Catalyst-free activation of kraft lignin in air using hydrogen sulfate ionic liquids

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ABSTRACT

In this research we use ionic liquids in combination with mild process conditions to provide a selective increase in the content of carbonyl groups in the kraft lignin structure. Such modification can improve the properties of the pristine biopolymer. In this study, aromatic substituted ionic liquids were synthesized using $[C_4C_1Im][HSO_4]$ as a template structure. The substituents were intended to increase the affinity of the ionic liquid to the aromatic structure of kraft lignin, and to increase access to the oxidizing agent, which was atmospheric oxygen. [Benzyl $(C_2OC_1)Im][HSO_4]$ and $[benzylC_4Im][HSO_4]$ activate the surface of the biopolymer more effectively than $[C_4C_1Im][HSO_4]$. This was confirmed based on X-ray photoelectron spectroscopy, which showed the content of C=O groups to be almost doubled compared with unmodified lignin. The analysis also revealed targeting of the hydroxyl groups of lignin to the carboxyl groups during activation in $[C_4C_1Im][HSO_4]$.

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1. Introduction

Ionic liquids (ILs) are a subject of constant interest both in scientific research [1] and in the development of innovative solutions in technology [2]. Much research is being done on the use of these organic salts as media in biomass processing. The method by which ILs are used to treat biomass is called the ionosolv process [3]. These compounds enable the selective isolation of components forming wood cells [4], and this property can be enhanced due to the possibility of designing ionic liquids [5, 6]. Because of this, they can be used not only to dissolve but also to modify the components of wood cell biopolymers. Studies on biopolymers, including lignin, are justified from the point of view of their wide availability and biodegradability. In addition, they can be a platform for obtaining functional materials with a wide range of applications. They may be used in particular for the development of packaging compositions or more complex products such as hydrogels [7, 8].

Ionic liquids can be used to obtain small-molecule organic compounds [9] and also serve as a platform for obtaining energy from biomass [10]. Moreover, ionic liquids can be used for the modification of wood, cellulose or lignin. They have been used to carry out acetylation, benzoylation and carbanilation reactions of lignocellulosic material [11]. An alternative solution is to perform partial autohydrolysis of the lignocellulosic feedstock in the ionic liquid, so as to obtain a raw material for the production of fibers or films [12, 13]. Cellulose derivatives have been successfully obtained in the reaction medium of $[C_4C_1Im][Cl]$ [14, 15]. Ionic liquids can also be used in the preparation of functional gels and cellulose aerogels. Such materials, after further functionalization with additives, can offer a broad spectrum of properties ranging from defined hydrophobicity to antibacterial activity [15]. In turn, the use of ionic liquids in lignin modification has led to the development of a method for obtaining lignin of very good quality and unified polydispersity. Treatment with ILs also reduces the molecular weight of the final lignin [16]. Research on the use of ionic liquids in lignin chemistry is mainly focused on the chemical transformation of the ether bond β-O-4 [17]. The primary purpose is to break this bond, which is widely represented in the structure of lignin [17]. In most studies the aim is the oxidation and consequent depolymerization of lignin [4, 18–20]. Ionic liquids act as a solvent, and facilitate and catalyze the contact of an oxidizing agent with the biopolymer [4, 18–20]. As a consequence of the oxidation of lignin, low-molecular-weight organic compounds are obtained.

The aim of the present study is to bring about the controlled oxidation of kraft lignin in mild conditions using ionic liquids and oxygen from the air. Such process parameters are unique, and led to effective activation of the biopolymer. The modification is directed towards the oxidation of hydroxyl groups to carbonyl groups. Of particular interest are the quinone groups, which can ensure the efficient transport of protons and electrons in a designed lignin-based electrode material [21]. Various new ionic liquids were synthesized with substitution of an aromatic ring at the cation. The selected initial structure was $[C_4C_1Im]$

[HSO$_4$], which has already been analyzed and shown to be a good reaction medium for lignin processing [22–25]. A number of potential applications of 3-butyl-1-methylimidazolium hydrogen sulfate are mentioned in the literature; for example, it can be used in electrochemistry [26], hydrometallurgy [27] and organic synthesis [28–30]. In addition, ionic liquids with the hydrogen sulfate anion are characterized by relatively simple synthesis methodology and a relatively low price, especially in the case of protic ILs [31]. The cost of producing such ionic liquids is only several times higher than commonly used organic solvents. Moreover, the price of an ionic liquid is determined by the complexity of its synthesis. For this reason, it is important to preserve a "golden mean" to ensure the validity of the research. The next step in the economic justification for the use of ionic liquids is the development of an effective methodology for regeneration and re-use of the ionic liquids [32]. Furthermore, the synthesis and regeneration of ionic liquids are still improving. It is also possible to propose a number of combinations of anions (Cl$^-$, HSO$_4^-$ or MeSO$_4^-$) and cations (tetraalkylimidazolium or alkylammonium) which will enable the production of relatively cheap ILs [33].

Lignin is used chiefly as an energy source, although there are recent literature reports on other applications, for example in electrochemistry. In one study, a cathode material was developed using lignin in combination with polypyrrole [21], and the resulting composite enabled the reversible transport of electrons and protons. Gnedenkov et al. investigated the use of Klason lignin as a cathode material in lithium-ion batteries [34]. In our earlier research we performed electrochemical tests for modified lignins in ILs, leading to a potential anode material for Li-ion batteries [32]. Based on the promising results, it was possible to propose a combination with manganese (VI) dioxide, leading to a material offering better reversibility of the intercalation of lithium ions compared with pure MnO$_2$ [35].

Previous work has included the optimization of the use of hydrogen sulfate ionic liquids as effective media in the activation of kraft lignin. An imidazolium cation substituted with aliphatic chains was used. Protic and aprotic ionic liquids were also compared as an effective environment for the activation of kraft lignin using oxygen as an activating agent [32, 35]. In addition, lignin modified in ionic liquids was successfully used for the production of MnO$_2$-lignin hybrid materials. As a result, promising material was obtained for further work on the development of lithium-ion cell material [35]. In this research the goal of increasing the asymmetry of the cation, with potentially good affinity of the ionic liquid to the aromatic skeleton of lignin, was successfully achieved. As a result, modified lignins were obtained with a significantly increased content of carbonyl groups, as confirmed by a number of analytical techniques.

2. Experimental

2.1. Materials

1-benzylimidazole, chloromethylethyl ether, 1-bromobutane, methyl iodide, and the solvents acetonitrile and heptane were obtained from Sigma-Aldrich (Germany). Kraft lignin was also purchased from Sigma-Aldrich. Hydrochloric acid and hydrogen peroxide (30% solution) were purchased from POCh S.A., currently Avantor Performance Materials Inc. (Poland).

2.2. Synthesis of ionic liquids

1-butyl-3-methylimidazolium hydrogen sulfate [C$_4$C$_1$Im][HSO$_4$] (**IL1**) was synthesized based on the methodology previously described by De Gregorio et al. [5]. This IL was chosen due to the low rate of the resulting lignin depolymerization reaction, as previously described [5]. The aim of the study was to oxidize lignin without degrading it. On the basis of this IL, new ionic liquids were designed, substituted with aromatic fragments.

The synthesis of new acidic imidazolium ionic liquids consisted of three steps.

In the first step, imidazolium chloride, bromide or iodide was obtained in the reaction of 1-benzylimidazole with chloromethylethyl ether (Scheme S1 – see Supplementary Information), 1-bromobutane (Scheme S2 – see SI) or methyl iodide (Scheme S3 – see SI).

Preparation of 1-benzyl-3-ethoxymethylimidazolium chloride: an anhydrous solution of 0.1 mol of 1-benzylimidazole in acetonitrile was added to 0.11 mol chloromethyl ethyl ether in acetonitrile. Chloromethyl ethyl ether is readily hydrolyzed in the presence of a small amount of water to form HCl, which in turn gives 1-benzylimidazolium hydrochloride. Separation of the quaternization product and 1-benzylimidazolium hydrochloride is practically impossible. For this reason, the quaternization reaction was conducted under strictly anhydrous conditions. The reaction was continued for 1 h at 50 °C, and then the solvent was evaporated in vacuum. The product was purified by extraction with heptane at 50 °C. The yield was 92.7%.

Preparation of 1-benzyl-3-butylimidazolium bromide: an anhydrous solution of 0.1 mol of 1-benzylimidazole in acetonitrile was added to 0.11 mol of 1-bromobutane. The reaction was carried out for 1 h under reflux, and then the solvent was evaporated in vacuum. The product was purified by extraction with heptane at 50 °C. The yield was 88.1%.

Preparation of 1-benzyl-3-methylimidazolium iodide: an anhydrous solution of 0.1 mol of 1-benzylimidazole in acetonitrile was added to 0.12 mol of iodomethane. The reaction was carried out for 1 h at 30 °C, and then the solvent was evaporated in vacuum. The product was purified by extraction with heptane at 50 °C. The yield was 82.3%.

In the second step, the chloride, bromide or iodide anion in 1-benzylimidazolium chloride, bromide or iodide was exchanged with a hydroxide anion on an ion exchange resin (Dowex Monosphere 550 A UPW OH form resin) (Schemes S1–S3 – see SI).

Preparation of imidazolium hydroxide: 0.07 mol of imidazolium chloride, bromide or iodide was dissolved in water and passed through a column filled with Dowex Monosphere 550 A UPW OH form resin.

In the third step, the obtained imidazolium hydroxides were immediately reacted with sulfuric acid to produce the corresponding imidazolium hydrogen sulfate (Schemes S1–S3 – see SI). Water was evaporated in vacuum. Three imidazolium hydrogen sulfates were synthesized: 1-benzyl-3-ethoxymethylimidazolium hydrogen sulfate [benzyl(C$_2$OC$_1$)Im][HSO$_4$] (**IL2**), 1-benzyl-3-butylimidazolium hydrogen sulfate [benzylC$_4$Im][HSO$_4$] (**IL3**) and 1-benzyl-3-methylimidazolium hydrogen sulfate [benzylC$_1$Im][HSO$_4$] (**IL4**). The respective yields were 97.1%, 96.8% and 99.1%.

1-benzyl-3-ethoxymethylimidazolium hydrogen sulfate IL2 [benzyl(C$_2$OC$_1$)Im][HSO$_4$]:
^{1}H NMR (600 MHz, temp. 25 °C, DMSO d_6, TMS): δ [ppm] = 1.10–1.13(t, J = 7.0 MHz, 3H); 3.55–3.58(m, 2H); 5.51(s, 2H); 5.60(s, 2H); 7.39–7.50(m, 5H); 7.91(s, 1H); 7.92(s, 1H); 9.59 (s, 1H).
^{13}C NMR (150 MHz, temp. 25 °C, DMSO d_6, TMS): δ [ppm] = 14.63; 52.13; 64.99; 78.22; 122.49; 122.94; 128.54; 128.84;129.04; 134.80; 136.84.

1-benzyl-3-butylimidazolium hydrogen sulfate IL3[benzylC$_4$Im][HSO$_4$]:
^{1}H NMR (600 MHz, temp. 25 °C, DMSO d_6, TMS): δ [ppm] = 0.88–0.90(t, J = 7.3 MHz, 3H); 1.23–1.26(t, J = 7.5 MHz, 2H); 1.77–1.80(t, J = 7.6 MHz, 2H); 4.20–4.22(t, J = 7.2 MHz, 2H); 5.47(s, 2H); 7.36–7.49(m, 5H); 7.86(s, 1H); 7.87(s, 1H); 9.47(s, 1H).
^{13}C NMR (150 MHz, temp. 25 °C, DMSO d_6, TMS): δ [ppm] = 13.24; 18.79; 31.28; 48.48; 51.88; 122.52; 122.86; 128.41; 128.70; 128.96; 134.99; 136.20.

1-benzyl-3-methylimidazolium hydrogen sulfate IL4 [benzylC$_1$Im][HSO$_4$]:
^{1}H NMR (600 MHz, temp. 25 °C, DMSO d_6, TMS): δ [ppm] = 3.15 (s, 3H); 5.44(s, 2H); 7.38–7.47(m, 5H); 7.74(s 1H); 7.82(s, 1H); 9.31 (s, 1H).