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Plant Biomass Fractionation Meets Catalysis**

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Several technologies for biomass pretreatment aim to make the cellulosic fibers more accessible to glycoside hydrolases. The enzymatic hydrolysis of cellulose is markedly enhanced upon physical disruption of the plant tissue and, in some cases, through its delignification by stoichiometric reactions. These pretreatments starkly contrast with the emerging catalytic methods for biomass fractionation. In light of recent progress, the earlier technologies appear to be unnecessarily harsh and waste- and energy-intensive. Through catalytic processes, the deconstruction of plant biomass may be efficiently achieved at low temperatures (100–180 °C). In some cases, sugars are directly produced.[1] This feature obviates the need for expensive enzymes for cellulose hydrolysis. Beyond the deconstruction of plant biomass, the emerging processes are directed towards the isolation of tailor-made fractions *through* and *for* catalysis, to exploit the full potential of catalysis in the conversion of biomass fractions into chemicals and fuels.

The plant cell wall is a complex composite that consists of cellulose, hemicellulose, and lignin. Evolution has brought these biopolymers together in very distinguished architectures, leading to great biodiversity from the molecular to the macroscopic level. The biopolymers are hierarchically organized (Figure 1). Cellulose is embedded in a complex matrix composed of hemicellulose and lignin. In some respects, this structure resembles a core–shell system in which the cellulose core is protected by a comparatively more reactive lignin–hemicellulose shell. Based on this simplified view, a categorization of the recently developed processes for catalytic fractionation is proposed:

1. “Deep depolymerization”: Lignocellulose is first depolymerized by acid catalysis to such an extent that the oligosaccharides that are obtained in addition to a complex mixture of lignin fragments become soluble in the solvent system (Figure 1 a). The carbohydrates are isolated by the precipitation of lignin either through addition of an antisolvent or through chemical reactions.

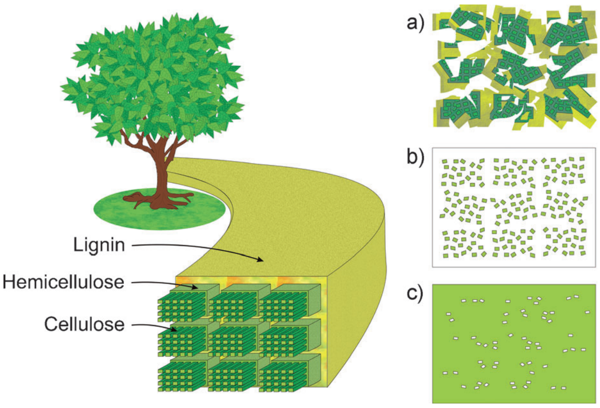

Figure 1. Simplified view of the lignocellulosic matrix and schematic representation of the outcome of a catalytic fractionation process through a) deep depolymerization, b) shell peeling, and c) core leaching.

2. “Shell peeling”: Lignin and, to a tunable degree, hemicellulose are detached from the lignocellulosic matrix by either acid- or base-catalyzed solvolysis (Figure 1 b). Thereby, lignin fragments and hemicellulose sugars are formed while cellulosic fibers are preserved from extensive depolymerization.
3. “Core leaching”: Cellulose and hemicellulose are extracted either as polymers or as monosaccharides. Lignin remains behind as a (degraded) polymeric residue in a collapsed matrix (Figure 1 c).

Very recently, Dumesic et al.[1] introduced a fractionation process that is based on the beneficial effects of γ-valerolactone (GVL) on acid-catalyzed saccharification.[2] Deep depolymerization was achieved by passing an acidic solution of GVL/H_2O (80:20, w/w, 0.05–0.1 mol L^{-1} H_2SO_4) through a heated, packed bed of biomass (e.g., corn stover, maple wood, and loblolly pine). As hemicellulose undergoes hydrolysis more easily than cellulose, proper selection of the temperature ramping enables a highly selective transformation to C_5 sugars (ca. 150–180 °C); the hydrolysis of cellulose to glucose takes place at higher temperatures (ca. 180–220 °C). As the process is performed in flow, a very good separation of xylose from glucose was obtained. Remarkably, the sugar feed can be concentrated either by extraction of GVL with liquid CO_2 or by addition of NaCl to the acidic GVL/H_2O solution that contains the sugars. As a result, a clear aqueous solution containing the sugars at concen-

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trations of up to 127 g L^{-1} (i.e., 65–85 % of the highest concentrations obtained by enzymatic hydrolysis) was produced.[1] Overall, the isolation of fermentable sugars in high yields together with a favorable preliminary techno-economic analysis make this process a very attractive alternative for the large-scale production of sugars for catalytic or biological upgrading.

Solvent-free processes for the deep depolymerization of purified cellulose[3] as well as real plant biomass[4] have also been reported. In this context, Rinaldi and Schüth et al.[4a] recently developed a simple process using mechanocatalysis for the deep depolymerization of lignocellulose. This method serves as a platform for the fractionation of plant biomass upon saccharification of the water-soluble oligosaccharides. Sugars (in high yields; e.g., 88–92 % glucose, 3.5–8 % glucose dimers, and 93–98 % xylose relative to the glucan and xylan fractions, respectively) and sulfur-free lignin precipitates were thus obtained from beechwood, pinewood, and sugarcane bagasse.[4a] The use of mechanical force is invariably associated with a considerable energy demand. However, a preliminary analysis of the laboratory-scale process show that the mechanocatalytic approach can become both an economically and energetically sustainable process.[3b,4b]

Leitner and Domínguez de Maria et al.[5] reported a catalytic fractionation process that leads to the full fractionation of the biomass components in a single operation unit. The so-called “organocat process” fractionates biomass by shell peeling through the selective solvolysis of lignin and hemicellulose catalyzed by oxalic acid or formic acid under low-severity conditions (80–140 °C). As this process is performed in a biphasic system (water and 2-methyltetrahydrofuran), the water-soluble hemicellulose sugars are separated from the lignin fragments. The sugars stay in the aqueous phase, while the lignin fragments are extracted by the organic solvent. Cellulose is separated as a slightly yellowish solid, and its hydrolysis by commercial cellulases was demonstrated.

More recently, Welton et al.[6] have demonstrated the deconstruction of *Miscanthus giganteus* using 1-butylimidazolium hydrogen sulfate, an inexpensive and chemically robust ionic liquid (IL). This process contrasts sharply with earlier methods for the acid-catalyzed depolymerization of cellulose in dialkylimidazolium ILs and is another key example for the shell-peeling-type fractionation, which removes lignin and, to some extent, hemicellulose from the lignocellulosic matrix. Importantly, the addition of water to the IL liquor leads to the precipitation of lignin and pseudo-lignin (humins formed from the decomposition of hemicellulose sugars), allowing for the sustainable recycling of the IL. Finally, subjecting the pulp to enzymatic saccharification allowed recovery of up to 90 % of the glucan as fermentable glucose.

The core-leaching methods encompass most of the experience garnered on the acid-catalyzed saccharification of wood over the past 100 years. However, the introduction of ionic liquids as solvents for cellulose by Rogers et al.[7] added important perspectives towards the saccharification of wood under low-severity conditions.[8] However, the practical utilization of dialkylimidazolium ILs in the core-leaching processes is hindered by several issues, such as the difficult isolation of sugars from the ILs, their debatable thermal and chemical stability, and their recycling.

In summary, significant progress in the fractionation of plant biomass was achieved through the development of several catalytic approaches. These new methods provide carbohydrate fractions either as monosaccharides or as polymers that are more amenable to enzymatic hydrolysis and chemocatalytic conversion. Nonetheless, a catalytic fractionation through a shell-peeling process in which lignin is selectively separated from the carbohydrate fraction and isolated as low-molecular-weight phenol derivatives is a valuable process to explore further.[9] Such a process could hold the key to better tackle the challenge of lignin valorization and its conversion into chemicals and fuels, thus enabling the utilization of the entire plant biomass to its fullest.[10]

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