

Soaking of Pine Wood Chips with Ionic Liquids for Reduced Energy Input during Grinding

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Abstract

Ionic liquids are of great interest as potential solvents/catalysts for the production of fuels and chemicals from lignocellulosic biomass. Attention has focussed particularly on the pretreatment of lignocellulose to make the cellulose more accessible to enzymatic hydrolysis. Any biomass processing requires a reduction in the size of the harvested biomass by chipping and/or grinding to make it more amenable to chemical and biological treatments. This paper demonstrates that significant energy savings can be achieved in the grinding of pine wood chips when the ionic liquid is added before the grinding operation. We show that this is due to the lubricating properties of the ionic liquids and not to physico-chemical modifications of the biomass. A brief impregnation of the chipped biomass results in higher savings than a longer treatment.

Keywords

Ionic liquid, biomass, biorefinery, grinding, wood.

Introduction

Ionic liquids are becoming increasingly important as potential process solvents¹. An area of particular interest in the last few years has been their use as solvents for biomass pretreatment to produce renewable fuels and chemicals². It has been demonstrated that the size of the wood particles used in pretreatment processes affects their dissolution rates, since smaller particles have a greater surface area to volume ratio³. Hence, most studies to date have focused on the use of pre-ground biomass, with the assumption that any biomass-to-fuels process using ionic liquids will begin with

harvest and reduction to chips, probably at or close to that location, followed by grinding to powder. However, it has been noted that the energy consumption for grinding untreated wood to powder could be a process-limiting cost for any lignocellulose based fuel and/or chemicals production process⁴. Hence the question arises of whether a more energy efficient process can be achieved by adding the ionic liquids to the biomass chips prior to grinding.

Our previous investigations of the action of ionic liquids on pine wood chips (10 x 10 x 5 mm) showed that ionic liquids have a range of effects upon the wood, from considerable swelling of the chips with some ionic liquids to no swelling at all with others⁵. This study also showed that ionic liquids with strongly hydrogen-bonding anions gave partial dissolution of the biomass, via dissolution of cellulose, whereas in another study we showed that ionic liquids of the [HSO₄]⁻ anion gave other ionic liquids gave partial dissolution of the biomass, via dissolution of lignin.⁶ Hence, here we investigate a number of ionic liquids with known effects on pine chips, considerable swelling and partial dissolution via cellulose dissolution, partial-swelling and partial dissolution via lignin dissolution and non-swelling, non-dissolving. No other combination of these behaviours is currently available.

Experimental

Synthesis

All reagents were purchased from Aldrich, unless otherwise stated. 1-Methylimidazole (Acros Organics) and 1-butylimidazole were distilled under vacuum from potassium hydroxide. 1-Chlorobutane was distilled over P₂O₅. Ethyl acetate and acetonitrile were supplied by VWR and distilled over calcium hydride. Ethanol, methanol, DMSO, dimethyl carbonate, sodium citrate, citric acid, petroleum spirit, perfluorohexane, high-boiling silicone oil (Acros Organics) and perfluoropolyether (PFPE, Fomblin Y 06/6) were used as received. 1-Butyl-3-methylimidazolium *bis*(trifluoromethylsulfonyl)imide ([C₄C₁im][NTf₂]) and 1-butyl-3-methylimidazolium hydrogen sulfate ([C₄C₁im][HSO₄]) were prepared using literature procedures.^{6,7} The synthesis of 1-butyl-3-methylimidazolium acetate ([C₄C₁im][MeCO₂]) is detailed in the electronic supplementary information (ESI). The ionic liquids were dried *in vacuo* at elevated temperature. Particle size analysis was performed using a set of Griffin & George test sieves and a Retsch AS 200 basic Vibratory Sieve Shaker.

Preparation of wood chips

Pine (*Pinus radiata*) sapwood was obtained from a 15 year old tree harvested at Silwood Park, Ascot, in June 2008. All wood was taken from material sawn from the main trunk. Pine sapwood specimens of dimensions 8 mm x 7 mm x 7 mm were prepared. Specimens were stored air-dried at room temperature and humidity in the laboratory. The moisture content of the pine wood was 7% on an oven-dry basis.

Ionic liquid soaking of wood chips

Eight wood chips (*ca.* 1.25 g) were placed in a wide-mouthed Pyrex culture tube with screw cap and Teflon-lining, and 5 mL of the treatment liquid was added. The tubes were placed in an oven and held at 90 °C for the specified time. Subsequently they were allowed to cool to room temperature and the wood chips were removed and placed on paper towel to remove any excess liquid from their surface.

Grinding experiments

A Yellow Line A10 analytical grinder with stainless steel cutter from IKA Works Inc. was connected to a Voltech PM300 power analyser, via purpose-built wiring which allowed the meter's ammeter to be connected in serial and its voltmeter in parallel (Figure 1).

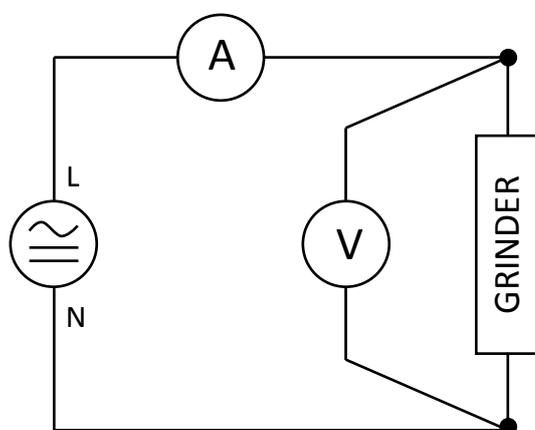


Figure 1: Circuit diagram for measuring power consumption of the grinder

The inbuilt water cooling apparatus was employed at all times (using tap water) to avoid overheating during grinding. Each sample was ground for 30 seconds as this was sufficient to grind the wood chips to a powder, and power consumption (current x voltage) was integrated over this period. Each experiment was replicated at least three times. It was observed that running the grinder empty prior to each experiment lead to increased reproducibility. Although an insert was used to reduce the working volume of the grinder, occasionally some chips would adhere to the sides of the chamber away from the blades and not be ground. This happened more frequently with viscous mixtures of liquid and wood powder. The data of such experiments were not used. Grinding energy was calculated per gram according to Equation (1).

$$\text{grinding energy per gram} = \frac{\text{power consumption} - \text{empty}}{\text{sample weight (air - dried)}} \quad (1)$$

Where *empty* is the average power consumption of the grinder running empty. Energy saving was calculated relative to untreated wood according to Equation (2), where *untreated* is the average energy required to grind 1 g of untreated wood chips.

$$\text{energy saving} = \frac{\text{untreated} - \text{grinding energy per gram}}{\text{untreated}} \times 100\% \quad (2)$$

Error bars in all figures represent the standard error associated with each data point, calculated according to Equation (3).

$$\text{Standard error} = \frac{\text{standard deviation}}{\sqrt{\text{no. of replicates}}} \quad (3)$$

Particle size analysis

After grinding, samples were soaked overnight in 20 mL of an appropriate volatile solvent (in all cases methanol, except petroleum spirit used for silicone oil and perfluorohexane for Fomblin). They were then filtered, rinsed twice with 5 mL of the solvent and left to air-dry for at least 24 hours. The resulting dry powder was gravimetrically checked for significant quantities of residual treatment liquid. The powder was then passed through a nested column of sieves with decreasing pore sizes (2 mm – 53 μm) by shaking on a vibratory sieve shaker for 8 minutes. The percentage weight of material retained by each sieve was measured, and from this data the log-normal distribution mass median diameter (D_{50}) was calculated, *i.e.* the particle size that 50 % of the sample is smaller than by mass. It is used herein as a measure of the wood powder's average particle size, and was calculated by linear interpolation⁸ using Equation (4).

$$D_{50} = 10^{\left[(\log x_2 - \log x_1) \times \left(\frac{50 - y_1}{y_2 - y_1} \right) + \log x_1 \right]} \quad (4)$$

Where x_1 and x_2 are the pore sizes of the sieves which allowed just under and just over 50% of the sample to pass through by weight, respectively, and y_1 and y_2 are the percentages of material passing through those sieves.

Enzymatic saccharification

Enzymatic saccharification was performed according to laboratory analytical procedure (LAP) "Enzymatic saccharification of lignocellulosic biomass" (NREL/TP-510-42629) on the washed and air-dried biomass samples. Using sieves, 150 mg portions of a known particle size range were prepared from each sample. The 180-850 μm range was used in most cases, except for those in which unground chips or a finer fraction (53-150 μm) were also investigated. The enzyme preparations used were Celluclast, a cellulase mix from *Trichoderma reesei*, and Novozyme 188 β -glucosidase (both from Sigma-Aldrich) which can also hydrolyse hemicellulose due to its hemicellulolytic activity. 60 μL of each preparation was used. Glucose and hemicellulose (mannose, xylose and galactose) yields were analysed using a JASCO HPLC system with RI detector, equipped with an Aminex HPX-87H column from Biorad using a 10 mM sulfuric acid mobile phase, 0.6 ml/min flow rate and a column temperature of 35°C. The yields are given as a percentage of the oven-dried sample weight

after treatment. The moisture content of the air-dried wood powder samples was determined according to LAP “Determination of Total Solids in Biomass and Total Dissolved Solids in Liquid Process Samples” (NREL TP-510-42621). 300 – 500 mg of air-dried biomass was wrapped in aluminium foil and heated to 105 °C overnight. The samples were weighed after cooling in a desiccator for 5 minutes, and the moisture content calculated according to Equation (5). The moisture content was in the range 5 – 9%.

$$\text{moisture (\%)} = \frac{m_{\text{air dried}} - m_{\text{oven dried}}}{m_{\text{oven dried}}} \times 100\% \quad (5)$$

Results and discussion

The aim of this study is to compare the energy demand for grinding wood chips with or without an ionic liquid treatment. For this purpose the effect of different ionic and molecular liquids were investigated as well as process variables such as soaking time and water addition (Table 1 and Figure 2). As with our previous investigations with pine chips,^{5,6} the wood was used in air-dried form and thus contained a significant amount of water. Rigorous drying would require a substantial additional energy input which would be an undesirable cost for any biomass pretreatment process. Due to the presence of water in the system the ionic liquids were not extensively dried prior to use. The moisture contents of the two hydrophilic ionic liquids used in this study [C₄C₁im][HSO₄] and [C₄C₁im][MeCO₂] were 1 wt% and 6 wt%, respectively. These differences arise because the moisture content of the ionic liquids in equilibrium with air varies widely with the ions present, particularly the anion⁹.

Grinding energy

Our previous work on the effects of a variety of ionic liquids on pine wood chips demonstrated that different anions led to different degrees of swelling of the chips⁵. We hypothesised that this would have an impact on the energy required to grind the chips. Hence, we selected three ionic liquids for this study, each of which gives different degrees of swelling and varying ability to dissolve cellulose or lignin. [C₄C₁im][NTf₂] does not induce swelling and there is no evidence for dissolution of cellulose nor lignin; [C₄C₁im][HSO₄] gives some pine wood swelling; it extracts and dissolves lignin, but is not able to dissolve cellulose;⁶ [C₄C₁im][MeCO₂] gives significant swelling of pine chips and can dissolve cellulose and lignocellulosic materials.⁵ Our studies and of others to date suggest that the effect of changing the ionic liquid cation on the swelling of pine chips is secondary to the anion effect and so the cation was kept constant throughout this study.

The grinder running empty was found to consume 0.93 Wh over the measured 30 seconds (Table 1). The energy demand to grind untreated wood chips was 1.04 Wh (normalised to one gram of wood) giving an additional energy requirement of 0.11 Wh/g (Equation (1)). We use this value for comparison with the treated wood, e.g. an energy requirement of 0.98 Wh when grinding one gram of wood indicates a saving of approximately 50% in comparison to the untreated sample (Equation (2)). The particle size distribution of the ground wood was also measured for each sample and the average particle size calculated to determine whether any energy savings were related to less effective grinding (Figure 4 and **Error! Reference source not found.**).

Table 1: Energy consumption (normalised to 1 g), relative energy saving and particle size of resulting powder for grinding of pine wood chips.

Treatment Liquid	Treatment Conditions	Energy Consumption (Wh)	Energy saving relative to dry wood (%)	Average particle size (D_{50} , μm)
[C ₄ C ₁ im][NTf ₂]	90°C, 1 h	0.956	75	219
[C ₄ C ₁ im][HSO ₄] _{80%}	90°C, 1 h	0.970	62	392
[C ₄ C ₁ im][HSO ₄]	90°C, 1 h	0.974	59	223
[C ₄ C ₁ im][MeCO ₂] _{80%}	90°C, 1 h	0.986	49	466
Silicone oil	90°C, 18 h	0.991	44	302
Silicone oil	90°C, 1 h	0.993	43	318
PFPE Fomblin Y 06/6	90°C, 1 h	0.992	43	243
[C ₄ C ₁ im][MeCO ₂]	90°C, 1 h	1.000	36	416
DMSO	90°C, 1 h	1.007	31	458
Organosolv	90°C, 1 h	1.008	29	826
[C ₄ C ₁ im][HSO ₄] _{80%}	90°C, 18 h	1.026	14	457
Untreated wood	N/A	1.042	N/A	789
Empty grinder/silicone oil	N/A	0.936	N/A	N/A
Empty grinder	N/A	0.926	N/A	N/A

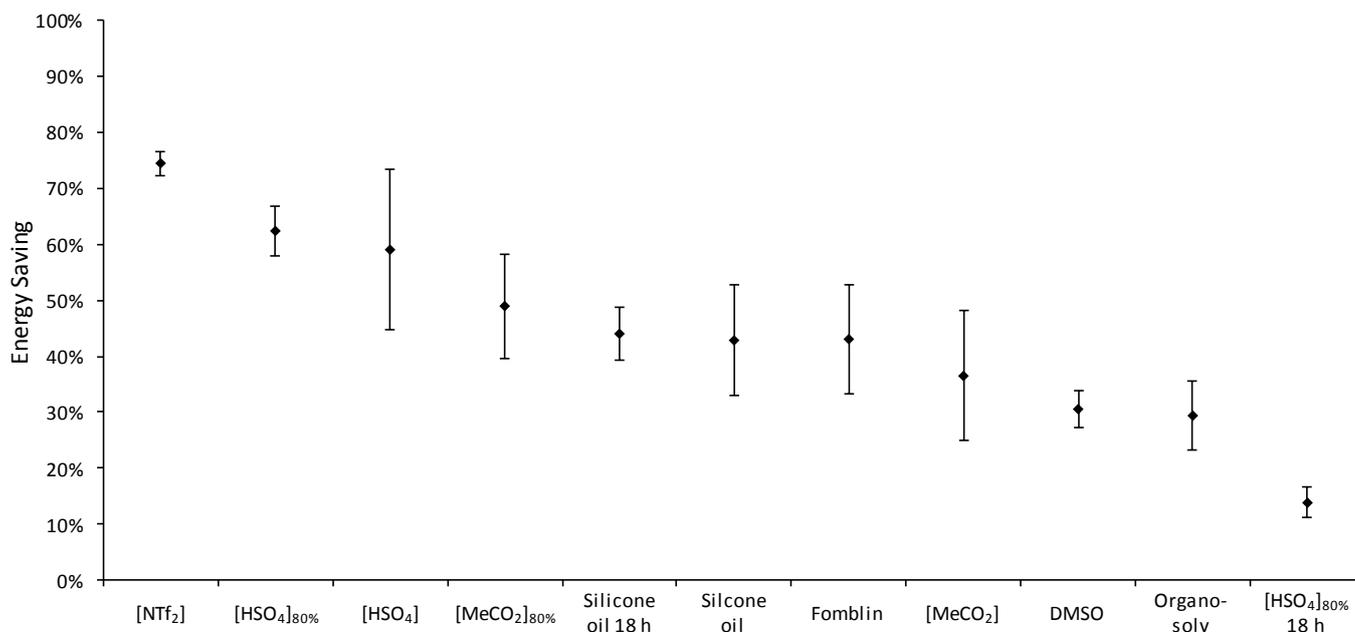


Figure 2: Energy savings for grinding of pine wood chips treated with various liquids (90 °C for 1 h except where otherwise stated) relative to untreated wood chips. Cation of all ionic liquids is [C₄C₁im].

The first three tests used pine chips that had been soaked either with $[\text{C}_4\text{C}_1\text{im}][\text{NTf}_2]$, $[\text{C}_4\text{C}_1\text{im}][\text{HSO}_4]$, or $[\text{C}_4\text{C}_1\text{im}][\text{MeCO}_2]$ at 90°C for 1 h. This time was chosen because we observed in preliminary experiments that it was sufficient to completely infuse wood chips with the liquids. This was checked by visual inspection of chips which had been cut in half in axial direction at the end of the soaking period. The effect of a longer impregnation time will be discussed in a separate section.

Figure 2 shows the standard errors of the energy savings between individual runs which are fairly large. This is due to the base consumption of the grinder being high compared to the energy consumed for the actual grinding. For example, the grinding of untreated wood accounted for only 11% of the total energy consumption. This imbalance is due to the small scale of the experiment.

Nevertheless we were able to observe clear trends. The energy input necessary to grind wood chips impregnated in the presence of $[\text{C}_4\text{C}_1\text{im}][\text{NTf}_2]$, $[\text{C}_4\text{C}_1\text{im}][\text{HSO}_4]$ or $[\text{C}_4\text{C}_1\text{im}][\text{MeCO}_2]$ for 1 h was reduced by 75%, 59% and 36% compared to air-dried wood, respectively. These savings are substantial and potentially process significant. This is the reverse order of the degree of swelling and dissolution of biomass fractions that is observed for these ionic liquids when used as pretreatments for pine chips.^{5,6} This demonstrates that it is not biomass decomposition that is leading to these savings.

Our previous work indicates that the sugar yield from the enzymatic saccharification of biomass with $[\text{HSO}_4]^-$ ionic liquids is improved by the addition of water to the system,⁶ whereas the presence of water significantly reduces the dissolution of cellulose by $[\text{MeCO}_2]^-$ ionic liquids. Therefore, we investigated the effect of increased water content on the grinding energy consumption as compared to the pure ionic liquid. We used two ionic liquid water mixtures, $[\text{C}_4\text{C}_1\text{im}][\text{HSO}_4]_{80\%}$ and $[\text{C}_4\text{C}_1\text{im}][\text{MeCO}_2]_{80\%}$, both containing 80 volume % ionic liquid, the remainder (20 vol%) being water. The use of $[\text{C}_4\text{C}_1\text{im}][\text{HSO}_4]_{80\%}$ did not lead to an energy saving significantly different to that of the pure ionic liquid (62% and 59%, respectively), while the use of $[\text{C}_4\text{C}_1\text{im}][\text{MeCO}_2]_{80\%}$ increased the energy saving compared to $[\text{C}_4\text{C}_1\text{im}][\text{MeCO}_2]$ (49% and 36%, respectively).

Ionic liquids have been demonstrated to be excellent lubricants¹⁰. To test whether the power savings were due to lubrication by the ionic liquid, we repeated the grinding experiments using wood chips that had been treated with other widely used lubricants. They were selected to be hydrophobic and therefore unable to chemically interact with the wood matrix. Both high-boiling silicone oil and perfluoropolyether gave an energy reduction of 43%, which is a substantial saving but lower than some of the savings observed for ionic liquids.

To exclude the possibility that the entire reduction of grinding energy was simply the result of wetting the sample, we repeated these measurements with DMSO and a 1:1 water ethanol mixture, representing the solvent mixture used for Organosolv pulping.¹¹ These liquids are not noted to be effective lubricants. The presence of the Organosolv mixture gave an energy reduction of 29%, and the presence of the polar organic solvent DMSO reduced the energy demand similarly by 31%. Although both solvents provided some energy reduction, it was lower than the savings achieved by either the ionic liquids or the established molecular lubricants.

Finally, we excluded the possibility that the energy savings were due to these liquids simply lubricating the grinding mechanism of the instrument, with the observation that the empty grinder with added silicone oil (1 mL) gave almost the same values as for the completely empty grinder. Therefore the energy savings must be due to interaction between the liquid, biomass and blades.

Particle size after grinding

It is generally true that, all else being equal, grinding energy is largely proportional to the ratio between initial and final particle size.¹² Since in our study the starting particle sizes were all the same, it was possible that the energy savings were related to lesser grinding and larger final particle sizes. Therefore the particle size distribution after grinding was measured. Figure 3 shows that the wood was, in fact, ground to a *smaller* particle size when ionic liquids or lubricants were present, as a larger percentage of the particles could pass through the finer sieves. This is also indicated by the smaller average particle size D_{50} of the wood powder after immersion in ionic liquid or lubricant (Table 1, right column).

The smallest average particle size was measured for chips ground after a 1 h incubation in $[C_4C_1im][NTf_2]$ (219 μm) and neat $[C_4C_1im][HSO_4]$ (223 μm). The use of the lubricants Fomblin (243 μm) and silicone (318 μm) also resulted in production of smaller particle sizes compared to air-dried wood (789 μm). The particle size was considerably higher in the presence of the cellulose dissolving $[C_4C_1im][MeCO_2]$ (416 μm) compared to the other ionic liquids. The average particle size of the biomass was reduced in the case of DMSO (458 μm), while the Organosolv case (826 μm) produced on average larger particles than untreated wood. The presence of 20 vol% water in the ionic liquid seems to increase the D_{50} (329 $\mu m > 219 \mu m$ for $[C_4C_1im][HSO_4]$ and 466 $\mu m > 416 \mu m$ for $[C_4C_1im][MeCO_2]$).

Figure 4 illustrates that the energy savings are not connected to larger final particle sizes. It is rather the opposite: in most cases the energy savings exist despite an improved particle size reduction (with the exception of the Organosolv case) and we can confirm that the energy savings are indeed due to lubrication effects.

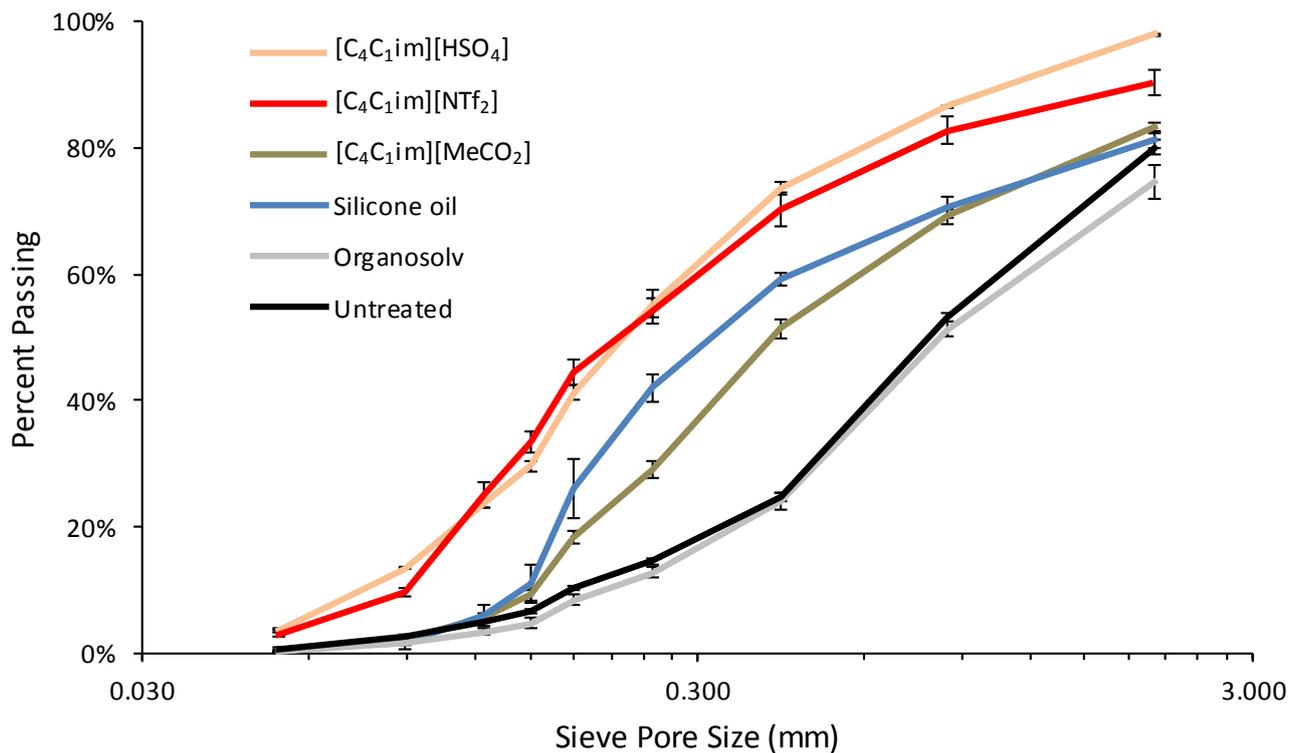


Figure 3: Particle size distributions of ground pine wood chips treated with different liquids (90°C, 1 h), shown as percentage weight of sample passing through different sieve pore sizes (log scale).

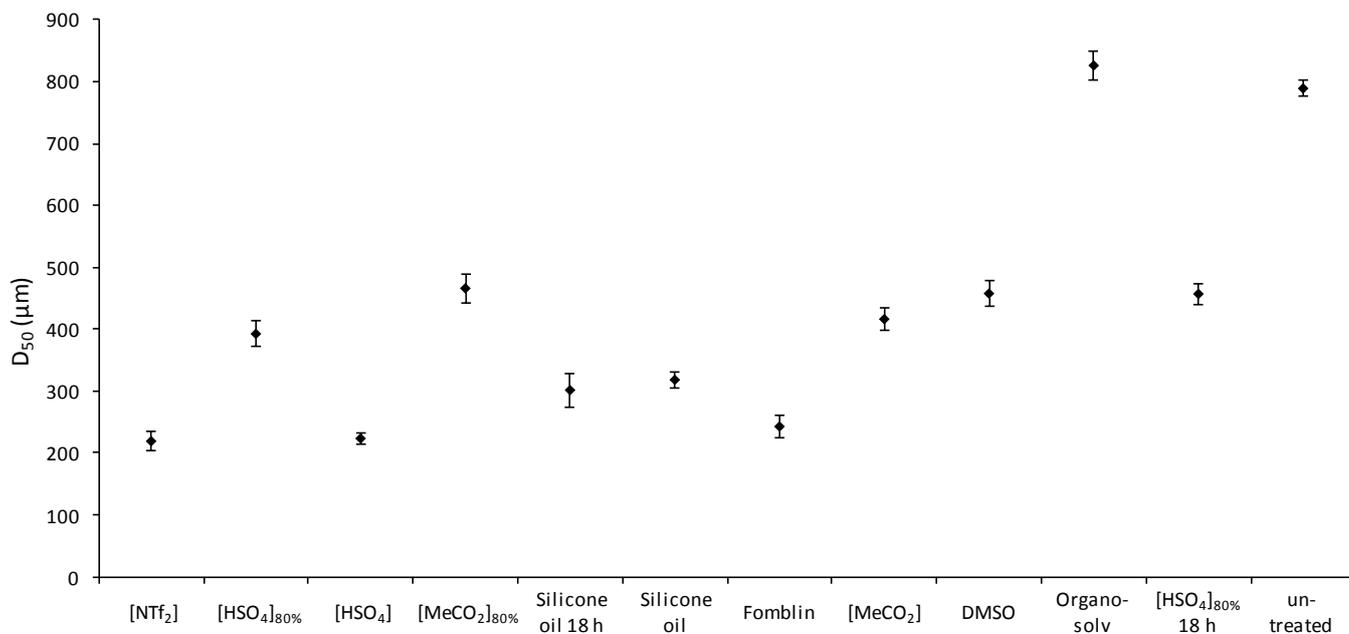


Figure 4: Average particle size (D_{50}) of ground pine wood chips treated with various liquids (90 °C for 1 h except where otherwise stated). Cation of all ionic liquids is $[C_4C_1im]$. The data are ordered according to the energy savings (highest saving on the left).

Morphology

The morphology of the wood powder was visibly different depending on which treatment liquid the wood chips had been exposed to (Figure 5). Wood chips treated with Organosolv or DMSO gave long and relatively large particles, whereas those treated with silicone oil and Fomblin resulted in a fluffy powder. Treatment with ionic liquids resulted in a more grainy appearance.

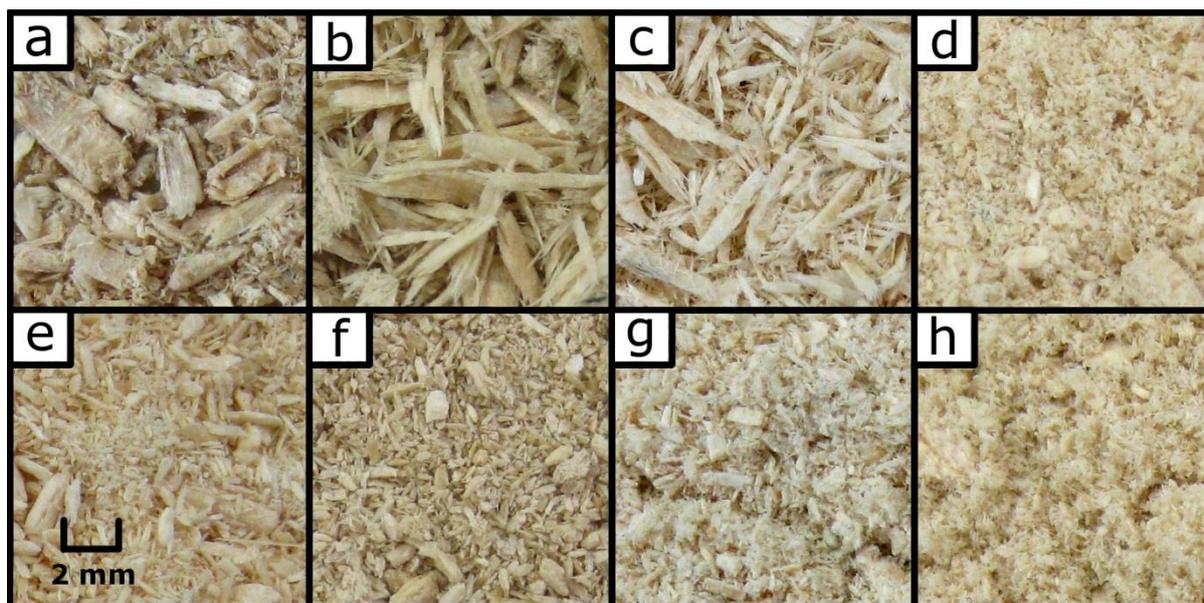


Figure 5: Photographs of ground wood chips after treatment at 90°C for 1 h with various liquids: a) no liquid, b) Organosolv, c) DMSO, d) silicone oil, e) $[C_4C_1im][HSO_4]$, f) $[C_4C_1im][MeCO_2]$, g) $[C_4C_1im][NTf_2]$, h) Fomblin.

Effect of soaking time

We compared the energy demand for grinding pine chips treated with either $[C_4C_1im][HSO_4]_{80\%}$ or silicone oil for a longer time. Collecting energy data for wood chips treated with $[C_4C_1im][MeCO_2]$ and $[C_4C_1im][NTf_2]$ at 90°C for 18 hours was not possible, as the chips adhering to the walls of the grinder's chamber prevented complete grinding. Our previous results showed that longer ionic liquid pretreatment results in greater breakdown of the wood's structure.⁶ For wood chips treated at 90°C for 18 hours, silicone oil gave an almost identical energy saving and average particle size to those treated for only 1 hour (44%, 302 μm and 43%, 318 μm , respectively). In the case of $[C_4C_1im][HSO_4]_{80\%}$ on the other hand, diminished energy saving and a larger particle size were observed when the chips were treated for 18 hours compared to 1 hour (14%, 457 μm and 62%, 392 μm , respectively). We attribute this to increased elasticity/ductility of wood chips, which have had sufficient pretreatment with the ionic liquid to induce significant swelling and modification of the wood matrix. It is known that grinding of ductile materials consumes more energy than grinding brittle substrates.¹³

Further optimisation of the impregnation time is certainly desired and the optimum time (and temperature) may well vary for different feedstocks and ionic liquids.

Enzymatic saccharification

To investigate whether the wood structure was affected by impregnation with ionic liquids, the powdered samples were subjected to a standardised enzymatic saccharification procedure and the sugar release was measured (data shown in the ESI). In our previous study we showed that treatment of pine wood with ionic liquids can lead to increased saccharification yields and that the yields are related to changes in the composition of the wood.^{5,6}

In general, the digestibility of the pine wood was not significantly altered by any of the incubation experiments. Only one of the treatment conditions, soaking in undiluted [C₄C₁im][MeCO₂] at 90°C for 1 h, gave a glucose yield significantly higher than untreated wood (see ESI). The increased yield (7.5% compared to 2.8%) suggests that the structure of the wood was somewhat altered by the impregnation making the cellulose more accessible to cellulases. Interestingly, this treatment delivered the second-lowest energy saving among the ionic liquid containing solvents. Incubation with [C₄C₁im][HSO₄]_{80%} for 18 h, which gave the lowest energy saving of all, did not lead to enhanced glucose release. However, there was a greater yield of hemicellulose sugars compared to untreated wood (3% compared to less than 1%) and a measurable mass loss (data also shown in ESI).

This suggests that significant structural changes during ionic liquid soaking are accompanied by lower energy savings and larger final particle sizes. Therefore we conclude that the impregnation step should be brief and conducted at low temperature, in order to harness the lubricating properties of the ionic liquids as well as the low elasticity of untreated wood chips.

Conclusions

Soaking pine wood chips with ionic liquids gives significantly more efficient grinding of these, by giving reduced energy requirement for the grinding and a greater size reduction at constant grinding time. This behaviour arises from their tribological properties and not from chemical or structural modification of the wood. The best savings (50-70%) were obtained when the ionic liquid impregnation was short and alteration to the wood structure appeared to be minimal. Our results suggest that for any future biomass-to-fuels process using ionic liquids the most energy efficient process will begin with harvest and size reduction to chips, with current assumptions probably at or close to that location, followed by soaking with ionic liquid under conditions that do not lead to biomass decomposition, then grinding and then pretreatment at higher temperature.

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