Pretreatment of Crop Residues for Bioconversion

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Decreasing the dependence on fossil resources as raw materials for the production of fuels, platform chemicals, and commodities is an imperative requirement of today’s industry and society in order to alleviate the threats related to climate change. Processing lignocellulosic biomass in biorefineries provides an alternative route for producing fuels and most of the chemicals that today are produced from fossil resources. Crop residues are a realistic option of lignocellulosic feedstock for biorefineries considering their large availability, low cost, and renewable nature. The generation of crop residues is increasing as a result of the expansion of the agricultural production necessary to support the increase in the global population. The harvest of cereals [1], other food crops [2], and non-food agricultural products [3] generates large amounts of residues, whose proper management poses huge challenges. Although the environmental impact of disposing crop residues by burning has not been as mediatic as that of industrial and vehicular emissions, its contribution to air pollution is an issue of major significance in many countries [4].

The bioconversion of crop residues via sugar-platform processes, in which polysaccharides are hydrolyzed to sugars for further conversion through microbial, enzymatic, or chemical processing, is a highly promising option for producing fuels and chemicals required for the sustainable development of human society. The enzymatic saccharification of cellulose is a selective approach for deconstructing biomass, but it requires a pretreatment for removing or weakening the barriers causing the inherent recalcitrance of lignocellulosic feedstocks [5]. In spite of the intensive research in the area, pretreatment of crop residues is still an open question. Pretreatment effectiveness is feedstock-dependent [6–8], and further research is required to develop efficient methods enabling the commercial operation of bioconversion processes based on crop residues of different nature.

This Issue

In this Special Issue, fourteen original research papers and one review covering some of the latest advances in pretreatment and bioconversion of crop residues are presented. Research results dealing with wheat straw, corn stover, sweet sorghum bagasse, hazelnut shells, oil palm empty fruit bunch, olive tree pruning biomass, soybean husks, oat husks, sugar beet pulp, rice straw, wheat bran, barley straw, as well as biomass from trees used in intercropping systems, and other residues of crop harvest and processing are discussed. Pretreatment methods such as auto-catalyzed and acid-catalyzed hydrothermal processing, steaming, alkaline methods, and different organosolv approaches are reported. Bioconversion with enzymes and microbes for producing fermentable sugars, xylitol, and biomethane are also included.

Wheat (*Triticum aestivum* L.) straw is a crop residue of high relevance for bioconversion, and hydrothermal pretreatment is one of the methods of higher interest for agricultural residues. In a comprehensive study backed with advanced analytical techniques, Ilanidis et al. clarified correlations between pretreatment conditions and critical aspects of biochemical conversion of wheat straw, including susceptibility to enzymatic saccharification, by-product formation, and inhibitory effects on enzymatic hydrolysis and ethanolic fermentation [9]. It was found that auto-catalyzed hydrothermal pretreatment is a better approach than sulfuric acid-catalyzed hydrothermal pretreatment to achieve high sugar yields from wheat straw while minimizing by-product formation.
Pretreatment of corn (Zea mays L.) stover, another well-studied crop residue, was also included in this Special Issue. Krafft et al. pretreated corn stover using a combination of steam refining and alkaline extraction of lignin, and they evaluated how different operational conditions affect enzymatic hydrolysis [10]. The proposed approach was found to be suitable for corn stover. According to the authors, steam refining at severities below 3.5 combined with alkaline extraction deserves being tested for other agricultural residues as well.

Organosolv pretreatment as a fractionation strategy for biorefinery applications is presented in two articles. In the first one, Mondylaksita et al. assess the feasibility of low acid-catalyzed organosolv pretreatment using ethanol as a solvent for fractionating oil palm (Elaeis guineensis J.) empty fruit bunch (OPEFB) [11]. A high delignification degree (90%) with consequent recovery of high-purity lignin (71% purity) and highly-digestible glucon (94% enzymatic digestibility) were achieved using low sulfuric acid concentration (0.07%). The study demonstrated the possibility of deconstructing OPEFB into high-quality fractions using remarkably lower acid concentrations than the typically reported ones. In the second article, Domínguez et al. report formosolv pretreatment for fractionating biomass of Paulownia (Paulownia elongata × fortunei), which is a fast-growing tree used in intercropping agricultural systems [12]. Under optimal conditions, formosolv treatment resulted in the solubilization of 78.5% of the initial lignin and in a cellulose-enriched pulp (80%). The study included also a complete characterization allowing us to verify lignin structural changes resulting from the formosolv process.

Processing hazelnut (Corylus avellana L.), one of the major nut crops commercialized worldwide, generates large amounts of waste shells. Two articles in this Special Issue present novel studies on the pretreatment of hazelnut shells for biorefining them to value-added products. Rivas et al. report on the hydrothermal pretreatment of hazelnut shells at different temperatures, with further refining of the resulting liquor by membrane processing to yield substituted oligosaccharides (OS) with the purity required for food use [13]. The antioxidant activity found in the produced OS reveals their potential as bioactive components of functional food formulations, cosmetics, or pharmaceuticals, and the presented data provide the basis for assessing large-scale manufacture. In another study, López et al. evaluate the biorefining of hazelnut shells by a combination of autohydrolysis for removal hemicelluloses and delignification by either alkaline treatment or different organosolv approaches [14]. By reaching an effective fractionation of the main components, the investigated biorefinery schemes provide an innovative way for the integral valorization of hazelnut shells. Consecutive stages of autohydrolysis and acid-catalyzed organosolv resulted in 47.9% lignin removal, yielding solids of increased cellulose content (55.4%) and low content of hemicelluloses. The enzymatic hydrolysis of cellulose resulted in 74.2% conversion.

The production of cellulose nanofibers as a valorization alternative for olive tree (Olea europaea L.) pruning biomass (OTPB), a crop residue of relevance in Mediterranean countries, is presented by Sánchez-Gutiérrez et al. [15]. In that study, mechanical pretreatment and TEMPO-mediated oxidation were applied to OTPB, and the influence of residual lignin content on pretreatment effectiveness was evaluated. The characterization in terms of chemical composition, morphology, thermal stability, and crystallinity revealed the high potential of the produced nanofibers for application in different sectors.

A techno-economic study revealing the challenges of producing biodiesel by transesterification of castor oil with ethanol produced from lignocellulosic residues of the same plant (Ricinus communis L.) is reported by Rahimi et al. [16]. The oil extraction residues are subjected to alkaline pretreatment, enzymatic hydrolysis, and fermentation, and the resulting ethanol is combined with oil for biodiesel production. Although the results showed that biodiesel production is more profitable when fossil-based methanol is used, using ethanol produced from castor plant residues is a highly relevant approach because of its environmental benefits. The study on the castor biorefinery is a good reference for
other non-edible oilseeds, whose potential for ethanol production has previously been reported [17,18].

Bioconversion of the large variety of crop residues available in different latitudes requires efficient cocktails of hydrolytic enzymes. This Special Issue includes four papers on assessment of in-house developed enzymes. Karp et al. report an evaluation of crude preparations of *Penicillium verruculosum* cellulases and xylanases in saccharification of acid- and alkali-pretreated sugarcane (*Saccharum officinarum* L.) bagasse, soybean (*Glycine max* L.) husks, and OPEFB [19]. Soybean husks, regardless of pretreatment method, and alkali-pretreated sugarcane bagasse were efficiently saccharified, while OPEFB resulted in low sugar yields. *P. verruculosum* B1 cellulase/xylanase preparation was the best enzyme choice for bagasse, while a combination of B1 preparation with the crude obtained by recombinant expression of *Penicillium canescens* xylanase in the *P. verruculosum* B1 host strain gave the highest hydrolysis yield for soybean husks. In another work using the *P. verruculosum* cellulase complex, Osipov et al. evaluated the hydrolysis of 69 samples of pretreated and non-pretreated agricultural and agro-industrial residues, such as wheat straw, sunflower peels, sugarcane bagasse, sugarbeet pulp, oat husks, soybean husk, and corn stover [20]. The effectivity of *P. verruculosum* cellulases for hydrolyzing cellulose-containing materials to sugars was shown.

Another two articles covering in-house developed enzymes for the bioconversion of crop residues deal with novel termite metagenome-derived cellulases and hemicellulases. In the first one, Mkabayi et al. optimize the synergistic action of two termite feruloyl esterases and an endoxylanase from *Thermomyces lanuginosus*; then, they applied them to hydrothermally pretreated and acid-pretreated corn cobs, resulting in a high production of xylo-oligosaccharides (XOS) and hydroxycinnamic acids [21]. In the second paper, Mafa et al. compare the efficacy of two alkaline pretreatment approaches, with either lime or NaOH, for sweet sorghum (*Sorghum bicolor* (L.) Moench) bagasse and corn cobs, and they assess the hydrolysis of the pretreated biomass using a holocellulolytic cocktail of termite metagenome-derived enzymes [22]. The study concluded that alkaline pretreatment was more effective for corn cobs than for sweet sorghum bagasse, and it revealed the multifunctionality of the enzyme system, which makes it suitable for the hydrolysis of hemicelluloses and amorphous cellulose. The authors propose using their holocellulolytic enzyme cocktail for the hydrolysis of crop residues in the biorefinery industry.

The bioconversion of pretreated wheat bran and rice (*Oryza sativa* L.) straw to xylitol is reported by Bedö et al. [23]. After investigating the effects of xylose concentration and aeration on xylitol production by *Candida boidinii* in a semi-defined xylose medium, models predicting the conditions leading to maximum yield and volumetric productivity were developed. The adequacy of the models was tested in fermentations of hemicellulosic hydrolysates obtained by acid pretreatment of wheat bran and rice straw. The models were successfully verified for wheat bran hydrolysate, which was found to be an outstanding substrate for xylitol production by *C. boidinii*, while the use of rice straw hydrolysate requires further research. In another article on bioconversion, Morales-Polo et al. report the anaerobic digestion of barley (*Hordeum vulgare* L.) crop residues for energy uses [24]. Substrate characterization and analysis of the anaerobic digestion process through all phases are discussed, and the potential for biogas and methane generation is determined. Using Spain as a case study, the article estimates the energy potential of biogas from barley crop residues and the expected reduction of CO$_2$ emissions from using this renewable energy source to replace fossil sources.

A review paper on consolidated bioprocessing (CBP) of crop residues for the production of biofuels completes this Special Issue. In the review, Olguín-Maciel et al. present an in-depth assessment of CBP, which involves not only technical issues of this innovative approach but also societal and economic aspects [25]. The role of CBP in the bioconversion of crop residues and other lignocellulosic materials to ethanol and other products in a single process and in a sustainable way is highlighted.
The guest editor cordially thanks all the authors who contributed to this Special Issue. In their contributions, the authors focus from different perspectives on the study of the pretreatment of crop residues for bioconversion. The papers compressing this Special Issue show the level of advancement achieved in this research area. However, the remaining challenges are still significant. Therefore, the current efforts for the development of technologies enabling massive implementation of commercial-scale biorefineries based on crop residues are expected to continue for the foreseeable future.

Conflicts of Interest: The author declares no conflict of interest.

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