Pretreatment of Cellulosic Biomass by Glycol-Functionalized Ionic Liquids and Aqueous Ionic Liquids

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Since cellulosic biomass is recalcitrant to enzymatic hydrolysis, the pretreatment of lignocelluloses is known to be a key to the fast enzymatic hydrolysis of cellulose. Recently, certain ionic liquids (ILs) were found capable of dissolving and pretreating cellulose, leading to improved cellulose saccharification. There are, however, a number of challenges to using current ionic solvents at large scales (imidazolium-based salts, in particular), including their relatively high costs and viscosities and their sluggish biodegradability. Aiming to overcome these hurdles, we have prepared a new series of poly(ethylene glycol) (PEG)-functionalized ILs comprising inexpensive alkylammonium or piperidinium cations paired with acetate anions. Some of these new ILs are capable of dissolving 8–12 wt% cellulose, while displaying low viscosities and acceptable thermal stabilities at the required process temperature. Our XRD and SEM data further confirm that regenerative pretreatment of cellulose by these PEGylated ILs can effectively transform the cellulose I structure to cellulose II, reducing the crystallinity of cellulose and increasing the structural homogeneity. Most excitingly, cellulose regenerated from these ILs can be rapidly hydrolyzed to glucose, in ~90% glucose yield after 2 h, using a commercial cellulase supplemented with β-glucosidase. In addition, to gain an in-depth understanding of pretreatment mechanisms afforded by aqueous IL systems, we evaluated the Avicel cellulose pretreatment by aqueous solutions (1.0 and 2.0 M) of 20 different ILs, correlating enzymatic hydrolysis rates of pretreated cellulose with various IL properties such as hydrogen-bond basicity, polarity, Hofmeister ranking, and hydrophobicity. The pretreatment efficiencies of neat ILs may be loosely correlated to the hydrogen-bond basicity of the constituent anion and IL polarity; however, the pretreatment efficacies for aqueous ILs are more complicated and cannot be simply related to any single IL property. Several aqueous IL systems have been identified as effective alternatives to neat ILs in lignocellulose pretreatment. An integrated analysis afforded by X-ray diffraction, scanning electron microscopy, thermogravimetric analysis and cellulase adsorption isotherm of lignocellulose samples is further used to deliver a more complete view of the structural changes attending aqueous IL pretreatment.