



Partial dissolution of ACQ-treated wood in lithium chloride/*N*-methyl-2-pyrrolidinone: Separation of copper from potential lignocellulosic feedstocks

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ABSTRACT

A cellulose solvent system based on lithium chloride (LiCl) in *N*-methyl-2-pyrrolidinone (NMP) was used to assess the merits of partial dissolutions of coarsely ground wood samples. Alkaline Copper Quaternary (ACQ)-treated pine wood was of particular interest for treatment given the potential to generate a copper-rich stream apart from solid and/or liquid lignocellulosic feedstocks. Treatment with NMP alone gave yields of soluble materials that were higher than typical extractives contents thereby suggesting a limited degree of wood dissolution. Inclusion of LiCl, which disrupts hydrogen bonding, gave lower wood residue recoveries (i.e., higher dissolution) with higher LiCl concentration. Lower wood residue recoveries coincided with lower Klason lignin and hemicellulose-derived sugar contents in the wood residues. After treatment with 8% LiCl in NMP, subsequent filtration afforded 34% of the ACQ-treated sapwood as a wood residue retaining only 2% of the original copper. Pouring the filtrate over an excess of water resulted in the recovery of 30% of the solids and 50% of the copper together as a copper-enriched lignocellulosic precipitate. Results demonstrate a solvent system showing potential as a means to separate heavy metals from preservative-treated wood and to recover lignocellulosic feedstocks that may be suitable for use in a biorefinery.

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1. Introduction

Under the biorefinery concept, the production of biofuels and/or chemical feedstocks can complement current industrial consumers of woody biomass by the extraction of wood flakes/chips before their use in composites/paper products (Ragauskas et al., 2006; Huang et al., 2009; Naik et al., 2010). Alternatively, a biorefinery may focus on converting the bulk of the wood polysaccharides to bioethanol (via saccharification and fermentation); thermochemical options include conversions to bio-oil (via pyrolysis) or synthesis gas (via gasification). Seemingly still on the fringe of the biorefinery concept is the dissolution of wood (Stark, 2011; Sun et al., 2011).

Ionic liquids, which are low-melting point salts, represent a relatively new class of solvents for cellulose and wood dissolution (Kilpelainen et al., 2007; Pu et al., 2007; Xie et al., 2007; Mäki-Arvela et al., 2010). Another option is the cellulose solvent system of lithium chloride (LiCl) in *N,N*-dimethylacetamide (DMAc) which continues to receive attention for the dissolution of both pure cellulose (Dupont, 2003; Henniges et al., 2011) and more complex lignocellulosic substrates (Berthold et al., 2004; Furuno et al., 2006); while the

mechanisms of dissolution are a matter of debate, it is generally accepted that lithium ions link to the solvent carbonyl leaving the chlorine anion as an efficient nucleophile that can disrupt hydrogen bonding (Dupont, 2003; Pinkert et al., 2010). In either case, applying such solvent systems to wood is particularly interesting given the possibility of selectivity in the dissolution of individual lignocellulosic polymers (e.g., cellulose, hemicelluloses, lignin) or distinctive lignocellulosic fragments (Furuno et al., 2006).

Analogous to LiCl/DMAc, LiCl added to *N*-methyl-2-pyrrolidinone (NMP) can also be used to dissolve cellulose (Dawsey and McCormick, 1990). For decades, NMP has been viewed as a relatively benign solvent with widespread uses in coatings, agricultural chemicals, and even personal care products (Reisch, 2008). NMP is an efficient solvent used for the extraction of tars from coal and their analysis by size exclusion chromatography (Herod et al., 2000). Richaud et al. (2000) used NMP at room temperature and reflux to extract not only coal, but also forest biomass for comparison; interestingly, the extract yields from the forest biomass at room temperature and under reflux were high at 12% and 32%, respectively. These unusually high yields of soluble materials suggested not only the recovery of those biomass constituents commonly identified as extractives, but also raises the possibility of the partial dissolution of the lignocellulosic matrix.

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While partial dissolution of wood may indeed provide avenues to the production of biofuels and/or chemical feedstocks from a renewable resource, it may also provide recycling options for wood waste currently sent to landfills. For example, partial dissolution may allow the separation of toxic heavy metals from preservative-treated wood taken out of service. Widespread recycling of preservative-treated wood by chemical extraction has yet to materialize because of technical limitations, logistical issues, and/or excessive costs (Shupe and Hse, 2006). Liquefaction has shown promise for separating heavy metals as precipitates apart from a degraded and reacted liquid wood product, the latter being used in phenolic adhesive resins systems (Lin and Hse, 2005). It remains to be determined whether the partial dissolution of preservative-treated wood with a cellulose solvent system can result in similar avenues for separating heavy metals from treated wood and provide solid and/or liquid lignocellulosic feedstocks for the generation of biofuels and/or chemicals.

The objective for the present study was to explore the functionality of NMP with and without the addition of LiCl, for the partial dissolution of wood. Given the potential for selectivity in lignocellulosic polymer dissolution, preservative-treated wood samples were used to explore the concept of selective heavy metal removal in concert with partial dissolution of the lignocellulosic matrix.

2. Materials and methods

2.1. Sample preparation

Southern pine (primarily loblolly pine, *Pinus taeda* L.) wood chips and peeled bark were obtained from a local paper mill and dried under ambient conditions. Samples were ground in a Wiley mill equipped with a 2 mm mesh screen; wood chips were first split into matchstick-sized pieces to facilitate grinding. An Alkaline Copper Quaternary (ACQ)-treated timber (ca 14 cm × 14 cm × 2.4 m) was purchased from a local lumberyard and cut with a table saw to obtain cross sections. Clearly discernable heartwood and sapwood zones were processed as above to obtain heartwood and sapwood particle samples. All samples were classified on a Rotap shaker to obtain particles passing through a 35 mesh (0.5 mm) screen and retained on an 80 mesh (0.18 mm) screen. Moisture contents were determined by drying samples in an oven at 103 ± 2 °C.

2.2. Solvent extractions

Wood particle samples were extracted with ethanol:toluene (7:3, 6 h) and then ethanol (6 h), using a Soxhlet apparatus (ASTM, 1996). Extracts were concentrated by rotary evaporation, transferred to small vials, dried under a stream of dry nitrogen, and then dried completely *in vacuo* before weighing to determine extractives yields. Extractive-free wood samples were dried in a fume hood and then in an oven (103 ± 2 °C) for comparison. For extractions with NMP, oven-dried wood particle samples (2 g each) were suspended in NMP (25 mL) in a round bottom flask and refluxed (bp 202 °C) under nitrogen for 1 h (Richaud et al., 2000; Álvarez et al., 2004). Wood residues were filtered over a Whatman GF/A filter in a Büchner funnel and then briefly rinsed with NMP and water before drying in an oven. Although the soluble materials obtained by refluxing in NMP could be recovered by freeze drying, they were generally discarded.

2.3. Partial lignocellulosic matrix dissolution

Lithium chloride and oven-dried (103 ± 2 °C) wood particle samples were stored over desiccant (Drierite). To an oven-dry 3-

neck flask (50 mL), containing a magnetic stir bar, were added dry wood particles (2 g), LiCl (Sigma–Aldrich, 99%+) and NMP (Alfa Aesar, 99.5%+) under a gentle purge of dry nitrogen; the amounts of LiCl and NMP were varied to obtain 1%, 2%, 4%, 6% and 8% (w/w) LiCl concentrations with an approximate total volume of the LiCl/NMP complex being 25 mL. The contents of the flask were stirred and heated to reflux. After a treatment time of 1 h, the contents were cooled slightly and then vacuum filtered warm over a Whatman GF/A filter. The retained wood residues were rinsed with NMP (75 mL) to obtain a filtrate that was set aside for later processing. Wood residues were then rinsed with deionized water until the aqueous filtrates were essentially colorless (ca 400–1000 mL). The wood residues were oven-dried and weighed. Each LiCl/NMP filtrate from above was poured over water (1500 mL) with vigorous stirring, typically resulting in the generation of a flocculent precipitate. The resultant suspension or turbid solution was allowed to stand overnight before vacuum filtering over previously dried and weighed Whatman GF/A filter. The precipitate on the filter was dried in an oven and weighed. Filtrates at this stage of the experiment were discarded.

2.4. Sample analyses

Klason lignin and sugar analyses were carried out on extractive-free and NMP treated samples using an established method (Davis, 1998). The acid-insoluble residue (Klason lignin) was washed with hot water, dried and weighed. Klason lignin values were corrected for residual ash content. Sugars present in the hydrolysates were determined by anion-exchange high-performance liquid chromatography on a system equipped with a Carbo-Pac PA1 column and detection using a pulsed amperometric detector.

Determinations for elemental copper were carried out by inductively coupled plasma atomic emission spectrometry (ICP-AES) (Jobin Yvon Ultima, Horiba Scientific) using American Wood Protection Association (AWPA) Standard Method A21-08 (AWPA, 2010a). Prior to ICP-AES analysis, samples were subjected to microwave assisted digestion in a solution of nitric acid and hydrogen peroxide using AWPA Standard Method A7-04 (AWPA, 2010b).

Fourier transform infrared (FTIR) spectra were collected using a Thermo Nicolet Nexus 670 spectrometer equipped with a Thermo Nicolet Smart Golden Gate MKII single reflection ATR accessory. Specimens were placed on the diamond crystal and pressure applied with the anvil affixed to the accessory clamping mechanism. Three spectra were collected for each sample and averaged.

3. Results and discussion

3.1. Refluxing with NMP alone

3.1.1. Partial lignocellulosic matrix dissolution

Partial dissolution of the lignocellulosic matrix of wood appeared feasible given a report that refluxing of woody biomass with NMP resulted in yields of soluble materials (Richaud et al., 2000) that were much higher than extractives contents typically obtained with standard solvent systems. In an attempt to

Table 1
Average yields of soluble materials from wood and bark samples after standard Soxhlet extraction or refluxing in NMP.

Sample	Soxhlet extracted (%)	NMP reflux (%)
ACQ-treated sapwood	3.9	13.0
ACQ-treated heartwood	10.2	14.6
Pulp mill chips	2.2	11.0
Pulp mill bark	8.2	41.8

Table 2

Copper determinations for ACQ-treated wood samples before processing and after standard Soxhlet extraction or refluxing in NMP (na = not applicable).

Sample	Sapwood		Heartwood	
	Copper concentration (mg g ⁻¹)	Copper removed (%)	Copper concentration (mg g ⁻¹)	Copper removed (%)
Before processing	9.69	na	0.29	na
Soxhlet extracted	8.41	13.2	0.23	21.5
NMP reflux	9.40	3.0	0.18	40.5

reproduce these findings, wood and bark samples were refluxed in NMP and gave yields of 11% and 42%, respectively (Table 1). The forest biomass used by Richaud et al. (2000) was likely rich in bark given the reported high yields of soluble materials (32%). For comparison, standard Soxhlet extraction of our wood and bark samples gave typical total extractives contents of 2% and 8%, respectively (Table 1). The higher total extractives content for the heartwood sample (10%), compared to the sapwood sample (4%), was expected. We account for the much higher yields of soluble materials with NMP, especially for the ACQ-treated sapwood (13%) and pine pulp mill chips (11%, control), to the partial dissolution of at least one of the lignocellulosic polymers (i.e., cellulose, hemicelluloses and/or lignin).

3.1.2. Copper retention

Residual ACQ-treated wood particles from the standard Soxhlet extractions and NMP treatment (under reflux) were subjected to elemental analysis to determine any differences in copper retention/removal. It should be recognized that the wood preservation industry focuses on treating the decay susceptible sapwood, and not the decay resistant heartwood, which in pines, is naturally infused with water-repellent resinous extractives. The much higher concentration of copper in the unextracted control for the ACQ-treated sapwood (9.69 mg g⁻¹), relative to that in the heartwood (0.29 mg g⁻¹), was therefore expected (Table 2). Both the standard Soxhlet extractions and NMP treatment of the ACQ-treated sapwood and heartwood samples gave wood residues with lower copper concentrations. Standard Soxhlet extraction appeared more effective for removing copper from the sapwood than the heartwood. Given the low concentration of copper present in the heartwood, the relatively high proportions of copper removed should be interpreted with caution. The results for the sapwood indicated that the extractives, and any lignocellulosic polymers possibly dissolved by the NMP treatment, did not have a significantly higher association with the copper from the preservative treatment. In practical terms, refluxing ACQ-treated wood with NMP would not give two product streams providing a bulk separation of copper apart from a lignocellulosic feedstock.

3.1.3. Sugar and lignin analyses

Standard analyses often used to characterize the chemical composition of wood (e.g., Klason lignin, sugars) were applied here with samples of the above “extractive-free” wood samples to assess whether refluxing with NMP was at all selective in dissolving

any of the lignocellulosic polymers (i.e., cellulose, hemicelluloses, lignin). Data were normalized to 100% for direct comparisons. Results showed the Klason lignin and sugar data to be similar for all samples (Table 3). This suggested that any partial dissolution of the lignocellulosic matrix achieved by refluxing with NMP was not particularly selective.

3.2. Refluxing with NMP and LiCl

3.2.1. Partial lignocellulosic matrix dissolution

To increase the level of lignocellulosic matrix dissolution, it seemed prudent to modify our approach by disrupting those bonds holding the lignocellulosic polymers together, in particular, the hydrogen bonds in the cellulose framework. Recent research has focused on the dissolution of cellulose, wood pulps, and even the completely lignified cell walls of wood sawdust, in ionic liquids (Kilpelainen et al., 2007). However, the concept of dissolving cellulose in a solvent system having an ionic character is not new; cellulose solvent systems based on LiCl in DMAc have a longer history of use (Dupont, 2003). The mechanism of functionality suggested here is that the lithium ions are strongly associated with the carbonyl group of DMAc leaving the chloride anion as a highly active nucleophile for disrupting hydrogen bonds. The use of NMP, as an alternative to DMAc, has only been occasionally noted. Continuing our study using NMP, we decided to pursue the addition of LiCl to NMP and assess any enhancement of lignocellulosic matrix dissolution in terms of lignocellulosic polymer selectivity as well as the impact of any such selectivity on the partitioning of copper in ACQ-treated sapwood apart from the bulk of the lignocellulosic matrix.

Special care was taken during the experiments with LiCl to eliminate water since it was suggested to limit cellulose complex formation during treatments with DMAc (Dupont, 2003). To prevent oxidation, we continued to carry out all reflux treatments with a nitrogen purge. The concentration of LiCl, as a percent of the solvent mixture (w/w), ranged from 1% to 8% in NMP, the optimal range for LiCl in DMAc was reported to be from 5% to 9% (w/w) (Dawsey and McCormick, 1990). Results shown in Table 4 demonstrate that increased lignocellulosic matrix dissolution was achieved upon the addition of LiCl. Increasing concentrations of LiCl resulted in a linear decrease ($R^2 = 0.97$) in weights of wood residue recovered (Fig. 1). For comparison, the pulp mill chip control was treated under the same conditions and gave a similar

Table 3

Klason lignin and polysaccharide sugar contents for wood residues from ACQ-treated wood, and pulp mill chips, after refluxing in NMP. (Standard Soxhlet extracted pulp mill chips included as a control).

Treatment	Sample	Klason lignin (%)	Polysaccharide sugars (%)					
			Arabinan	Galactan	Rhamnan	Glucan	Xylan	Mannan
NMP reflux	ACQ-treated sapwood	30.6	0.5	2.6	0.0	51.1	6.0	9.2
	ACQ-treated heartwood	30.2	0.3	5.5	0.0	47.1	6.2	10.8
	Pulp mill chips	30.4	1.0	3.4	0.0	46.4	7.5	11.2
Soxhlet extracted	Pulp mill chips	30.0	1.1	2.1	0.1	47.1	6.7	12.9

Table 4
Average recoveries and copper determinations for wood residues and precipitates from ACQ-treated sapwood after refluxing in NMP with LiCl. (Copper concentration of ACQ-treated sapwood was 6.71 mg g⁻¹; nd = not determined).

LiCl (%)	Wood residue recovered (%)	Copper concentration in residue (mg g ⁻¹)	Copper recovered in residue (%)	Precipitate recovered (%)	Copper concentration in precipitate (mg g ⁻¹)	Copper recovered in precipitate (%)
1	62	0.10	1.5	0.12	nd	nd
2	57	0.09	1.4	0.02	nd	nd
4	50	0.14	2.1	0.02	nd	nd
6	44	0.07	1.1	0.02	nd	nd
8	34	0.16	2.3	30	11	54

relationship between LiCl concentration and wood residue recovered ($R^2 = 0.93$) albeit shifted to somewhat higher recoveries.

Complete dissolution was not achieved under the experimental parameters we employed. The highest level of dissolution achieved was approximately 66% for the ACQ-treated sapwood. Using that value and the total volume of the treatment mixture, the concentration of lignocellulosic material in solution was estimated to be 5%. This compares well to the reported 8% solubility of Norway spruce sawdust using an ionic liquid at an elevated temperature (110 °C) for 8 h (Kilpelainen et al., 2007). In an analogous manner as described for ionic liquids, we also attempted to form a “regenerated wood” by pouring the lignocellulosic-containing solution over an excess of water (Kilpelainen et al., 2007). Pouring the dark-colored filtrates we recovered over an excess of water gave turbid and dark-amber-colored liquids for all concentrations of LiCl, except 8%. In that case, a voluminous flocculent precipitate could be recovered by filtration that comprised about 30% of the starting mass of the original wood sample (Table 4). Analysis of this precipitate by FTIR spectroscopy gave a nondescript spectrum (not shown) that was similar to the spectra obtained from the wood residues, thus this precipitate represented our “regenerated wood”. For this treatment in particular (8% LiCl), approximately 36% of the starting mass of wood particles remained in solution.

3.2.2. Copper retention

Wood residues and precipitates recovered during the experiments with 8% LiCl in NMP were also analyzed for copper content to determine if the greater level of dissolution could provide the desired partitioning of a copper-rich stream apart from potential lignocellulosic feedstocks. Unlike the wood residue recovered by refluxing in NMP alone, the addition of LiCl resulted in wood residues for which the copper concentration was minimal, with copper recoveries of about 1% to 2% (Table 4). For the LiCl concentrations of 1% through 6%, the copper concentrations of the precipitates were not determined because of the minimal amount of material recovered. The precipitate from the 8% LiCl treatment was analyzed and had a much higher copper concentration (11%) than the corresponding wood residue (ca 0%); the amount of copper recovered in the precipitate accounted for nearly 54% of that in the original wood particle sample. The mechanism(s) by which the use of LiCl in NMP under reflux allows the copper to be partitioned remains to be determined. Nevertheless, here we demonstrate that under

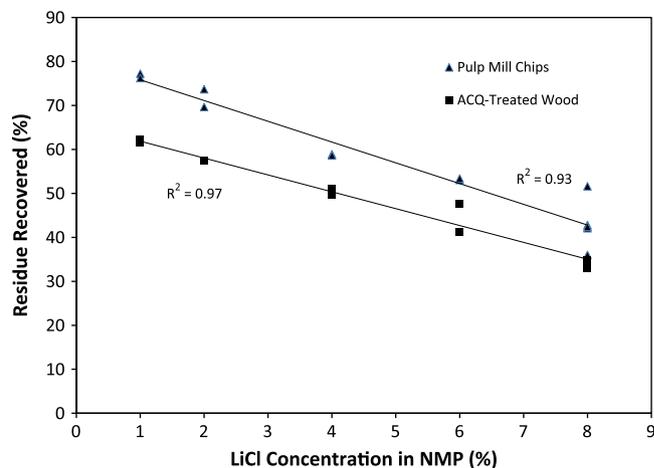


Fig. 1. Recoveries of wood residues from ACQ-treated sapwood and pulp mill chips after refluxing in NMP with LiCl.

conditions resulting in partial dissolution, preservative-treated wood may afford a copper-rich stream for recycling apart from copper-depleted lignocellulosic feedstocks for generating biofuels and/or chemicals.

3.2.3. Sugar and lignin analyses

Parallel to the copper determinations, the wood residues from the ACQ-treated sapwood samples refluxed in NMP with LiCl were subjected to Klason lignin and sugar analyses. Prescreening of these samples by FTIR spectroscopy showed a trend of decreasing aromatic signals (ca 1600 and 1500 cm⁻¹) coinciding with decreasing wood residue recoveries (spectra not shown). Indeed, with increasing LiCl concentration from 1% to 6%, there was a decrease in the Klason lignin content coinciding with an increase in sample dissolution (Table 5). As the proportions of xylose and mannose decreased, the proportion of glucose increased. Together, these results suggest that the more aggressive dissolution conditions had greater selectivity for lignin and hemicelluloses than the cellulose, ironically, with such solvent systems being described in the literature as cellulose solvents. A curious finding was that there appears to be a threshold in these dissolutions given that the trend ends at

Table 5
Klason lignin and polysaccharide sugar contents for wood residues from ACQ-treated sapwood after refluxing in NMP with LiCl.

LiCl (%)	Klason lignin (%)	Polysaccharide sugars (%)					
		Arabinan	Galactan	Rhamnan	Glucan	Xylan	Mannan
1	34.0	0.2	0.8	0.0	56.6	3.5	5.0
2	31.3	0.1	0.6	0.0	61.5	2.4	4.1
4	28.2	0.0	0.3	0.0	67.5	1.3	2.7
6	23.1	0.0	0.1	0.1	73.9	0.7	2.1
8	28.7	0.0	0.2	0.0	68.7	0.7	1.8

8% LiCl, with the Klason content trending higher and the glucose content trending lower. This can be rationalized in that as the dissolution approaches completion, the seemingly more resistant cellulose ultimately dissolves.

4. Conclusions

Treatments of wood with NMP, under reflux, appear to result in a limited dissolution of the lignocellulosic matrix. Upon the addition of LiCl to NMP, significantly greater levels of dissolution can be achieved with the amount of wood residue recovered being inversely related to concentration of LiCl used. Decreasing wood residue recovery generally coincides with decreasing contents of Klason lignin and the sugars comprising hemicelluloses. Use of 8% LiCl in NMP affords about one third of ACQ-treated sapwood as a wood residue retaining little copper. A significant proportion of the dissolved lignocellulosic matrix can be recovered as a precipitate rich in copper. These results demonstrate the potential of LiCl solvent systems for separating heavy metals from preservative-treated wood and providing lignocellulosic feedstocks for the production of biofuels and/or chemicals.

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