

Editorial

Biovalorization of Lignocellulosic Waste

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The swift and successful transition towards a fossil fuel-free economy is amongst the most complex challenges ever faced by humanity, implicating intricate connections and trade-offs with the so-called water–energy–food nexus [1]. In particular, the sustainable production of bioenergy and biofuels, i.e., energy and fuel sources generated from renewable biomass, must avoid conflicts with water and food security. In such a delicate context, the energetic valorization of the most abundant source of waste biomass, i.e., lignocellulosic materials (LMs), generated by large bioeconomy sectors such as agriculture and forestry, offers a powerful and sustainable alternative to the use of primary edible biomass. Although, on the one hand, the generation of heat and power through LM combustion, or the combustion of liquid and gaseous fuels (e.g., syngas) through pyrolysis and gasification, represents an established option, on the other hand, the biological valorization of LMs, alone or in combination with other treatments and/or wastes, offers the advantage of a more versatile and diverse platform, enabling the conversion of substrates with a high moisture content into biofuels such as biomethane, biohydrogen and bioethanol. In view of this, the increasing research efforts on the biological conversion of LMs, mainly aimed at overcoming the bio-recalcitrance of lignocellulosic biopolymers (i.e., cellulose, hemicellulose and lignin) [2], are thus set to play a major role in empowering the energetic valorization of overabundant LMs.

This editorial on “Biovalorization of Lignocellulosic Waste” includes eight recent articles on different processes enabling the bioconversion of LMs into renewable bioenergy and biofuels. The scientific works here overviewed involve: the anaerobic digestion (AD) through mechanical and chemical pretreatments, or co-digestion, of hemp biomass residues (HBRs) [3,4]; the effect of trace elements’ (TEs) supplementation on the AD of rice straw [5]; the combination of hydrothermal carbonization (HTC) and AD employing LMs alone [6] or in combination with other feedstocks [7]; the dark fermentation (DF) of LMs aimed at biohydrogen production, also in combination with photo fermentation [8,9]; and, finally, the production of ethanol from LMs and how this impacts and is impacted by a greenhouse gas (GHG) emission reduction obligation system [10]. A summary of the content of these eight articles is reported below.

The conversion of waste LMs in bioenergy (biogas) or biofuel (biomethane, CH₄) through AD is amongst the most promising and investigated bioprocesses, but still faces relevant issues of low rates and yields. To overcome these limitations, chemical and mechanical pretreatments enabling a faster and more complete biodegradation are often used. Matassa et al. [3] evaluated the use of mechanical and chemical (i.e., acid and alkaline) pretreatments on HBRs, a typically overabundant waste LM. The use of mild alkaline (24 h at 30 °C with a 1.6% weight-to-weight (w/w) NaOH solution) or mechanical (particle size reduction to 1–2 mm) pretreatments led, in both cases, to an almost 16% increase in the biochemical methane potential (BMP) as compared to the untreated feedstock. This study confirms how the removal of the lignocellulosic barrier by means of chemical pretreatment, thereby providing an easier and more complete cellulose biodegradation, or the increase in the surface available to the enzymatic hydrolysis through a mechanical pretreatment,



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can significantly improve the CH₄ production from waste LMs. In addition to mechanical or chemical pretreatments, the AD of waste LMs in combination with substrates having different structures and properties represents another interesting option to improve the BMP and, thus, the bioconversion of LMs. Papirio et al. [4] demonstrated how the BMP of HBRs can be enhanced by almost 11% by co-digesting hemp hurds and cheese whey in a 70:30 ratio (on a volatile solids (VS) basis). The co-digestion of LMs with other substrates is generally aimed at improving the carbon to nitrogen (C/N) ratio, increasing the availability of TEs (see below) or the content of readily biodegradable material. The latter, by stimulating a higher activity of enzymatic hydrolysis, was likely the predominant mechanism that improved the BMP from LMs in the presence of cheese whey.

Another strategy to enhance the BMP of LMs is to supplement essential TEs to improve the microbial growth and metabolism. Mancini et al. [5] proposed the addition of iron (Fe) and cobalt (Co) to the AD of rice straw, a typical abundant LM deficient in TEs. Besides investigating the effect of the addition of Fe and Co, in comparison with the condition with no metals added, the authors evaluated the change in metal speciation and bioavailability and how these could affect the biological conversion of rice straw into CH₄. The authors observed that, despite an increase in the Fe and Co bioavailable fractions by 23 and 48%, respectively, the BMP obtained from rice straw was not significantly enhanced. This was ascribed to the inoculum used in the BMP tests, i.e., a buffalo manure digestate, highly rich in bioavailable TEs. Hence, as also highlighted in the previous paragraph, the importance of using multiple substrates, having different physico-chemical characteristics and origins during AD, can also contribute to a more balanced presence of essential TEs for the microbial consortia involved.

Extending the potential of the AD of LMs characterized by a high water content is also possible through the integration with innovative thermochemical treatments such as HTC. This strategy is particularly promising, as it combines the production of a solid fuel, the so-called hydrochar, with the generation of process waters characterized by a chemical oxygen demand (COD) of more than 30 g/L, which can be further biovalorized through AD. The study by Brown et al. [6] proved how the combination of HTC and AD, treating grass as LM, can greatly improve the overall energy output. The authors showed how the combustion of the hydrochar and the generation of biogas from process waters (obtained through HTC from 150 to 250 °C for one hour) could increase the overall energetic output from 51 (AD alone) to 97% (HTC-AD). The beneficial effects of combining AD and HTC were also demonstrated by Parmar et al. [7], who co-processed waste LMs with sewage digestate to investigate the effect on the generated hydrochar and on the BMP of process waters. The blending of LMs with a substrate having different characteristics improved the BMP by about 26% as compared to the AD of process water obtained from the HTC of the single substrates. Both studies on the combined HTC-AD of single and co-processes LMs also highlight how the biovalorization of the liquid fraction through AD is likely to lead to better energetic outcomes when the HTC temperature is lower (150–200 °C), thereby limiting the formation and solubilization of inhibitory compounds such as phenols, hydroxymethylfurfural (HMF) and furfural, or when the presence of co-substrates with a high water content (e.g., sewage digestate) exerts a positive dilution effect on inhibitors of AD.

Hydrogen (H₂) will play a pivotal role in the future low-carbon economy. The large availability of LMs can propel the production of clean H₂, for instance through biological routes such as DF. In their review, Liu et al. [8] examined the technological development of DF, with an emphasis on constructed artificial neural networks to establish correlations among carbon sources (i.e., glucose and xylose, obtained from pretreated lignocellulosic fermentation broths), the potential inhibitors (e.g., acetate, furfural and aromatic compounds) and H₂ production yield and rate. The authors found that their approach allowed them to identify the optimal composition, in terms of glucose and acetate concentrations, leading to the highest H₂ production yield and rate, providing useful insights for the steady-state operation of continuous-flow DF bioreactors. Notwithstanding this, the management of the fermentate obtained from DF can often be an issue given the still high carbon concentra-

tions. The work of Kucharska et al. [9] proposed a sequential process coupling DF to photo fermentation, with the second treatment/valorization step being employed to further convert the residual organic acids into H₂ or other valuable products (e.g., precursors of deep eutectic solvents). The authors observed an increase in H₂ production up to approximately 820 mL/L medium and an 82% removal of COD from the DF broth.

Ethanol is another biofuel which is firmly considered to drive future sustainability strategies. Ethanol can be obtained from the biological transformation of LMs through hydrolysis and fermentation via the solventogenesis route. Bioethanol is nowadays used in vehicles' engines and can be blended with fuels obtained from fossil sources to reduce the environmental impact and GHG emissions of the transportation sector. In this context, Haus et al. [10] investigated how the economic competitiveness of sawdust-based ethanol could be influenced by the GHG emission reduction system imposed in Sweden for the road transportation sector. It was observed that sawdust-based ethanol can lead to a saving of 83–97% of GHG emissions compared to traditional fossil liquid transportation fuels. According to the authors, this will likely increase the cost competitiveness of lignocellulosic ethanol in the near future, although the allocation of additional economic incentives is needed to favor the introduction of new forms of bioethanol in the market.

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