ACIDOLYSIS OF WOOD IN IONIC LIQUIDS

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BACKGROUND

In our earlier work we have shown that wood can be dissolved in some ionic liquids (ILs), including 1-butyl-3-methyl- and 1-allyl-3-methylimidazolium chlorides ([Bmim]Cl and [Amim]Cl) with high wood regeneration yield. When these ILs were used for additional wood pretreatment cycles, it was observed that the wood dissolution rate of cellulose increased, accompanied by lignin degradation. As such, it became of interest to investigate the effect of small amounts of acid in ILs on wood degradation and its hydrolytic conversion during such a pretreatment stage. In this effort we are comparing three wood species pretreated with dilute hydrochloric acid in water and in [Amim]Cl. The lignin contents of the regenerated wood were determined, and the components that remained within the recycled IL were examined.

After pretreatment of wood in ILs, the carboxylic acid from hemicelluloses was accumulated in the recovered ILs (Fig. 1). When the recovered ILs were used for wood pretreatment cycles, it was observed that the hydrolysis rate of cellulose increased, accompanied by lignin degradation. (Fig. 2)

The recovered ILs were extracted by ethyl acetate. The extracted hydrophobic compounds were characterized by 31P-NMR spectrometry and GC-MS. The identified compounds include typical chemicals from degradation of wood polysaccharide and lignin such as 5-hydroxymethylfurfural (HMF), furan-2-carboxylic acid, catechol, methylcatechol, methylguaiacol, acetoguaiacone, and acetol. (Figure 8, Table 3)

The optimal conditions of wood acidolysis in ILs were: 120 °C for 5h when the acid concentration was fixed at 0.8 mmol of HCl/g of wood. (Fig. 3)

The recovered water after acid pretreatment of wood contained no lignin degradation products, since no signals in the phenolic-OH region (144-137 ppm) is apparent. However, the recovered ILs after acid pretreatment of wood contained significant amount of phenolic compounds from lignin degradation, especially for softwood species. (Fig. 7)

The aqueous hydrolysis conditions were effective only for hemicelluloses dissolution, whereas the acidic treatment in IL also caused the hydrolysis of cellulose. At an acid concentration of 1.4-1.5 mol of HCl/g wood, most of the carbohydrates were hydrolyzed (E. grandis, 95%; S. pine, 67%; and N. spruce TMP, 82%). Several low molecular weight hydrolysis products were identified within the recycled ILs such as 5-hydroxymethylfurfural (HMF), furan-2-carboxylic acid, and 1-hydroxy-2-propanone. An IL-based acid pretreatment of wood may offer a potential platform for the efficient conversion of woody biomass to readily digestible carbohydrates and other valuable chemicals.

CONCLUSION

The aqueous hydrolysis conditions were effective only for hemicelluloses dissolution, whereas the acidic treatment in IL also caused the hydrolysis of cellulose. At an acid concentration of 1.4-1.5 mol of HCl/g wood, most of the carbohydrates were hydrolyzed (E. grandis, 95%; S. pine, 67%; and N. spruce TMP, 82%). Several low molecular weight hydrolysis products were identified within the recycled ILs such as 5-hydroxymethylfurfural (HMF), furan-2-carboxylic acid, and 1-hydroxy-2-propanone. An IL-based acid pretreatment of wood may offer a potential platform for the efficient conversion of woody biomass to readily digestible carbohydrates and other valuable chemicals.

LITERATURE


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