Corn stalks as a lignocellulose substrate for biorefinery applications

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Biomass captures CO_2 from the atmosphere when growing. In the same time, approximately 1,4 Gt of available renewable biomass is annually wasted while cereal straw wastes contribute to that with 66%. Corn is among the dominant cultures in Europe with annual production of over 69,960 thousand metric tons (US Department of Agriculture, 2022). The significant amount of stalks, husks and leaves remains after the harvest and huge portion of these residues is still burnt, while it is the source of bioactives, fermentable sugars and only natural aromatic polymer-lignin. For example, lignin is among the most abundant aromatic polymers on planet with estimated amounts of over 300 billion tons and with annual increments estimated by around 20 billion tons (Kouris, 2020). The main obstacle for valorization of biomass is the recalcitrant nature of dominantly present lignocellulose and variability in biomass composition which decreases already modest efficiency of acid/alkaline thermal treatment conventionally used in biorefineries. Conventional treatments have low selectivity, generate inhibitory compounds for enzymes or microorganisms used in biorefineries and have high environmental footprint.

Cold plasma treatment (CPT) can induce modifications of cellulosic and hemicellulosic fraction as well as oxidation and depolymerisation of lignin, but CPT lacks selectivity in complex substrates such as agri-food wastes. Medium used during CPT significantly affects efficiency of carbohydrate or lignin degradation and influence chemical changes induced in both fractions. We combined CPT with water, ethanol, Fenton and hydrogen peroxide media under acidic and basic conditions for treatment of corn stalks as significant lignocellulose agri-industrial waste. Chemical properties of treated samples were analyzed by FTIR and mercury porosimetry, acetyl bromide soluble lignin content was determined by spectrophotometric methods, while carbohydrate fractions were subjected to enzymatic hydrolysis followed by spectrophotometric analysis to assess its potential for fermentations. Lignin fraction which is often neglected (Ponnusamy et al., 2019) was also examined as a source of antioxidants.

We proved that some delignification can be achieved with CPT and further enhanced in combination with other oxidative treatments, particularly Fenton and alkali hydrogen peroxide treatment, while significantly decreasing treatment time and duration. After CPT assisted pretreatments, the enzymatic hydrolysis of carbohydrate fractions was preserved or even enhanced. This was explained by textural changes of lignocellulose substrates after CPT. CPT induced up to two times larger pores in treated biomass and maintained its stability. This effect correlated with the CPT duration and made substrate surface more approachable to enzymes. Different chemical modifications were obtained depending on conditions of CPT treatment or media composition (Fe/hydrogen peroxide ratio or hydrogen peroxide concentration). It was confirmed that CPT as low energy treatment combined with other oxidative treatments significantly improves delignification and carbohydrate accessibility while decreasing overall processing time and energy consumption.

Combination of CPT proved beneficial in corn stalks fractionation, but based on the obtained results it seems promising that process can be further improved to use lower concentration of chemicals (acid, bases or Fe ions) by careful optimization of CPT treatment. This can also significantly elevate application potential of lignin fraction which are usually too aggregated and modified after conventional treatments. This can significantly contribute to move towards more advanced biorefineries where process sustainability will be achieved through valorization of both lignin and carbohydrates present in biomass.

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