignocellulosic materials into non-derivatizing media such as imidazolium-chlorides. Note: although at present, cellulose dissolving ILs (commonly imidazolium acetates (34), chlorides (10), dialkylphosphates (35) and formates (36)) are regarded as non-derivatizing, a recent report by Ebner and Rosenau(37) suggests that imidazolium cations have the potential to react with reducing end groups in cellulose, catalyzed by basic species, in solution. This has however only been confirmed for the imidazolium acetates and considering the abundance of reducing end groups per anhydroglucose unit (AGU), represents only a small and practically unobservable fraction of the molecules, by standard NMR techniques.

3.4.1. ^1H & ^{13}C NMR Analysis

Our work has shown that it is possible to dissolve a lignocellulosic sample into room temperature ILs such as AmimCl or 1,3-dimethylimidazolium dimethylphosphate ([mmim] Me_2PO_4) and run a homogeneous solution phase ^1H or ^{13}C NMR spectrum, in the absence of additional locking solvent. However, the biopolymer to solvent signals are poor (based upon a typical 5 % concentration of substrate) and a reduction in gain (and hence sensitivity) is required with significant losses in the resolution of the peaks. To date, no NMR analyses have been reported of lignocellulosic materials dissolved in pure perdeuterated ionic liquids.

In 2007, Fort and Rogers et al. (38) demonstrated that by the addition of 15% d_6 -DMSO to BmimCl followed by ^{13}C NMR analysis of heat treated samples, it was possible to progressively extract lignocellulose fractions from wood chips. A resonance at 57.2 ppm was thought to be indicative of the presence of 'OMe' functionalities from the lignin monomer units. The proportion of lignin to polysaccharides extracted was estimated by an integration of the 'OMe' to polysaccharide backbone carbon resonances. These were found to remain approximately constant, increasing with time at 80 °C and reaching to ~60% of the total content in 4 different wood species after 24 hr. Furthermore, these authors demonstrated that by the addition of a co-solvent, it was possible to precipitate (fractionate) relatively lignin-free polysaccharide from these solutions. The composition of this polysaccharide was suggested to be cellulose.

Dissolution of pulverized lignocellulose samples into ILs such as [amim]Cl and [mmim] Me_2PO_4 has also allowed for chemical modification of hydroxyl groups, regeneration of the product and subsequent dissolution into a low viscosity and polarity solvent such as CDCl_3 for high resolution NMR analysis of the complete intact sample. This has been demonstrated in the aforementioned publication by Kilpeläinen and Argyropoulos(18) whereby Norway spruce wood sawdust was dissolved in [amim]Cl and the hydroxyl groups acetylated completely using an $\text{Ac}_2\text{O}/\text{Pyr}$ mixture at 80°C over 18 hrs. The product was regenerated by addition of water. Complete functionalisation of all hydroxyls was determined by the absence of an 'OH' stretch in the IR spectra. This acylation reaction has also been reported to be achievable from [mmim] Me_2PO_4 by Olszewska, Argyropoulos et al. (39). The resulting product in CDCl_3 (Figure 3) shows significant proton resonances in the region around 2 ppm corresponding to 'OMe' and 'OAc' functionalities (not shown in Figure 3). In the region from 3-5.5 ppm, the polysaccharide and lignin-aliphatic backbones are clearly intact. Additionally, clearly resolved from this region is a small resonance at 6 ppm, corresponding to α -H resonances from the β -O-4 coniferyl alcohol monomers in softwood lignin. Downfield from this are the Ar-H resonances at 6.25-7.5 ppm from the lignin. Interestingly this acylation reaction is thought to predominantly occur by initial reaction of the acid chloride with the dialkylphosphate anion from the ILs to give the mixed anhydride. It is this species which acts as electrophile in the acetylation of the lignocellulose hydroxyls. Addition of significant quantities of AcCl to [mmim] Me_2PO_4 furnishes [mmim]Cl, which can be observed to crystallize from the reaction mixture. Although this procedure does not

provide satisfactory resolution of different polysaccharide aliphatics from lignin aliphatics, the technique in the future may allow for reasonable lignin content determinations, by integration of Ar-*H* or α -*H* against internal standards. With the formation of alternative acyl esters of lignocellulose, such as benzoylates, it may be possible to integrate 'OME' functionalities against both internal standard and α -*H*, yielding valuable information about the abundance of these functionalities in the pulverized native or processed lignocellulose sample in question.

3.4.2. Quantitative ^{13}P NMR Analysis

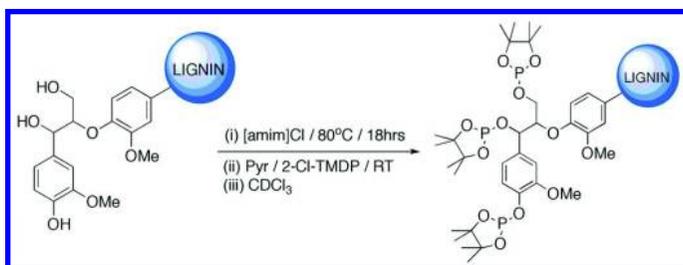
In relation to wood analysis, ^{31}P NMR has traditionally been used for the identification of aliphatic, phenolic (resolved condensed, syringyl, guaiacyl or *p*-hydroxyphenyl) and carbonyl (carboxylic acids) hydroxyls in extracted or enriched lignin preparates, such as milled wood lignin (MWL), cellulolytic enzyme lignin (CEL) and most recently enzymatic mild acidolysis lignin (EMAL) (27, 42, 54).

Typically, the solvent treatment required to pre-dissolve the lignin has been heating overnight in the polar aprotic solvent DMF. Under these conditions, cellulose (MCC) does not dissolve and is neither soluble after the introduction of the reactive species. ILs such as the imidazolium chlorides, such as AmimCl, have now provided a means for the pre-dissolution of MCC, in the pure ILs under mild conditions (80 °C, 2 hrs), followed by complete phosphitylation with 4,4,5,5-tetramethyl-2-chloro-1,3,2 dioxaphospholane (2-Cl-TMDP) and solubilisation in AmimCl/ CDCl_3 mixtures, as demonstrated in publications by King, Argyropoulos et al. (40). EMAL, as a high molecular weight lignin, was also found to be fully reacted and soluble in similar solvent mixtures (Scheme 3).

When this method was applied to Norway spruce sawdust dissolved in high purity, neutral (acid free) AmimCl (41), turbidity was observed both in the 'pre-dissolved' pure ILs mixture and the phosphitylated reaction mixture. This was accompanied by very low values for total observed ^{31}P nuclei, in comparison to an internal standard of known quantity. Actual values were 20% of those expected for MCC (18.52 mmol/g = $1000 \times 3/162$). These observations are an indication of insolubility and somewhat contradictory to the previous reports mentioned earlier concerning wood dissolution and analysis. To resolve this solubility issue, Norway spruce sawdust was pulverized in a planetary mill at 24 hrs intervals to a total milling time of 96 hrs. The ^{31}P labeling and analysis procedure was carried out at each interval and the total observable phosphate esters, in comparison to the internal standard, for each sample plotted as a function of milling time (Figure 4).

The observable phosphate esters for each sample are representative of the total number of available (or reactive) hydroxyls for each sample under these mild dissolution and reaction conditions. This is a measure of the solubility of the wood sample in the ILs, without applying harsh or acidic conditions for dissolution. From Figure 4, it is obvious that significant solubility is only achievable at around 40 hrs milling time. The values seem to maximize at a value of ~ 12.5 mmol/g which is representative of the total number of hydroxyls in Norway spruce wood.

Scheme 3. Typical phosphitylation reaction on a terminal lignin guaiacyl β -O-4 dimer residue.



Analysis of the lignin phenolics from these milled samples shows a similar trend of increasing abundance of phosphate esters with increasing milling time (Figure 4). In this case however, the guaiacyl functionalities, which are the most abundant phenolics in softwood, continue to increase at a faster rate (relative to total quantity in solution), in comparison to the total available hydroxyls values in Figure 4. This is accompanied by a similar rate of increase in carboxylic acids and is indicative of breakage of beta-O-4, corroborating previous reports concerning degradation of lignin functionalities with various mechanical treatments (42).

In Figure 5B, the klason content corrected ($100 * \text{mmol/g values} / \text{klason content} = 100\%$ values) guaiacyl hydroxyl abundance values at 50 hrs planetary milling time were found to be the same as those observed for the pure EMAL samples, which had been prepared using 28 days vibratory milling. Extrapolation of the values for the most soluble fractions (72 and 96 hrs) to 0 hrs milling time gives an approximate value (0.65 mmol/g) for the total free guaiacyl phenolic hydroxyls in Norway spruce wood sawdust.

Although no serious assignment about the carbon skeletons of lignin or hemicelluloses can be made, using ^{31}P NMR, ILs pre-dissolution and subsequent analysis has afforded a technique that can chart the relative abundance of, most valuably, the common free phenolics that can be observed in lignin from softwoods, hardwoods and grasses, without prior isolation or enrichment of the lignin (43). Continuing development of this technique will afford an excellent tool for analyzing the selectivity of potential bioprocessing methods based upon ILs pre-dissolution, especially in relation to the breakage of common ether bonds found in lignin.

3.5. Pyrolysis of Wood in Ionic Liquids

Fast pyrolysis is regarded as an important approach to produce valuable chemicals from biomass (44, 45). Corresponding problems of this traditional method that involves heterogeneous mass diffusion and transport are low activity and selectivity, cumbersome product separation and the need of high temperatures. Many attempts have been made to improve both the conversion and selectivity of biomass pyrolysis. It is claimed that pre-treatments, solubilization or the presence of additives can lead to increases in the degrees of conversion and the selectivities of the underlying reactions (46).

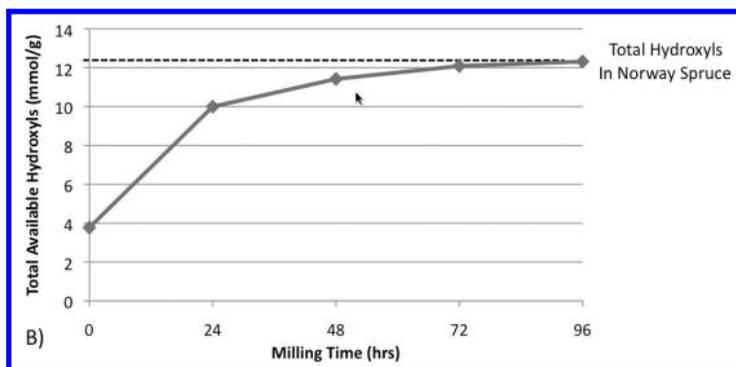


Figure 4. Total available (observable) hydroxyls in Norway spruce at different planetary milling times.

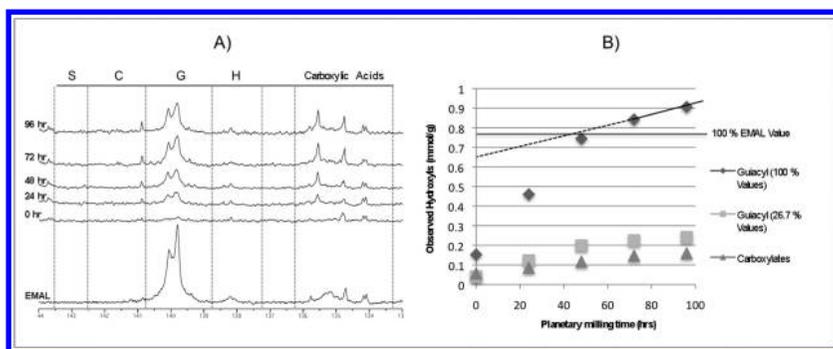


Figure 5. (A) ^{31}P NMR spectra of wood as a function of pulverization. (B) Guaiacyl phenolic hydroxyl and carboxylic acid content in planetary milled Norway spruce for 0 - 96 hrs planetary milling time and EMAL (from 28 days vibratory milling).

ILs are regarded as a good media for high temperature processes due to their negligible vapor pressure and high thermal stabilities (47). Furthermore, the solubilization environment provided by ILs (especially at elevated temperatures) may lead to high conversion and even stereoselectivity on functional group transformation (48). In 2007, Sheldrake et al. (49) reported that dicationic molten salts of ILs can act as good media for the controlled pyrolysis of cellulose to anhydrosugars. In addition, wood liquefaction and hydrolysis by ILs and improved transformation of sugars into valuable chemical intermediates have also been reported (50–52). This further demonstrated that the interaction between ILs and biomass can facilitate the transformation of biomass to valuable chemicals. Levoglucosan (LG) and levoglucosenone (LGO) are two significant molecules that can be produced from the pyrolysis of cellulose. They are highly functionalized compounds due to their carbon-carbon double bonds, the ketone group and the glycosidic linkage. These characteristics make them ideal precursors in organic transformations aimed at compounds of pharmaceutical significance (53). During our study, we used wood, chromated copper arsenate (CCA) treated wood and H_3PO_4 treated wood as our raw materials to investigate

Table 1. Effect of ionic liquids on the pyrolysis/thermolysis of wood samples

Entry	Pyrolysis Methods ^a	Samples	% Tar	% Distillate	% Char	% Total Recovery
1	A	Original wood (Southern pine)	54.5	12.5	27.5	94.5
2	A	CCA-treated wood	52.2	15.2	30.4	94.5
3	A	H ₃ PO ₄ treated	19.1	26.6	49.8	95.5
4	B	Original wood	65.0	22.0	13.0	100.0
5	B	H ₃ PO ₄ treated wood	36.0	24.5	15.0	75.5
6	B	Cellobiose	19.9	36.2	31.0	87.0
7	B	Cellulose	17.6	33.2	19.6	70.3

^a Pyrolysis conditions : A: 350 °C without ionic liquid; B: 180 °C in AmimCl.

the possibility of producing value-added chemical intermediates (LG, LGO) from pyrolysis tar products. Gas chromatography and quantitative ³¹P NMR spectroscopy were the analytical tools that proved to be invaluable for the analysis of these complex degradation mixtures (54–56).

The effective pyrolysis of wood usually requires temperatures in excess of 300 °C. During our work, the fact that the wood was actually dissolved, resulting in a homogeneous solution in ILs, allowed for increased mass and heat transfer during the pyrolysis and facilitated the dehydration reactions of the cellulose and its interaction with the catalytic additives. Consequently, this led to a significant reduction in the required pyrolysis temperatures and an increase in the efficiency of the wood pyrolysis reactions. In actual fact in the presence of ILs, the thermal requirements for the deconstruction of cellulose were so significantly reduced that prompted us in using the term “thermolysis” rather than “pyrolysis” to describe these reactions. As seen in Table 2, the combined yields of tar and distillate were vastly improved when the thermolysis was carried out under the homogeneous conditions provided by the ILs with concomitant reduction in the amounts of the remaining char. For wood alone, these numbers amount to an increase of tar and distillates of about 20% with an accompanying reduction of the char residue. It is also important to note that the homogeneous thermolysis conditions created by the ILs provided for greater amounts of more volatile products as evidenced by the higher percentages of distillate obtained. This can be very important since these distillates can be more readily refined and/or more completely incinerated as fuel or pyrolysis oils. In an effort to better understand the thermolysis of wood in ILs, the presence of H₃PO₄ in treated wood, cellobiose and cellulose was also examined (Table 1, Entries 3 & 5). As anticipated the catalytic effect of acids was apparent in the dehydration chemistry of cellulose and the model carbohydrates examined.

Quantitative ³¹P NMR spectroscopy and gas chromatography (GC-FID) were used as parallel analytical tools for the definition and identification of the chemical

compositions of the pyrolysis fractions. For example, pure LG and LGO resulted in signals of distinct chemical shift values in the ^{31}P NMR spectra centered at 146.6-148.1 and 135.8, respectively.

Typical ^{31}P NMR spectra of tar products obtained during our work are shown in Figure 6. The ^{31}P NMR spectrum (A) of tar product resulting from the heterogeneous pyrolysis of control wood is more complex than those obtained from H_3PO_4 treated wood (B) and the homogeneous thermolysis of original wood (C) in ILs. In addition, there is a large signal due to the presence of LG in spectrum (A) and a dramatically decreased signal for LG is apparent in spectra (B) and (C) accompanied with a new signal of LGO appearing compared to spectrum (A). This is indicative that the dehydration chemistry of cellulose is a lot more facile in the presence of acid catalysts (as anticipated) and in the presence of ILs.

Quantitative analyses of the tar fractions based on ^{31}P NMR and GC-FID confirmed that the yield of levoglucosan (LG) was significantly lower in the ILs thermolysis media (54, 55). In contrast, the yield of LGO was seen to increase when ILs were used as the reaction medium (approximately a 5 fold increase was seen compared to the conventional system; Table 2). For example, the yield of LG in the case of original wood decreased from 3.7% to 0.06%, and the yield of LGO increased from 0.6% to 2.8% when ILs were used (Table 2, Entries 1 & 8). These observations were also confirmed when thermolysis experiments were carried out with microcrystalline cellulose (Table 2, Entries 5 & 6) consisted with published results (50, 54, 55). The yields of LGO from lignocellulosic materials in ILs were seen to be even higher than those of the pyrolysis of pure microcrystalline cellulose (Table 2, Entries 5, 6, 8 & 9). Overall by considering LGO is a marker compound responding to the efficiency of the dehydration operating on cellulose our data indicates that ionic liquids promote this reaction. The lower yield of LG within the final products obtained using IL media indicates that the conversion of LG to LGO was more complete when the ILs were used.

4. Sustainability of the Ionic Liquids Based Biorefinery Platform

Due to their non-volatility, effectively eliminating a major pathway for environmental release and contamination, ionic liquids have been considered as having a low impact on the environment and human health, thus recognized as one of the green solvents for the future. Compared with other conventional solvents-based processing platforms for biopolymers, such as NMNO (57), LiCl/DMAC (58), ethylene diamine/salts (59), etc., ILs based biopolymer processing platforms display many properties, such as high recyclability and a broad applications range due to their relative high chemical and thermal stability. It is envisaged that a biorefinery concept based on ILs may contribute to sustainability by reducing the amount of waste assuming an effective recycling of raw solvents, with the potential for the entire process becoming carbon neutral. Our work on the recycling ability of ILs has shown a number of desirable traits as well as technical challenges to be overcome for diverse applications such as

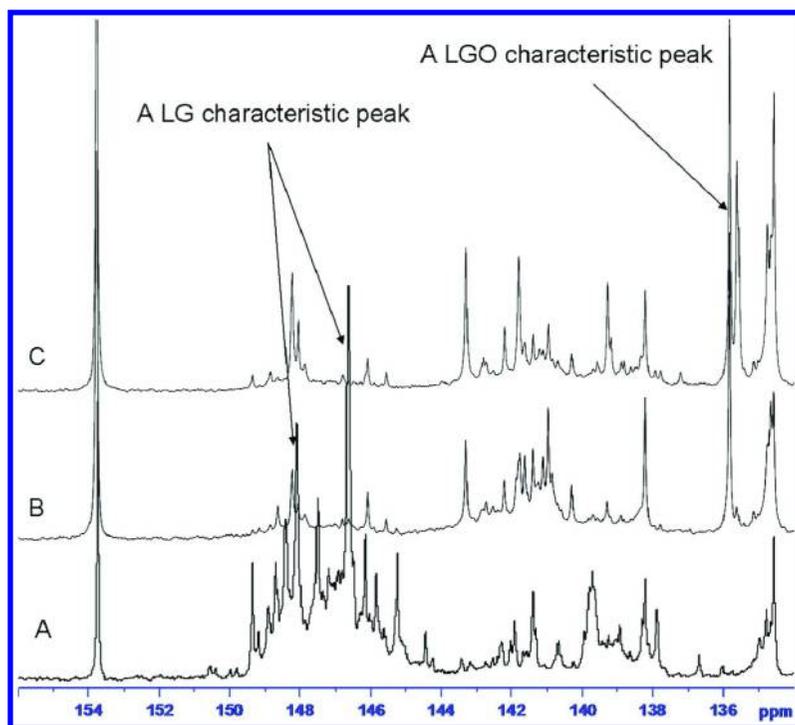


Figure 6. ^{31}P NMR spectra of tar fractions from pyrolysis of (A) Original wood with traditional method (54, 55); (B) H_3PO_4 -treated original wood in an ionic liquids.

Table 2. Analysis of the tar fractions

Entries	Samples	LG (%)	Yield of LGO (%)
1	Original wood	3.7	0.6
2	CCA-treated wood	18.3	0.9
3	H_3PO_4 -treated original wood	19.95	0.6
4	H_3PO_4 -treated CCA wood	20.53	1.3
5	Microcrystalline cellulose	42.5	1.5
6	Microcrystalline cellulose in an ionic liquid	40.5	2.7
7	Cellobiose in an ionic liquid		2.2
8	Original wood in an ionic liquid	0.06	2.8
9	H_3PO_4 -treated original wood in an ionic liquid	0.06	2.9

the wood dissolution process, wood chemical modification and wood thermolysis (18, 22–24, 56).

5. Conclusions & Outlook

The preparation of wood solutions not only extends the utilization of lignocellulosic materials from heterogenous to homogenous conditions but also creates a variety of new strategies for converting our abundant lignocellulosic materials to novel value-added bioproducts. Some potential applications of wood-ILs solution have been explored and include the following:

1. Highly substituted wood-based lignocellulosic derivatives have been obtained with high degrees of reproducibility through homogenous chemical modification in ILs. The resulting wood derivatives show distinct thermal transitions and uniform morphology. Compatible wood composite fibers have been successfully synthesized with polyolefins and polystyrene.
2. After a dissolution-regeneration treatment, wood cellulose can be efficiently digested to glucose.
3. *In-situ* NMR (^1H , ^{13}C & ^{31}P) methods using ILs have been developed for the elucidation of structural information of wood and wood components without the prior isolation of the individual component.
4. The first homogenous thermolysis of wood in ILs has been developed. Under such conditions the cellulose dehydration chemistry was found to be favoured.

Over thousands of years, wood has been used mainly as a raw material for building, fuel, and paper making. These wood processing strategies so far have been limited due to its insoluble characteristics. The dissolution of wood in ILs presents a range of possibilities to utilize wood in an efficient homogenous manner. Significant technological and scientific challenges, however, still remain to be addressed. Amongst others these are: economic syntheses on a large scale; definition of recycling pathways, biodegradation/bioaccumulation studies as well as toxicity and handling considerations.

References

1. Ragauskas, A. J.; Williams, C. K.; Davison, B. H.; Britovsek, G.; Cairney, J.; Eckert, C. A.; Frederick, W. J.; Hallett, J. P.; Leak, D. J.; Liotta, C. L.; Mielenz, J. R.; Murphy, R.; Templer, R.; Tschaplinski, T. *Science* **2006**, *311*, 484.
2. Stocker, M. *Angew. Chem., Int. Ed.* **2008**, *47*, 9200.
3. Bozell, J. J. *Clean: Soil, Air, Water* **2008**, *36*, 641–647.
4. Kamm, B. *Angew. Chem., Int. Ed.* **2007**, *46*, 5056–5058.
5. Morandini, F.; Salamini, F.; Gantet, P. *Curr. Med. Chem.: Immunol. Endocr. Metab. Agents* **2005**, *5*, 103.
6. Nolen, S. A.; Liotta, C. L.; Eckert, C. A.; Glaser, R. *Green Chem.* **2003**, *5*, 663–669.

7. Eckert, C. A.; Liotta, C. L.; Bush, D.; Brown, J. S.; Hallett, J. P. *J. Phys. Chem. B* **2004**, *108*, 18108–18118.
8. Parvulescu, V. I.; Hardacre, C. *Chem. Rev.* **2007**, *107*, 2615–2665.
9. Ritter, S. *Chem. Eng. News* **2004**, *82*, 4–4.
10. Swatloski, R. P.; Spear, S. K.H.; Rogers, R. D. *J. Am. Chem. Soc.* **2002**, *124* (18), 4974–4975.
11. Phillips, D. M.; Drummy, L. F.; Conrady, D. G.; Fox, D. M.; Naik, R. R.; Stone, M. O.; Trulove, P. C.; De Long, H. C.; Mantz, R. A. *J. Am. Chem. Soc.* **2004**, *126*, 14350–14351.
12. Xie, H. B.; Li, S. H.; Zhang, S. B. *Green Chem.* **2005**, *7*, 606–608.
13. Xie, H. B.; Zhang, S. B.; Li, S. H. *Green Chem.* **2006**, *8*, 630–633.
14. El Seoud, O. A.; Koschella, A.; Fidale, L. C.; Dorn, S.; Heinze, T. *Biomacromolecules* **2007**, *8*, 2629–2647.
15. Adler, E. *Wood Sci. Technol.* **1977**, *11*, 169–218.
16. Ämmälähti, E.; Robert, D.; Bardet, M.; Brunow, G.; Kilpeläinen, I. *J. Agric. Food Chem.* **1998**, *46*, 5113–5117.
17. Ralph, J.; Marita, J. M.; Ralph, S. A.; Hatfield, R. D.; Lu, F.; Ede, R. M.; Peng, J.; Quideau, S.; Helm, R. F.; Grabber, J. H.; Kim, H.; Jimenez-Monteon, G.; Zhang, Y.; Jung, H.-J. G.; Landucci, L. L.; MacKay, J. J.; Sederoff, R. R.; Chapple, C.; Boudet, A. M. Solution-state NMR of lignins. In *Advances in Lignocellulosics Characterization*; Argyropoulos, D. S., Ed.; Tappi press: 1999; pp 55–108.
18. Kilpeläinen, I.; Xie, H.; King, A.; Granström, M.; Heikkinen, S.; Argyropoulos, D. S. *J. Agric. Food Chem.* **2007**, *55*, 9142–9148 and reference therein.
19. Anderson, J. L.; Ding, J.; Welton, T.; Armstrong, D. W. *J. Am. Chem. Soc.* **2002**, *124*, 14253–14254.
20. He, C.; Wang, Q. *Polym. Adv. Technol.* **1999**, *10*, 487–492.
21. Järvi, P.; Olszewska, A. M.; King, A. W. T.; Granström, M.; Hietala, S.; Kilpeläinen, I.; Argyropoulos, D. S. Unpublished results.
22. Argyropoulos, D. S. U.S. Patent Application No. 12/026,997, World Patent No. WO2008098032, PCT Int. Appl., Filed Aug. 14, 2008.
23. Xie, H.; King, A.; Kilpeläinen, I.; Granström, M.; Argyropoulos, D. S. *Biomacromolecules* **2007**, *8*, 3740–3748 and reference therein.
24. Argyropoulos, D. S.; Xie, H. U.S. Patent Application No. 12/026,998, World Patent Application No. PCT/US2008/053151, Filed Feb. 6, 2008.
25. Wu, J.; Zhang, J.; Zhang, H.; He, J.; Ren, Q.; Guo, M. *Biomacromolecules* **2004**, *5*, 266–268.
26. Argyropoulos, D. S.; Bolker, H. I.; Heitner, C.; Archipov, Y. *Holzforschung* **1993**, *47*, 50–56.
27. Archipov, Y.; Argyropoulos, D. S.; Bolker, H. I.; Heitner, C. *J. Wood Chem. Technol.* **1991**, *11* (2), 137–157.
28. Rowell, R. M. *Handbook of Wood Chemistry and Wood Composites*; CRC Press: 2005; pp 365–380.
29. Hon, D. N. S.; Chao, W. Y. *J. Appl. Polym. Sci.* **1993**, *50*, 7–11.
30. Xie, H.; Jarvi, P.; Karesoja, M.; King, A.; Kilpeläinen, I.; Argyropoulos, D. S. *J. Appl. Polym. Sci.* **2009**, *111* (5), 2468–2467.

31. Lu, F.; Ralph, J. *Plant J.* **2003**, *35* (4), 535–544.
32. Wang, Z.; Tomoya, Y.; Chang, H. *EWLP Proceedings* **2008**, *O4*, 13–15.
33. Rencoret, J.; Marques, G.; Gutiérrez, A.; Nieto, L.; Santos, I.; Jiménez-Barbero, J.; Martínez, Á. T.; del Río, J. I. *European Workshop on Lignocellulosics & Pulp Proceedings EWLP* **2008**, *PII-19*, 340–343.
34. Köhler, S.; Liebert, T.; Schöbitz, M.; Schaller, J.; Meister, F.; Günther, W.; Heinze, T. *Macromol. Rapid Commun.* **2007**, *28*, 2311.
35. Fukaya, Y.; Hayashi, K.; Wada, M.; Ohno, H. *Green Chem.* **2008**, *10*, 44–45, 46.
36. Fukaya, Y.; Sugimoto, A.; Ohno, H. *Biomacromolecules* **2006**, *7*, 3295–3297.
37. Ebner, G.; Schiehsler, S.; Potthast, A.; Rosenau, T. *Tetrahedron Lett.* **2008**, *49*, 7322–7324.
38. Fort, D. A.; Remsing, R. C.; Swatloski, R. P.; Moyna, P.; Moyna, G.; Rogers, R. D. *Green Chem.* **2007**, *9*, 63–69.
39. Olszewska, A. M.; Järvi, P.; King, A. W. T.; Kilpeläinen, I.; Argyropoulos, D. S. *European Workshop on Lignocellulosics & Pulp Proceedings* **2008**, *PI-21*, 222–225.
40. King, A. W. T.; Kilpeläinen, I.; Heikkinen, S.; Järvi, P.; Argyropoulos, D. S. *Biomacromolecules* **2009**, *10*, 458–463.
41. King, A. W. T.; Kilpeläinen, I.; Järvi, P.; Olszewska, A.; Heikkinen, S.; Argyropoulos, D. S. *European Workshop on Lignocellulosics & Pulp Proceedings* **2008**, *O9*, 32–35.
42. Guerra, A.; Filpponen, I.; Lucia, L. A.; Saquing, C.; Baumberger, S.; Argyropoulos, D. S. *J. Agric. Food Chem.* **2006**, *54*, 5939–5947.
43. King, A.; W., T.; Zoia, L.; Filpponen, I.; Olszewska, A.; Xie, H.; Kilpeläinen, I.; Argyropoulos, D. S. *J. Agric. Food Chem.* **2009**, *57*, 8236–8243.
44. Mohan, D.; Pittman, C. U.; Steele, P. H. *Energy Fuels* **2006**, *20*, 848–889.
45. Amidon, T. E.; Wood, C. D.; Shupe, A. M.; Wang, Y.; Graves, M.; Liu, S. J. *Journal of Biobased Materials and Bioenergy* **2008**, *2*, 100–120.
46. Dobeles, G.; Rossinskaja, G.; Telysheva, G.; Meier, D.; Faix, O. *J. Anal. Appl. Pyrolysis* **1999**, *49*, 307–317.
47. Ye, C. F.; Liu, W. M.; Chen, Y. X.; Yu, L. G. *Chem. Commun.* **2001**, 2244–2245.
48. Zhao, H. B.; Holladay, J. E.; Brown, H.; Zhang, Z. C. *Science* **2007**, *316*, 1597–1600.
49. Sheldrake, G. N.; Schleck, D. *Green Chem.* **2007**, *9*, 1044–1046.
50. Xie, H. L.; Shi, T. J. *Holzforchung* **2006**, *60*, 509–512.
51. Li, C. Z.; Wang, Q.; Zhao, Z. K. *Green Chem.* **2008**, *10*, 177–182.
52. Li, C. Z.; Zhao, Z. K. B. *Adv. Synth. Catal.* **2007**, *349*, 1847–1850.
53. Witczak, Z. J. In *Levogluconone and Levoglucosans: Chemistry and Applications*; Witczak, Z. J., Ed.; ATL press: Mount Prospect, 1994. Witczak, Z. J. In *Materials, Chemicals and Energy from Forest Biomass*; ACS Symposium Series No. 954; Argyropoulos, D. S., Ed.; The American Chemical Society: Washington, DC, 2006; ISBN: 978-0-8412-3981-4, February 2007.

54. Fu, Q.; Argyropoulos, D. S.; Tilotta, D. C.; Lucia, L. A. *Ind. Eng. Chem. Res.* **2007**, *46*, 5258–5264.
55. Fu, Q.; Argyropoulos, D. S.; Tilotta, D.; Lucian, L. A. Understanding the Pyrolysis of CCA-Treated Wood, Part II, Effect of Phosphoric Acid. *J. Anal. Appl. Pyrolysis* **2008**, *82*, 140–144.
56. Argyropoulos, D. S. U.S. Patent Application No. 12/026,993, World Patent Application No. 12026993, Filed Feb 6, 2008.
57. Augustine, A. V.; Hudson, S. M.; Cuculo, J. A. In *Cellulose Sources and Exploitation*; Kennedy, J. F., Philipps, G. O., Williams, P. A., Eds.; E. Horwood: New York, 1990; p 59.
58. Dupont, A. L. *Polymer* **2003**, *44*, 4117–4126.
59. Frey, M. W.; Li, L.; Xiao, M.; Gould, T. *Cellulose* **2006**, *13*, 147–155.