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ARTICLE

Fractionation of 'water-soluble lignocellulose' into C_5/C_6 sugars and sulfur-free lignins

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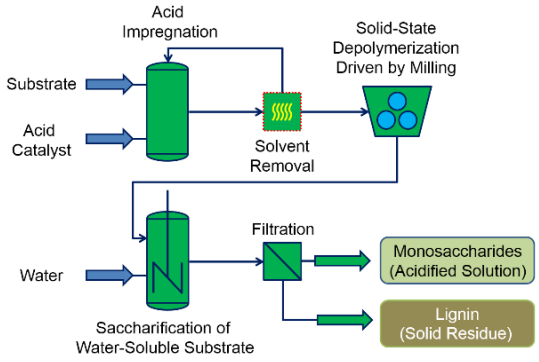
Recently, we demonstrated the mechanocatalytic depolymerization of lignocellulosic substrates as a powerful methodology that fully converts lignocellulosic substrates into 'water-soluble lignocellulose.' We now show that the saccharification of the aqueous solution of depolymerized beechwood, pinewood and sugarcane bagasse (at 140 °C for 1 h) produces a high yield of sugars (*e.g.* 88-92 % glucose, 3.5-8 % glucose dimers and 93-98 % xylose relative to the glucan and xylan fractions, respectively) and leads to precipitation of sulfur-free lignins. Noteworthy, the formation of furfurals is suppressed because the 'water-soluble lignocelluloses' undergoes hydrolysis at relatively low temperatures. At 140 °C, 5-hydroxymethylfurfural and furfural are formed in yields not exceeding 1.4 and 5.7 %, respectively. The separation of the carbohydrate fraction (as C_5 and C_6 sugars) from the lignin fraction is thus feasible by simple filtration.

Introduction

Mechanical forces have been exploited for wood processing for the past few hundreds of years. A representative example is the mechanical pulping of wood, which has been in place for more than 100 years. As such, the paper industry produces about 35 million tons of pulp per year.[1] In mechanical pulping, the internal processes leading to the deconstruction of wood are predominantly physical in nature.[2] Surprisingly, although mechanical processing of biomass has been long established,[3, 4] the combination of acid catalysis and mechanical forces in a 'one-pot process' has not yet been extensively studied for performing processes that are chemical in nature, such as catalytic biomass conversion. Only recently have some reports on solvent-free approaches for the acid-catalyzed depolymerization of cellulose – driven by mechanical forces – emerged in literature.[5-11] In this context, the high depolymerization efficiency, that is, the full conversion of plant biomass into water-soluble products, was realized through the impregnation of cellulosic fibers with catalytic quantities of HCl or H_2SO_4 before milling of the dry substrate, as recently demonstrated by us.[8]

The impregnation of acid onto the cellulose surface mitigates contact problems found by Blair *et al.*[5] for the reaction in the presence of solid acids. Hence, cellulose undergoes deep depolymerization and is thus fully converted into 'water-soluble oligosaccharides' (WSO) within 2 h of milling.[8] We demonstrated the WSO as a unique replacement for glucose and xylose, enabling high-yield production of sugar alcohols[9] or furfural and 5-hydroxymethylfurfural (HMF).[12] Moreover, first analyses of the results on lab-scale indicate that the mechanocatalytic depolymerization of lignocellulosic biomass could well become both economically and energetically sustainable.[8]



Scheme 1. Schematic representation of the method for fractionation of plant biomass into water-soluble monosaccharides and lignins.

Recently, we reported that the full conversion not only of cellulose, but also of native lignocellulosic substrates (*e.g.* pinewood, beechwood, switchgrass and sugarcane bagasse) into 'water-soluble wood' can also be achieved by the mechanocatalytic approach.[8] The separation of the water-soluble oligosaccharides from the water-soluble lignin fragments, however, has remained an unsolved challenge until now.