Green Solvents in Biomass Delignification for Fuels and Chemicals

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Lignin is considered by many as the ultimate barrier that impedes biomass conversion to fuels and chemicals. Several delignification strategies have been developed so far, but alkaline extraction remains the most widely used. However, this technology has a high chemical demand, consumes large amounts of water, and generates effluents that are hard to handle. Organosolv pulping is a good option for such application, but the impact of solvent losses and harmful emissions may be unsustainable. To this end, the use of greener alternatives such as water, biobased solvents, ionic liquids, and deep eutectic solvents, under sub- or supercritical conditions, may pave the road for the development of sustainable biorefineries.

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The Problem

Delignification has been recognized by many as an efficient technique for biomass fractionation and the ultimate solution for optimal enzymatic hydrolysis of lignocellulosic materials (Silveira *et al.* 2015). Besides, delignified cellulosic materials are precursors of many valuable products, such as cellulose for pulp and paper, dissolving pulp, cellulose-based food additives, microcrystalline cellulose, hydrogels, and bio-based nanomaterials. In addition, delignified fibers produce enzymatic hydrolysates with low inhibitory impact on microbial fermentation for fuels and chemicals. Some delignification strategies yield sulfur-free lignin streams that are useful for other valuable applications (Suota *et al*. 2021). The most widely used delignification technique is alkaline extraction, which may be performed over milled native lignocellulosic materials to produce partially delignified fibers in which hemicelluloses are partly retained or over hydrothermally or dilute acid-pretreated materials to produce partially delignified fibers with hemicelluloses around 2-3% (Da Silva *et al*. 2016). However, large quantities of sodium or potassium hydroxide are typically required to achieve high delignification levels. Also, alkaline pretreatment liquors must be neutralized (critical for lignin recovery) before disposal, while substrate conditioning for enzymatic hydrolysis (and fermentation) generates massive amounts of alkaline washing waters, making it hardly unsustainable. In general, alkaline extraction is expensive for large scale processes unless value-added products are obtained from biomass along with bulk chemicals (*e.g.*, liquid fuels) and/or materials. However, in some bio-based industries such as kraft pulping, alkaline pretreatment (black) liquors are concentrated and burned in biomass boilers to provide combined heat and power and chemical recovery in the form of green liquor. Delignification with organic solvents may also be achieved after pretreatment (either physical, chemical, or thermochemical). Still, this option involves high solvent recovery costs, complex unit operations, high energy demand, and low yields due to mass transfer limitations and poor solubility of technical lignins.

The Green Alternative

Organosolv pretreatments offer a good alternative to alkaline extraction because solvents from the pretreatment liquor are quickly recovered by evaporation/distillation for reuse, depending on their boiling point. The process involves fractionating biomass using one or more organic solvents at temperatures beyond 170 °C (Chu *et al*. 2021). At optimal conditions, organosolv processes produce fibers with good strength properties, substrates with good accessibility for enzymatic hydrolysis, and sulfur-free lignin streams (Mesa *et al*. 2016). For this, water plus an acid or basic catalyst is often added to induce hydrolysis of plant polysaccharides (mostly hemicelluloses). However, the impact of solvent losses and harmful emissions must be controlled and/or avoided in organosolv processes. The most widely used solvents for organosolv pretreatment are ethanol, methanol, and acetone, assisted or not by an exogenous catalyst. Besides, these solvents can be obtained from biomass to pretreat biomass, bringing further improvements to the greenness of the pretreatment process. In this regard, ethanol seems to be a better option because it is more sustainable, less toxic, and more easily accessible than other organic solvents at a relatively low cost (Silveira *et al.* 2015).

In recent years, green solvents in organosolv processes have become a hot topic for biomass conversion (Mesa *et al*. 2016). Green solvents are advantageous over petrochemical solvents because they are less toxic and fully biodegradable. Conventional organic solvents may be replaced by green solvents, such as ionic liquids (ILs), deep eutectic solvents (DES) (Escobar *et al*. 2022), and bio-based molecular solvents, such as 2-methyl tetrahydrofuran (2-MeTHF) and γ-valerolactone (GVL) (Soh and Eckelman 2016). Also, fatty acid alkyl esters and glycerol-based solvents from lipid-based feedstocks have been seen as potential green solvents (Winterton 2021). In addition, terpenes such as farnesene from microbial fermentation and *d*-limonene from citrus peel wastes can replace hexane in biomass extractions, acting as an attractive green solvent for producing valuable chemicals (Soh and Eckelman 2016).

In addition to applying bio-based chemicals, organosolv pretreatments can be much more efficient when operating at aimed conditions with supercritical carbon dioxide ($scCO_2$). The $scCO_2$ dissolves most organic solvents, decreasing their viscosity and surface tension (Escobar *et al*. 2020). Also, diffusion of acid or basic catalysts is facilitated when these are present in the reaction system (Daza-Serna *et al*., 2015). Depending on the reaction conditions, suitable substrates for hydrolysis are produced while lignin is recovered in high purity (Escobar *et al*. 2022). Also, $scCO_2$-assisted processes do not generate fermentation inhibitors, and CO_2 can be recycled after depressurization (Hermsdorff *et al*. 2023). It is worth noting that neither bio-based molecular solvents nor $scCO_2$ can beat the advantages of water as a sustainable solvent, since it is practically omnipresent and not harmful to the environment or health. Hydrothermal processing, with water at sub and supercritical conditions, is also a promising alternative. Supercritical water (scH_2O) also lowers the system viscosity enabling a better diffusion of chemicals into the lignocellulosic matrix, facilitating the reactive extraction and/or solubilization of organic compounds (Escobar *et al*. 2020). Changing the temperature and pressure may profoundly affect the water properties so that water behaves as an organic solvent, such as methanol, at supercritical conditions. This condition favors extraction, gasification, fractionation, and partial depolymerization processes crucial for biomass valorization. Also, water can act either as acid or base at sub- and supercritical conditions enabling the recovery of a wide variety of chemicals from biomass (Adschiri 2014).

The Future Ahead

Despite their being highly effective and highly selective for biomass conversion to fuels and chemicals, it is undeniable that some ionic liquids and deep eutectic solvents are toxic, expensive, or even hard to recover. These issues can partially rule out their application as green solvents for biomass fractionation. Even safer ILs and DES to the environment or health can find difficulties in complying with the greenness demanded because production on a large scale can be problematic. Biobased solvents such as 2-MeTHF and GVL also struggle with bottlenecks to be extensively available and cost-effective to make biomass pretreatment viable. Nevertheless, green (biobased) organosolv pretreatment processes are promising for biomass conversion to fuels and chemicals. Indeed, organosolv can involve higher operational and installation costs compared to alkaline delignification due to the solvent cost and high-energy demands. However, it is worth mentioning that such a process can be technologically and economically feasible if equipment is optimized and both heat and energy are integrated. The choice for biobased solvents such as first (saccharinic) or second (cellulosic) generation ethanol could be used for pretreatment, helping to close the loop and to improve the process economics. Finally, solvents at supercritical conditions, such as $scCO_2$ and scH_2O, are promising green approaches for biomass pretreatment that must be considered. With this, biomass conversion to fuels and chemicals can be made fully sustainable, elevating green organosolv, supercritical, and hydrothermal pretreatments as the pillars for advanced biorefineries and further developments in the implementation of a viable low carbon bioeconomy (Silveira *et al.* 2015).

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