

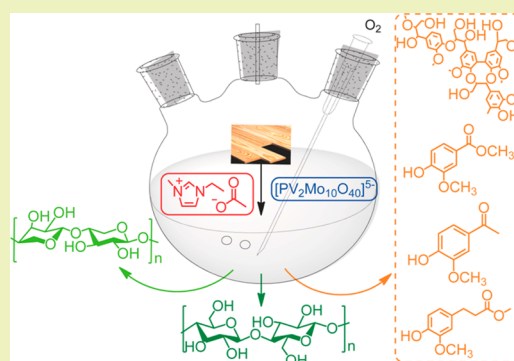
Oxygen Enhances Polyoxometalate-based Catalytic Dissolution and Delignification of Woody Biomass in Ionic Liquids

Fangchao Cheng,^{†,‡} Hui Wang,[†] and Robin D. Rogers^{*,†}[†]Center for Green Manufacturing and Department of Chemistry, Box 870336, Shelby Hall, 250 Hackberry Lane, The University of Alabama, Tuscaloosa, Alabama 35487, United States[‡]Key Laboratory of Bio-based Material Science and Technology of Ministry of Education of China, College of Material Science and Engineering, Northeast Forestry University, 26 Hexing Road, Harbin 150040, China

Supporting Information

ABSTRACT: Complete dissolution and over 90% delignification of Southern yellow pine (<0.125 mm) can be achieved in the ionic liquid (IL) 1-ethyl-3-methylimidazolium acetate ([C₂mim][OAc]) at 110 °C for 6 h by the catalytic action of polyoxometalate in the presence of an appropriate O₂ feed. Cellulose-rich materials (CRMs), or pulps, and hemicellulose with a limited lignin content and free lignin were subsequently recovered by adding antisolvents to the IL solution, followed by filtration. Comparison of wood processing in [C₂mim][OAc]/POM with or without O₂ revealed that the presence of oxygen can greatly facilitate the dissolution, delignification, separation of hemicellulose, and oxidation of lignin. The main products from lignin oxidation were extracted from the IL using benzene and then tetrahydrofuran, and were shown by gas chromatography–mass spectrometry (GC–MS) to be methyl vanillate, acetovanillone, vanillic acid, methyl 3-(3-methoxy-4-hydroxyphenyl) propionate, and methyl 4-hydroxybenzoate. This study suggests that treating wood with a [C₂mim][OAc]/POM/O₂ system could be a viable strategy to separate wood components with high efficiency and obtain cellulose with high purity for materials or biorefinery applications, particularly those that desire smaller lignin oxidation fragments for further processing.

KEYWORDS: Ionic liquid, lignocellulosic biomass, lignin, polyoxometalate, oxygen, fractionation



INTRODUCTION

Ionic liquids (ILs), generally defined as salts that are liquid below 100 °C,¹ have been recognized as promising solvents for the processing of lignocellulosic biomass, one of the potentially sustainable energy sources.^{2,3} However, the complex recalcitrant structure and the entangled and covalently cross-linked polymeric matrix of wood, greatly hinder its rapid dissolution and efficient fractionation in ILs.^{3,4} In 2011, we showed that the polyoxometalate (POM, a transition metal oxide anionic cluster⁵) [PV₂Mo₁₀O₄₀]⁵⁻ could efficiently catalyze the dissolution and delignification of Southern yellow pine in 1-ethyl-3-methylimidazolium acetate ([C₂mim][OAc]).⁶ The time for complete dissolution of 0.5 g of pine in 10 g of [C₂mim][OAc] was reduced from 46 to 16 h in the presence of POM, and the recovered cellulose-rich materials (CRMs) had a lower lignin content (5.4–18.3 wt % vs 23.5 wt %), although the yield of isolated lignin decreased (8.0–27.0 wt % vs 31.4 wt %) due to degradation of lignin. Although the addition of POM greatly enhanced the dissolution of wood in the IL, it still required a relatively long time to completely dissolve the wood (e.g., 16 h at 110 °C for pine) and the lignin content of the recovered CRM was high, ranging from 5.4 to 18.3 wt %.

POMs have previously been explored in the delignification and bleaching of lignocellulosic pulp in aqueous solution,^{7,8} and

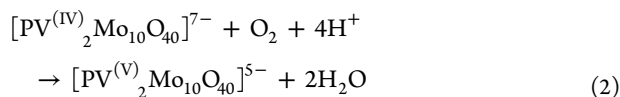
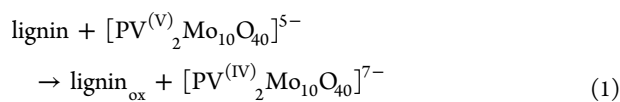
the oxidation of starch in ILs.⁹ Recently, Albert et al. reported the oxidation of woody biomass to formic acid at 90 °C under 30 bar O₂ in aqueous solution using POM (H₃PV₂Mo₁₀O₄₀) as the catalyst, and formic acid yields reached 15.8 wt % in the processing of pine.¹⁰ Besides POMs, metal chlorides, such as CrCl₃, CrCl₂, AlCl₃, and LiCl, have also been employed as selective catalysts for the production of furfural and 5-hydroxymethylfurfural from lignocellulosic biomass or the hydrolysis of both phenolic and nonphenolic lignin model compounds in ILs.^{11–15} In addition, Ru, Rh, or Pt nanoparticles, combined with a series of Brønsted acidic imidazolium ILs, can hydrogenate and deoxygenate phenolic lignin model compounds to nonaromatic hexane species.¹⁶

According to the reported mechanism of POM action (eqs 1 and 2),^{9,17–19} during the catalytic reaction, the vanadium in the POM ([PV₂Mo₁₀O₄₀]⁵⁻) anion is first reduced from V(V) to V(IV) and then oxidized from V(IV) to V(V) in the presence of O₂. There is no reported structural change of the POM anion during the reaction.

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O₂, as the oxidant, plays a major role in the catalytic degradation of lignin. We hypothesized that increasing the presence of O₂ during the IL processing of lignocellulosic biomass would facilitate the dissolution and delignification of wood in ILs by enhancing the breakdown of the lignin polymers. To test this hypothesis, Southern yellow pine was treated in [C₂mim][OAc]/POM solutions with an appropriate O₂ feed followed by recovery and analysis of the major biopolymer fragments and lignin oxidation products.

EXPERIMENTAL SECTION

Materials. Microcrystalline cellulose (MCC) with degree of polymerization 270 and xylan (from beechwood) were purchased from Sigma-Aldrich (St. Louis, MO). Indulin AT (lignin from the kraft pulping process) was provided by MeadWestvaco Corporation (Glen Allen, VA). Deuterated DMSO (DMSO-*d*₆) was purchased from Cambridge Isotope Laboratories, Inc. (Andover, MA). Deionized (DI) water was obtained from a commercial deionizer (Culligan, Northbrook, IL) with specific resistivity of 17.38 MΩ cm at 25 °C. [C₂mim][OAc] (>95%) was purchased from Iolitec USA (Ionic Liquids Technologies Inc., Tuscaloosa, AL). Acidic POM in hydrate form (H₅[PV₂Mo₁₀O₄₀].29H₂O) was donated by Japan New Metals Co. (Akita, Japan). [C₂mim]₄H[PV₂Mo₁₀O₄₀], an IL-compatible form of POM, was synthesized by mixing aqueous solutions of [C₂mim]Cl and H₅[PV₂Mo₁₀O₄₀] following our previous report.⁶ All other solvents were obtained from Sigma-Aldrich (St. Louis, MO) and used as received.

Southern yellow pine was received from Seaman Timber Co. (Montevallo, AL) as shavings. The biomass sample was ground into powder using a lab mill (Janke & Kunkel IkaLaborstechnik, Wilmington, NC), separated using brass sieves (IkaLaborstechnik, Wilmington, NC) to particles having diameters of less than 0.125 mm, and then dried overnight in an oven (Precision Econotherm Laboratory Oven, Natick, MA) at 90 °C until no further weight loss was observed.

Dissolution and Delignification of Biomass in IL with POM and Oxygen. POM (acid form or IL-compatible form, 0.01–0.1 g) was added to 10 g of [C₂mim][OAc] in a three-necked flask vented through a pressure-release bubbler and O₂ was fed through a needle with a flow rate of 120 mL/min. Our previous work has shown that when POM and [C₂mim][OAc] are mixed together, some of the POM is reduced immediately.⁶ Therefore, prior to addition of biomass, O₂ was bubbled through the system at 110 °C for 1 h to ensure all of the POM was oxidized. Subsequently, 0.5 g of pine was added to the IL/POM solution and heated at 110 °C for 5 or 6 h with stirring (650 rpm) at the same O₂ feed rate described above. For controls, the process without O₂ and without POM and O₂ were carried out under the same conditions while directly exposed to air.

Regeneration and Separation of Biopolymers. Procedure A (Separation of Undissolved Residue). DMSO (10 mL) was added to the pine/IL/POM solution after dissolution of pine to reduce the viscosity and assist separation of the solution from any undissolved residue. After the solution was mixed, the IL solution was separated from the residue by vacuum filtration, and the residue was further washed with DMSO (3 × 10 mL) to strip any dissolved substances adsorbed or trapped within the solid texture. Then it was further washed with DI water (3 × 20 mL), filtered, dried overnight at 90 °C, and weighed. CRM was precipitated by pouring the biomass/IL/POM/DMSO solution into 200 mL of acetone/water (1:1, v/v) in a 300 mL beaker with magnetic stirring at room temperature for 1 h.

The solution with suspended CRM was then centrifuged and the precipitated solid was further washed with an acetone/water (1:1, v/v) mixture and then DI water to ensure all the free lignin and IL were washed out. The CRM was finally separated using vacuum filtration through a ceramic funnel with nylon filter paper (10 μm). The regenerated CRM was dried overnight in the oven at 90 °C.

Procedure B (recovery of CRM, Hemicellulose, and Lignin). Because the use of DMSO did not allow the regeneration of lignin or hemicellulose, pine/IL solutions with residual yield <0.1%, without addition of DMSO, were used to recover all the biopolymers. CRM was obtained by the addition of 200 mL of acetone/water (1:1, v/v) mixture to the biomass/IL solution, and separated following the methods described in Procedure A. The filtrate after the filtration of CRM was concentrated using rotary evaporator (Büchi Rotary R-210, Flawil, Switzerland) at 50 °C for 2 h to remove most of the acetone and water. Hemicellulose was precipitated by the addition of 200 mL of ethanol (95%, v/v) to the concentrated IL solution, and separated from the remaining solution by vacuum filtration through a ceramic funnel with nylon filter paper (10 μm). Afterward, the ethanol in the filtrate was evaporated using a rotary evaporator, and 200 mL of DI water was added to the obtained IL solution to precipitate water-insoluble lignin, which was then recovered by vacuum filtration using the same equipment as CRM but with 0.8 μm nylon filter paper (due to the small particle size of the lignin). After filtration of water-insoluble lignin, 1 M aqueous hydrochloric acid solution was added to the filtrate drop by drop with manual stirring until the pH of the solution was lower than 2.0, determined with pH paper (Micro Essential Laboratory Inc., Brooklyn, NY), for precipitation of acid-insoluble lignin. The recovered acid-insoluble lignin was also separated by vacuum filtration following the same methods used for water-insoluble lignin. All the recovered biopolymers were dried overnight in the oven at 90 °C.

Extraction of Major Lignin Oxidation Products from the IL Solution. After the acid-insoluble lignin was separated, the IL solution was concentrated using the rotary evaporator at 50 °C to remove most of the water. To extract the lignin oxidation products, 20 mL of benzene was added to the IL solution and the combined solution was mixed thoroughly with a vortexer. After the solution was let stand for 0.5 h, a biphasic system formed and the top benzene phase was separated from the bottom phase with a pipette. This extraction was repeated 3 times (3 × 20 mL), the benzene solutions were combined and concentrated to about 0.5 mL by rotary evaporation, and then analyzed by gas chromatography–mass spectrometry (GC–MS). After benzene extraction, tetrahydrofuran (THF) extraction was subsequently performed to extract more products from the benzene extracted IL solution using the same procedures.

CHARACTERIZATION

The recovered biopolymers, Indulin AT, and acidic POM were characterized by Fourier transform infrared spectroscopy (FTIR) using a Bruker Alpha FTIR instrument (Bruker Optics Inc., Billerica, MA) with 24 scans at 2 cm⁻¹ resolution. MCC, xylan, Indulin AT, and the recovered biopolymers were also analyzed by ¹³C NMR using a Bruker AVANCE 500 MHz NMR spectrometer (Karlsruhe, Germany). The samples of MCC and CRM were prepared by cooking 5 wt % MCC or CRM in [C₂mim][OAc] at 100 °C for 6 h and diluting the solution with DMSO-*d*₆ (IL/DMSO-*d*₆, 85:15, w/w) as cellulose is insoluble in DMSO. A total of 20 000 scans were collected for ¹³C NMR of the MCC or CRM solutions at 125.76 MHz and 70 °C to get spectra with good resolution.²⁰ For other biopolymers, 5 wt % biopolymer/DMSO-*d*₆ solutions were prepared by heating the corresponding biopolymer and DMSO-*d*₆ at 90 °C for 15 min, and 10 000 scans were collected for ¹³C NMR at 125.76 MHz.

The benzene and THF solutions containing the lignin oxidation products were analyzed using GC–MS: Agilent

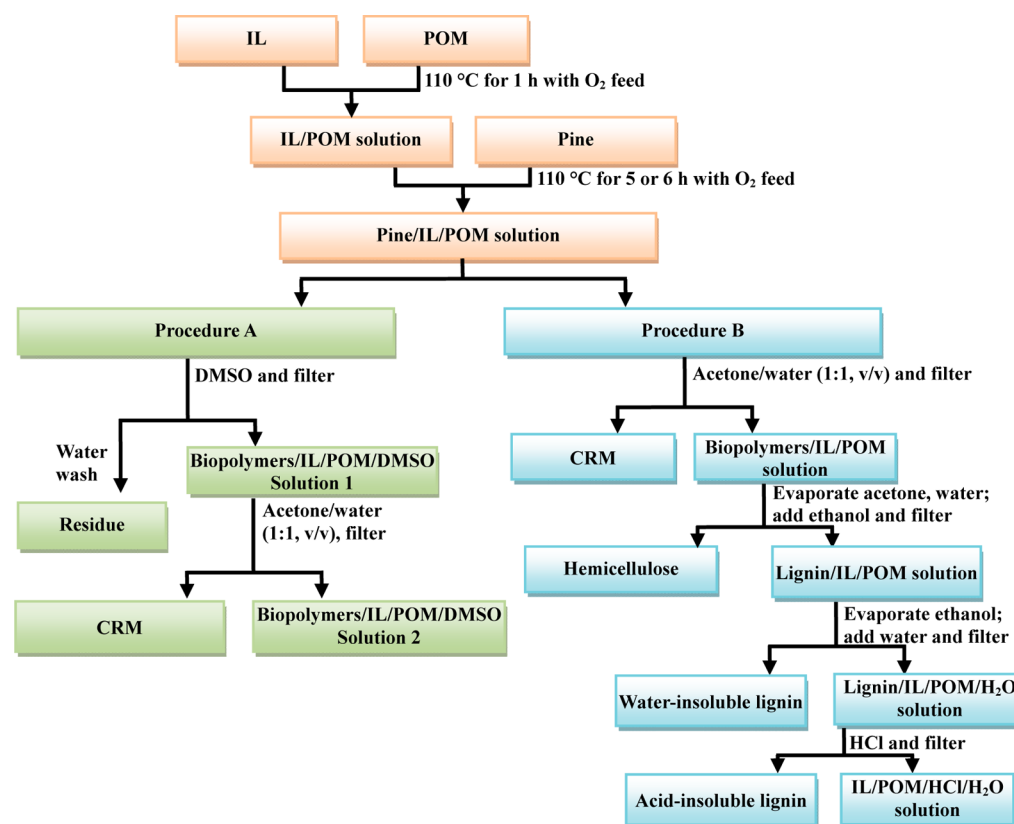


Figure 1. Flowchart for the IL/POM/O₂ processing of pine.

Table 1. Dissolution and Delignification of Pine under Various Conditions^a

trial	POM	O ₂	time (h)	CY ^b (%B)	CC ^b (%B)	LC ^b (%B)	LPC ^c (%CRM)	RY ^d (%B)
1			6	16.8	14.5	2.3	13.6	63.0
2	0.1 g [C ₂ mim]POM		6	36.1	32.3	3.8	10.5	44.5
3	0.1 g [C ₂ mim]POM	O ₂	6	3.1	3.1	— ^e	— ^e	<0.1
4	0.05 g [C ₂ mim]POM	O ₂	6	27.5	26.8	0.7	2.6	<0.1
5	0.01 g [C ₂ mim]POM	O ₂	6	30.9	27.9	3.0	9.6	<0.1
6	0.01 g [C ₂ mim]POM	O ₂	5	42.0	35.0	7.0	16.6	5.2
6b ^f	0.01 g [C ₂ mim]POM	O ₂	5	41.4	34.8	6.6	15.9	4.5
				(0.7%) ^g	(0.3%) ^g	(2.9%) ^g	(2.2%) ^g	(7.2%) ^g
7	0.05 g acidic POM	O ₂	6	26.6	26.0	0.6	2.1	<0.1

^a0.5 g of pine (<0.125 mm, lignin 32.0 wt %) was added to 10 g of [C₂mim][OAc] and the designated amount of POM, and then heated at 110 °C for 5 or 6 h at a stirring speed of 650 rpm. ^bCRM yield (CY), carbohydrates in CRM (CC), and lignin in CRM (LC) provide the mass percentage of these values related to the mass of original biomass used (%B). ^cLignin percentage of CRM (LPC) is the mass percentage of lignin related to the mass of CRM (%CRM). ^dResidue yield (RY) is the mass percentage of residue to the mass of original biomass (%B). ^eThe CRM obtained was not sufficient to measure the lignin content. ^fSecond run using the conditions of Trial 6. ^gCoefficient of variation (COV) for the results from Trials 6 and 6b.

HP6890N GC equipped with a DB-1701 capillary column (30 m long, 320 mm I.D., 1.0 mm stationary film thickness) and MicromassAutoSpec-Ultima™ MS with He as the carrier gas. Samples of 1.0 μL were injected with an autosampler in a split ratio of 20:1. The column was initially kept at 70 °C for 1 min, then was heated at a rate of 20 °C min⁻¹ to 250 °C, and maintained for 20 min. Identification of the products was done by comparing and matching the mass spectra with the standard spectra in the NIST05 EI mass spectral library.²¹

The lignin contents of the original pine and recovered biopolymers were determined by TAPPI methods with a scaled down process as described in our previous report.²⁰ Briefly, 0.1 g of the material was first hydrolyzed using 2 mL of 72 wt % H₂SO₄, and then the acid was diluted to 3% and refluxed for 4

h. The acid insoluble lignin was measured gravimetrically (Sartorius AC 210 P balance, Bohemia, NY) after drying in the oven. The acid soluble lignin was determined by UV spectroscopy using a Lambda XLS absorption spectrophotometer (PerkinElmer Ltd., Beaconsfield, UK) at 205 nm.

RESULTS AND DISCUSSION

Dissolution and Delignification of Pine in [C₂mim][OAc]/POM/O₂. Because O₂ has been shown to act as both reactant and accelerant for the degradation of lignin when POM is present,¹⁹ and POM has already been demonstrated to enhance the dissolution and delignification of wood in [C₂mim][OAc] at 110 °C when only exposed to air,⁶ we tested the combination of both POM and O₂ by bubbling

oxygen into a mixture of Southern yellow pine and [C₂mim]-[OAc]/POM. The IL/POM system was placed in a three-necked flask vented through a pressure-release bubbler and O₂ was fed through a needle with a flow rate of 120 mL/min. The mass of IL (10 g), choice of POM (acidic POM and IL-compatible salt form, [C₂mim]POM), mass of POM (0.05 g of acidic POM or 0.01–0.1 g [C₂mim]POM), mass and particle size of Southern yellow pine (0.5 g, <0.125 mm), and processing temperature (110 °C) were chosen based on our previous study.^{6,22} The use of [C₂mim]POM (MW = 2177.91 g/mol) instead of the acidic hydrated form H₃[PV₂Mo₁₀O₄₀]·29H₂O (MW = 2259.70 g/mol) eliminates the addition of any excess water to the system while providing a similar number of moles of the active POM per unit mass.

Southern yellow pine was first processed in [C₂mim][OAc] at 110 °C without O₂ and without O₂ or POM as the control experiments. Pine was then processed in [C₂mim][OAc] with different loadings of [C₂mim]POM (0.01–0.1 g)⁶ or acidic POM (0.05 g) with O₂ at 110 °C for 5 or 6 h. The residues were separated by adding 10 mL of DMSO (used to reduce the viscosity and assist separation of the solution from any undissolved residue) to the obtained IL solution followed by filtration. Cellulose-rich material (CRM), or pulp, was obtained by adding acetone/water (1:1, v/v) to the IL/DMSO solution followed by filtration (Procedure A, Figure 1).

As observed in Table 1 and Figure 2, the addition of POM to [C₂mim][OAc] leads to a lower residue yield (63.0 wt % for

Trial 1 vs 44.5 wt % for Trial 2) and a higher yield of CRM (16.8 wt % for Trial 1 vs 36.1 wt % for Trial 2) with lower lignin content (13.6 wt % for Trial 1 vs 10.5 wt % for Trial 2), in accordance with our previous results;⁶ nonetheless, the bulk of the pine sample remains undissolved under these conditions. It is apparent, however, that complete dissolution of the pine can be easily achieved when bubbling O₂ into the IL solution under the same cooking conditions (110 °C, 6 h) even when using only a small amount of POM (0.01 g [C₂mim]POM, Trial 5). The presence of the O₂ feed also significantly facilitates the delignification of pine in the [C₂mim][OAc]/POM system, leading to lower CRM yield (3.1–30.9 wt % for Trials 3–5 vs 36.1 wt % for Trial 2), but with much lower lignin content (2.1–9.6 wt % for Trials 3–5 vs 10.5 wt % for Trial 2).

Decreasing the loading of [C₂mim]POM (0.1, 0.05, and 0.01 g, Trials 3–5, Table 1, Figure 2) led to much higher CRM yield (3.1 to 30.9 wt %) and higher lignin content in the CRM (2.6 to 9.6 wt %). With high loading of POM (0.1 g), most of the carbohydrates were also degraded during the processing and only a small amount of CRM (3.1 wt % of added pine) could be recovered with limited lignin content (determined by FTIR, Figure S1, Supporting Information).

It is apparent that enhanced delignification is achieved at the cost of decreased CRM yield, which is consistent with traditional pulping,²³ as increased removal of lignin is normally accompanied by a certain amount of carbohydrate degradation.²⁴ In the present study, a POM loading of 0.05 g was chosen as the optimized catalyst loading to reach a compromise between high CRM yield and low lignin content.

Sufficient processing time was also shown to be necessary for the complete dissolution and high delignification of pine in the system. Shortening the processing time (Trial 5 vs Trial 6, Table 1, Figure 2) resulted in higher residue yield (5.2 wt % vs <0.1 wt %) and higher lignin content in CRM (16.6 wt % vs 9.6 wt %), although the CRM yield was also higher (42.0 wt % vs 30.9 wt %). Thus, 6 h was selected as the processing time to ensure the complete dissolution of pine in all combinations of processing conditions.

Once the effect of each set of conditions was known, repeatability was checked by re-examination of Trial 6, where both a measurable amount of residue and good catalytic activity were observed. As shown in Table 1 (Trial 6 vs 6b), repeatability was good with the coefficients of variation (COV) ranging from 0.3% to 7.2%.

Acidic POM was also studied as the catalyst using the same optimized conditions (Trial 7, Table 1, Figure 2) to investigate the effect of POM forms on processing efficiency. The use of

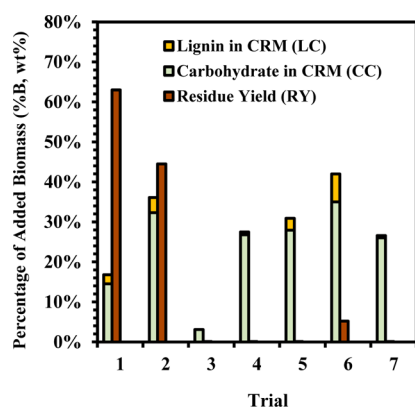


Figure 2. Mass balance for trials in Table 1 with different processing conditions.

Table 2. Mass Balance after Processing with the IL/POM/O₂ System

trial	POM	O ₂	CY ^a (%B)	CC ^a (%B)	LC ^a (%B)	LPC ^b (%CRM)	LR ^c (wt %)	HY ^d (%B)	LH ^e (%B)	WLY ^f (%B)	ALY ^g (%B)	ML ^h (%B)
8	0.05 g acidic POM		80.7	57.1	23.6	29.2	26.4	1.3	— ⁱ	2.8	6.3	8.9
9	0.05 g acidic POM	O ₂	27.9	27.0	0.9	3.2	97.2	19.6	2.8	<0.1	4.8	47.7
10	0.05 g [C ₂ mim]POM	O ₂	32.4	31.3	1.1	3.4	96.6	18.3	3.0	<0.1	8.2	41.1

^aCRM yield (CY), carbohydrates in CRM (CC), and lignin in CRM (LC) provide the mass percentage of these values related to the mass of original biomass used (%B). ^bLignin percentage of CRM (LPC) is the mass percentage of lignin related to the mass of CRM (%CRM). ^cLignin removed (LR) is the reduction of the lignin mass in the pulp (CRM) compared to the lignin mass in the original biomass. ^dHemicellulose yield (HY) is the mass percentage of the isolated hemicellulose related to the mass of original biomass (%B). ^eLignin in hemicellulose (LH) is the mass percentage of lignin in the isolated hemicellulose related to the mass of original biomass (%B). ^fWater-insoluble lignin yield (WLY) is the mass percentage of the isolated lignin to the mass of original biomass (%B). ^gAcid-insoluble lignin yield (ALY) is the mass percentage of the isolated lignin to the mass of original biomass (%B). ^hML is the mass percentage of lost components in the process to the mass of original biomass (%B). ⁱThe CRM obtained was insufficient to measure the lignin content.

acidic POM resulted in almost the same CRM yield (26.6 wt % for Trial 7 vs 27.5 wt % for Trial 4) and lignin content in CRM (2.1 wt % for Trial 7 vs 2.6 wt % for Trial 4) as those when $[\text{C}_2\text{mim}]\text{POM}$ was used. Both POM forms at 0.05 g loading were efficient at facilitating the dissolution of 0.5 g pine in 10 g $[\text{C}_2\text{mim}][\text{OAc}]$ at 110 °C within 6 h in the presence of O_2 . It should be noted that unlike our previous results where $[\text{C}_2\text{mim}]\text{POM}$ had a higher catalytic activity than acidic POM when the processing was conducted in air,⁶ here both forms of POM had essentially the same activity. We attribute this to the bubbling of O_2 through the system for 1 h prior to adding the biomass, which would allow sufficient time for either form of POM to be converted to the fully oxidized state.

Recovery and Separation of Biopolymers after Processing. The biopolymers were recovered and separated using Procedure B (Figure 1) to track the mass balance of all three major components after the $[\text{C}_2\text{mim}][\text{OAc}]/\text{POM}/\text{O}_2$ processing of pine. First, pine was processed in the $[\text{C}_2\text{mim}][\text{OAc}]/\text{POM}/\text{O}_2$ system with the optimized loading of POM (0.05 g, both the IL-compatible and acidic forms) at 110 °C for 6 h. The influence of oxygen on the mass balance of biopolymers during the processing was studied by comparing the dissolution of pine in $[\text{C}_2\text{mim}][\text{OAc}]$ with or without O_2 in the presence of the same loading of POM. All the biopolymers obtained with Procedure B were also characterized with NMR and FTIR.

Table 2 and Figure 3 present the mass balance of biopolymers in pine after processing. The O_2 feed into the

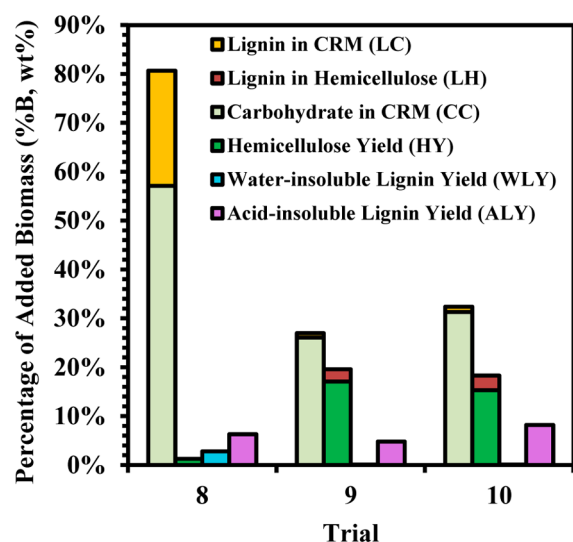


Figure 3. Mass balance for CRM, hemicellulose, and lignin. The numbers correspond to the trial numbers in Table 2.

$[\text{C}_2\text{mim}][\text{OAc}]/\text{acidic POM}$ solutions dramatically enhanced (a) the delignification of pine (97.2% for Trial 9 vs 26.4% for Trial 8; lignin content in CRM: 3.2 wt % for Trial 9 vs 29.2 wt % for Trial 8), (b) the separation of hemicellulose (19.6 wt % for Trial 9 vs 1.3 wt % for Trial 8), and (c) the oxidation of lignin (total lignin yield, 4.8 wt % for Trial 9 vs 9.1 wt % for Trial 8). The process with O_2 gives much lower CRM yield (27.9 wt % vs 80.7 wt %) and much higher mass loss (47.7 wt % vs 8.9 wt %) compared to the process without O_2 because of the removal and oxidation of lignin and degradation of carbohydrates. Interestingly, very limited amounts of water-insoluble lignin and even less acid-insoluble lignin were

obtained with the O_2 process, which also points to the enhancement of lignin oxidation when O_2 is used.

Both acidic POM and $[\text{C}_2\text{mim}]\text{POM}$ (Trials 9 and 10, Table 2, Figure 3) show high efficiency in the delignification of pine (97.2% for acidic POM, Trial 9 vs 96.6% for $[\text{C}_2\text{mim}]\text{POM}$, Trial 10; lignin content in CRM: 3.2 wt % vs 3.4 wt %, respectively) and in the separation of cellulose and hemicellulose when bubbling O_2 into the IL/POM solution. Compared to the $[\text{C}_2\text{mim}]\text{POM}$ process, the process with acidic POM resulted in slightly higher hemicellulose yield (19.6 wt % vs 18.3 wt %), lower lignin content in hemicellulose (14.3 wt % vs 16.4 wt %), lower acid-insoluble lignin yield (4.8 wt % vs 8.2 wt %), lower CRM yield (32.4 wt % vs 27.9 wt %), and higher mass loss of biopolymers (47.7 wt % vs 41.1 wt %). Considering the delignification of pine and carbohydrate loss in the process, $[\text{C}_2\text{mim}]\text{POM}$ is a slightly better catalyst than acidic POM on pine processing when introducing O_2 into this system, because it leads to higher CRM yield and lower mass loss with similar delignification.

Compared to the kraft pulping process, a lower pulp yield but with much lower lignin content was obtained for most of the current trials (Figure 4), because of the removal of both

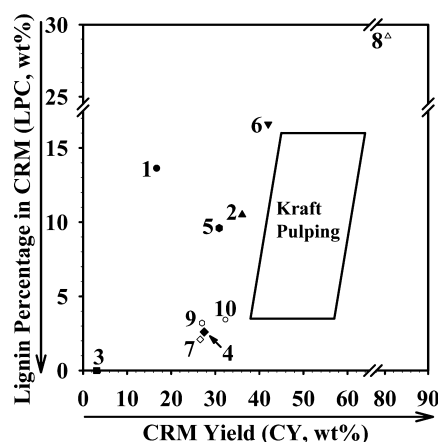


Figure 4. Comparisons of CRM yield (CY, %B; pulp) and percentage of lignin in the CRM (LPC, %CRM) in the IL/POM/ O_2 process with those obtained using kraft pulping. The numbers correspond to the trial numbers in Tables 1 and 2; the rectangular area encompasses literature reports for kraft pulping.²⁷

hemicellulose and lignin in the current process. Kraft pulping, as the most dominant pulping process, aims to obtain as much cellulose intact and undissolved as possible while degrading and dissolving hemicellulose and lignin during the process.²⁵ However, the IL/POM/ O_2 process has the advantage of completely dissolving all the biomass components,²⁶ and allows the separation of cellulose and hemicellulose from lignin with high purity, which can provide high quality feedstock for materials or biorefinery applications.

All the biopolymers obtained in the present study were characterized by ^{13}C NMR and FTIR. CRM obtained from the IL/POM/ O_2 process was confirmed as cellulose with limited hemicellulose and lignin by comparing the spectra with those of MCC, xylan, and Indulin AT (Figures S2 and S3, Supporting Information). The spectra of the recovered hemicellulose indicated it mainly contained xylan with minor amounts of lignin (Figures S2 and S3, Supporting Information). IR spectra showed the presence of POM in the acid-insoluble lignin after the process, while the CRM, hemicellulose, and water-insoluble

lignin did not contain any POM (Figures S3 and S4, Supporting Information).

Extraction and Analysis of Lignin Oxidation Products.

After recovery of lignin from the IL solution, the lignin oxidation products were extracted from the IL solution using benzene and then THF, both of which can form a biphasic system with $[C_2mim][OAc]$. The benzene and THF extracts were analyzed with GC-MS to identify the products and the major lignin oxidation product observed was methyl vanillate (Figures S5 and S6, Supporting Information). Other products (e.g., acetovanillone, vanillic acid, methyl 3-(3-methoxy-4-hydroxyphenyl) propionate, and methyl 4-hydroxybenzoate) were also found, although in minor amounts (Figures S5 and S6, Supporting Information).

CONCLUSIONS

Complete dissolution and over 90% delignification of Southern yellow pine were achieved in $[C_2mim][OAc]$ catalyzed by POM with O_2 at 110 °C for 6 h. CRMs, hemicellulose, water-insoluble lignin, and acid-insoluble lignin could be recovered from the pine/IL solutions by adding antisolvents in sequence. Comparison of wood processing in $[C_2mim][OAc]$ /POM solutions with or without O_2 indicated that the presence of oxygen can significantly facilitate the delignification of biomass, the separation of hemicellulose, and the oxidation of lignin, although much less CRM (pulp) could be recovered.

Both acidic POM and $[C_2mim]POM$ showed high efficiency in the delignification of wood, the separation of hemicellulose, and the oxidation of lignin. Characterization of the recovered biopolymers confirmed that the CRM was mainly cellulose with limited amounts of hemicellulose and lignin. The main lignin oxidation products were extracted from the IL solution with benzene and THF, and were shown to be methyl vanillate, acetovanillone, vanillic acid, methyl 3-(3-methoxy-4-hydroxyphenyl) propionate, and methyl 4-hydroxybenzoate. Overall, this study suggests that treating wood with $[C_2mim][OAc]$ /POM/ O_2 could provide a viable strategy to separate wood components with high efficiency and to obtain cellulose, hemicellulose, and lignin with high purity for materials or biorefinery applications.

ASSOCIATED CONTENT

Supporting Information

Characterization of biopolymers with NMR and FTIR and identification of lignin oxidation products. This material is available free of charge via the Internet at <http://pubs.acs.org>.

AUTHOR INFORMATION

Corresponding Author

*(R.D.R.) Tel.: +1 205-348-4323. E-mail: rdrogers@ua.edu.

Notes

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