Tandem extraction and catalytic depolymerization of lignin from lignocellulose yielding lignin oil and holocellulose

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Introduction

The first step towards the conversion of lignocellulosic biomass into biofuels or platform chemicals is its fractionation into phenolics (lignin) and carbohydrates (holocellulose, i.e. hemicellulose and cellulose). Unfortunately, due to the high complexity of the lignin polymer, stemmed from the condensation of lignin fragments formed within the fractionation process, problems are posed for the catalytic conversion of technical lignins. To obtain aromatics, the depolymerization and liquefaction of technical lignins often require high temperatures and high H₂ pressures. Herein, we demonstrate a catalytic biorefining method that exploits H-transfer reactions for the production of depolymerized lignin oils and pulps hydrolysable by cellulases. The lignin oils are highly stable upon storage and easier to upgrade than organosolv lignin.

Materials and Methods

Experimental details are provided in Ref. [1]. Figure 1 displays an overview of the proposed catalytic biorefining by H-transfer reactions. First, wood pellets and Raney Ni were suspended in an aqueous solution of 2-propanol (2-PrOH, 70%, v/v). Then, the suspension was heated under mechanical stirring (e.g., at 180°C for 3 h). The voluminous lignocellulosic feed was processed in the absence of molecular hydrogen. Next, the holocellulose stream was isolated by filtration and washed with the 2-PrOH/water solution. Raney Ni was easily removed from the holocellulose suspension with a magnet. In our experiments, this catalyst could be reused at least eight times. Finally, the lignin oil was isolated by solvent removal from the extracting liquor. Acetone generated by the H-transfer processes can be hydrogenated to 2-PrOH in gas-phase through a second, small reactor.

Results and Discussion

As we recently reported, the combination of Raney Ni and 2-PrOH constitutes an outstanding catalytic system for the transfer hydrodeoxygenation of aldehydes and ketones in addition to the transfer hydrogenolysis of diaryl and aryl alkyl ethers.[2] Nonetheless, this catalytic system is not capable of extensively depolymerizing organosolv lignin into defunctionalized products. However, the catalytic system is able to convert the low-molecular-weight lignin fragments that are released by solvolysis upon cooking wood in the solvent mixture of 2-PrOH/H₂O (7:3, v/v). This feature prevents the lignin fragments from condensation. As a result, the lignin stream is obtained as a stable viscous oil (Figure 2B). Gel Permeation Chromatography (GPC) shows the molecular weight distribution of a lignin oil sample, compared to that of organosolv lignin (Figure 2A). In Figure 2B, the prominent peaks below 500 Da (i.e. monomers and dimers) demonstrate that high depolymerization is achieved by the catalytic biorefining by H-transfer reactions.

Figure 1. Schematic representation of the catalytic biorefining method, and a visual comparison of the products of the catalytic biorefining and those of the organosolv process.

Figure 2. GPC analysis and pictures of (A) organosolv lignin and (B) lignin oil.

Enzymatic hydrolysis of the pulps using a commercial cellulase preparation (Celluclast) proves that the conversion of the pulps, obtained from the catalytic biorefining, into fermentable sugars are similar to those from organosolv pulp (84-87 wt% yield of glucose after 72 h).

Significance

We demonstrated an approach for lignocellulose biorefining that directly provides low-molecular-weight lignin intermediates, together with the cellulose and hemicellulose streams, to be effective in the whole plant biomass utilization for the production of platform chemicals.

References