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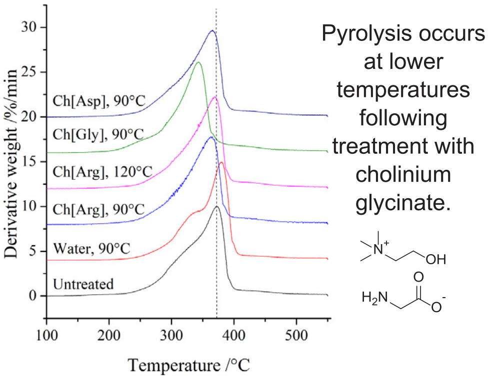
Pinewood pyrolysis occurs at lower temperatures following treatment with choline-amino acid ionic liquids

Manuel Brunner[a], Hua Li[a], Zhezi Zhang[b], Dongke Zhang[b], Rob Atkin[a,*]

[a] School of Molecular Sciences, University of Western Australia, 35 Stirling Highway, Perth, WA 6009, Australia
[b] Centre for Energy, University of Western Australia, 35 Stirling Highway, Perth, WA 6009, Australia

GRAPHICAL ABSTRACT



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ABSTRACT

Pinewoods are the dominant species in Australian softwood plantations and an important source of renewable lignocellulosic biomass. This work examines interactions between cholinium amino acid (Ch[AA]) ionic liquid (IL) – Water mixtures and pinewood. The Ch[AA] ILs employed were cholinium arginate (Ch[Arg]), cholinium glycinate (Ch[Gly]), and cholinium aspartate (Ch[Asp]), with water contents between 32 and 42 wt%. Pinewood and Ch[AA] ILs were mixed at 90 °C for all samples, and also 120 °C for Ch[Arg], as it dissolved the most biomass at 90 °C. Thermogravimetric analysis (TGA), scanning electron microscopy (SEM), x-ray diffraction (XRD), and compositional (CHNS) analysis were performed on the raw and treated biomass samples to reveal the changes in physical and chemical properties. While Ch[Arg] solubilised the greatest mass of biomass during treatment, the most pronounced changes in decomposition properties was obtained using Ch[Gly]. The TGA analysis revealed the maximum in the derivative weight loss data shifted to lower temperatures by 29 °C.

1. Introduction

Lignocellulosic biomass represents the most abundant source of renewable carbon on the planet and, if it can be effectively harnessed, is a green alternative to fossil fuel resources like coal, oil and gas [1–4]. Lignocellulosic biomass mainly consists of three building components, namely, cellulose, hemicellulose, and lignin and their contents and physical structure vary from feedstock to feedstock [5].

Pinewoods, which are the dominant species in Australian softwood plantations, are an important source of raw lignocellulosic biomass [6].

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[*] Corresponding author.
E-mail address: rob.atkin@uwa.edu.au (R. Atkin).

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Pinewood lignin network mainly consists of guaiacyl units which can crosslink at C5 position. C—C bonds formed at C5 cannot be hydrolysed by acids or bases, as a consequence softwoods are harder to deconstruct than hardwoods or grasses with lower guaiacyl content [5].

The most exciting potential biomass applications require treatment to disrupt the lignin network, and ideally separate the major components [7–9]. For example, thermo-chemical conversions like pyrolysis can be performed to produce gases (hydrogen, methane, carbon monoxide and carbon dioxide), charcoal and bio-oils [10]. Another potential application for lignocellulosic biomass is the preparation of composite materials using one or more biopolymers from the biomass feedstock with additional polymers or crosslinking agents [11–13].

Lignocellulosic biomass can be treated by various methods ranging from particle swelling and delignification processes [14] to partial or complete dissolution of the biomass [15]. To date, most established industrial treatment techniques utilize harsh, environmental unfriendly chemicals, for example strong acids or bases, or are highly energy intensive, e.g. mechanical extrusion [7,16].

Recently, ionic liquids (ILs) have attracted significant attention for biomass treatment [17–20]. ILs are low melting salts (T_m < 100 °C) which often have low vapour pressure, high thermal stability, wide liquid ranges and the ability to solvate a wide range of materials [21–24]. ILs and their mixtures can have pronounced nanostructures in the bulk and at interfaces [25–28], which is important for the use of ILs for biomass treatment. The major IL classes are aprotic (AILs) and protic ionic liquids (PILs). Common AILs combine cations with permanent charges (e.g. imidazolium, quaternary ammonium or pyridinium groups, etc.) with flouros anions to produce liquids with high stability. Until recently, studies of biomass treatment using ILs have mostly been limited to imidazolium based AILs [29,30]. However, AILs suffer from high synthesis costs, and are often toxic and poorly biodegradable [31,32].

In contrast to AILs, PILs are synthesized via a simple neutralization reaction between a Brønsted acid and base, meaning they are cheap to produce [33]. Recently, PILs synthesized from environmentally benign, biological compounds have attracted research interest. Choline amino acid ILs (Ch[AA]), also known as bio-ILs [34], are composed of a cholinium cation and an amino acid anion, have low toxicity as well as good biodegradability [35,36], and can be applied without removal of water following synthesis. Combined, these factors mean bio-ILs are more economically viable than AILs [37,38].

Recently our group investigated aqueous Ch[AA] mixtures with water contents of up to 59% as cost efficient treatment agents for lignite and thermal coal [38]. For both coals, cholinium arginate (Ch[Arg]) was clearly the most effective treatment agent (solubilised up to 68% of the coal mass). A second study revealed that Ch[AA] IL treatment of algae significantly increased the fraction of extractable lipids. In particular, treatment of *algae spirulina* with Ch[Arg] led to 96% of extraction of lipids, revealing the algae cell walls were effectively broken [37,38]. Several other papers have also found Ch[Arg] is the best performing IL for the treatment of lignocellulosic biomass [39,40].

We recently completed a computational study to reveal the atomic scale origin of the performance of Ch[Arg]. We used high-level G4(MP2) calculations to show that for R-OH···[Arg]Ch systems, [Arg] adopts a closed (ring) conformation, with the guanidine sp^2 nitrogen forming a H-bond with the H-bond donor group. The cation charge group associates closely with the anion charge centre, and the ring structure places the cation charge group in close proximity to the hydrogen bond formed by the H-bond donor and anion guanidine sp^2 nitrogen. This leads to polarisation of the H-bond: the charge on partial negative atoms becomes more negative, and the partial positive charge of the proton increases, leading to unusually strong H-bonds. This accounts for the effectiveness of Ch[Arg] for biomass treatment; the strong H-bonds it forms are best able to disrupt the biomass structure [41].

The interactions of Ch[AA]/pure water systems with pinewood are unexplored. While, Ren et al. used Ch[Arg] IL for pinewood treatment, it was in the presence of sea water (for reasons of downstream economics) which hinders fundamental interpretation and further does not address the effect of varying the anion type for studies of wood [40]. In this study we examine interactions of pinewood with Ch[AA] bio-ILs with different anions with focus on the characterization of the biomass residues. Elemental analysis and X-ray diffraction measurements were performed to elucidate compositional and structural changes and thermogravimetric analysis use to probe how these changes affect pyrolysis. We aim to better understand how the interactions of the bio-ILs with pinewood differ to those in our earlier work with coal and algae, in order to elucidate whether best performing anion structures differ between biomass types.

2. Materials and methods

Aqueous choline hydroxide solution (46 wt%), L-arginine (≥98%), L-aspartic acid (≥98%) and glycine (≥98.5%) were purchased from Sigma Aldrich and used without further purification. Ionic liquids were synthesized via simple acid base reaction as described by To et al. [38] and used without purification.

Australian Pinewood sawdust, obtained from local source, was ground to reduce the particle size below 60 mesh using a cutting mill. Prior to IL treatment the sawdust was dried under vacuum (~1.5 mbar) at 60 °C for 24 h. Experiments confirmed that no further mass loss can be observed after that time. The subsequent IL treatment was performed at a biomass load of 100 mg biomass per mL of IL at 90 °C or 120 °C for 24 h at ambient atmosphere under vigorous stirring. The treatment was stopped by adding approximately 25 mL of DI water to the samples. Samples were then centrifuged at 2500 rpm for 5 min using a Hettich Rotana 460 centrifuge. The solid residues were washed using 25 mL DI water seven times and subsequent centrifuging at 2500 rpm for 5 min; conductivity measurements of the final wash solution were the same as pure water within error. The solid residue was dried under vacuum (~1.5 mbar) at 60 °C for 24 h. The weight loss percentage of treated pinewood was determined by subtraction of the sample mass after treatment from the initial pinewood mass.

For the determination of volatile carbon and char content, TGA was performed on a TGA Q5000 (TA Instruments) under nitrogen flow of 150 $mL\,min^{-1}$. Approximately 4.5 mg of treated or untreated biomass sample was weight into a platinum pan and dried at 100 °C for 10 min. The sample was then heated at 10 $°C\,min^{-1}$ heating rate and equilibrated at 550 °C for 30 min. Measurements were performed in triplicate with only minor deviations observed.

XRD measurements were performed on a Bruker D8 Advance diffractometer equipped with a Cu Kα source. Samples that were collected in triplicate were combined to obtain an averaged sample for XRD. Scans were collected from $2\theta = 5°$ to 90° at a step size of 0.015° and a step time of 0.7 sec.

The morphologies of the raw and IL treated pine sawdust were investigated using a Zeiss 1555 field-emission scanning electron microscope (SEM). Samples were vacuum dried prior to imaging and mounted on aluminium stubs using conductive copper tape and sputter-coated with 6 nm of gold. Imaging was performed at a beam accelerating voltage of 10 kV.

Raw and treated pinewood were analysed using a FlashSmart CHNS/O analyser (ThermoFischer).

3. Results and discussion

This work investigates the treatment of pinewood with three Ch[AA] ILs, Ch[Arg], cholinium aspartate (Ch[Asp]) and cholinium glycinate Ch[Gly]. In earlier work, concerning coal and algae, Ch[Arg] and Ch[Gly] were the best performing bio-ILs [37–40], while typically Ch[Asp] performed poorly, so serves as a cross check and point of comparison. DI water was used under the same conditions as a control.