Fractionation of corncob biomass towards sustainable valorization in biorefinery processes

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Keywords: delignification, microwave, lignocellulose, lignin isolation, biorefinery.
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Corncob biomass is a type of secondary agricultural residue of lignocellulosic nature that is generated in huge amounts during corn processing. In developing countries, secondary agricultural residues are still underutilized, mostly being disposed of by field dumping, open burning, or used as firewood in boilers or furnaces (Gandam *et al*, 2022). The utilization of lignocellulosic biomass including corncob in higher-value biorefineries is still very limited. Focusing on the processing of one structural component of biomass, mainly carbohydrate polymers, many of these processes suffer from unsustainability. To expand the spectrum of biorefinery products new processes should enable efficient biomass fractionation with high selectivity while preserving the potential of not only cellulose, and hemicellulose but also lignin, assuring minimal wasting of resources (Gandam *et al*, 2022). In this work, we studied the fractionation of corncob biomass by applying short-term microwave-assisted peroxide treatment. The fractionation process was optimized to enable the simultaneous recovery of polysaccharide-rich residue and high-quality lignin fraction for the more sustainable and upgraded valorization of corncob biomass in biorefineries.

Corncob was kindly provided by a local farm in Vojvodina province, Serbia. A particle fraction between 0.5 mm and 1 mm was extracted with ethanol and obtained alcohol-insoluble residue was further subjected to microwave-assisted peroxide treatment using the Monowave™ 300 microwave reactor (Anton Paar, Austria). A Taguchi orthogonal array L9 (3^4) was applied to establish the optimum treatment conditions and to determine the contribution of individual process parameters (factors) to the target functions (responses). Four process parameters studied at three levels were the concentration of hydrogen peroxide, microwave power, pretreatment time, and liquid-to-solid ratio, while the lignin content in solid residue, total solid recovery, and yields of isolated lignin and hemicellulose were analyzed as process responses. The lignin content was determined spectrophotometrically by the acetyl-bromide method (Fukushima and Kerley, 2011). Total solid recovery and the yields of hemicellulose and lignin isolated from the pretreatment liquor were calculated and expressed as a percentage of starting biomass dry matter. The untreated and treated corncob biomass, and isolated lignin obtained by optimal treatment conditions were characterized in terms of compositional analysis (applying analytical NREL procedure) (Sluiter *et al*, 2008). Changes in the functional groups and crystallinity of obtained fractions were also analyzed by Fourier transform infrared spectroscopy (FTIR) and X-ray diffraction (XRD).

The analysis of the Taguchi design showed that higher lignin removal could be obtained when microwave power, treatment time, and concentration of hydrogen peroxide are high, and the liquid-to-solid ratio is low. The optimum delignification was obtained at a microwave power of 300W, a treatment time of 60 s, 2.5% of hydrogen peroxide, and a liquid-to-solid ratio of 10. After establishing the optimum treatment conditions, the response values under the optimum conditions were predicted and a confirmation experiment was conducted to validate the predicted results. The obtained results of a confirmation experiment demonstrated that the prediction of the Taguchi design was in good agreement with the experimental results. Studying the correlation between lignin content, total solid recovery, and yields of isolated hemicellulose and lignin after the conducted 9 treatment runs, it was observed that the lignin content and solid recovery were strongly positively correlated, while the yield of isolated lignin and hemicellulose were negatively correlated with the solid recovery (Table 1).

Table 1. Correlation between lignin content, yields of isolated lignin and hemicellulose, and total solid recovery obtained after 9 experimental runs in Taguchi optimization.

Parameter (%)	Total solid recovery	Lignin content in the solid residue	Hemicellulose yield
Lignin content in the solid residue	0.929699	1	
Hemicellulose yield	-0.90567	-0.90082	1
Lignin yield	-0.90333	-0.91894	0.956861892

Compositional analysis of treated and untreated biomass showed a decrease in lignin content of 76.5% and an increase in cellulose content of 60.4% after applying optimal treatment conditions. Also, XRD analysis showed significantly higher cellulose crystallinity after the treatment (63%) compared to untreated corncob biomass (45%). The results obtained in this study indicate that the lignin and hemicellulose were the target components in the microwave-assisted peroxide treatment and that the increase of cellulose content and crystallinity was mainly due to efficient biomass delignification. This suggests that better cellulose digestibility could be expected in enzymatic hydrolysis due to better cellulose accessibility and more reversible enzyme adsorption on treated biomass allowing more efficient utilization of corncob in the production of fermentable sugars. In addition, the lignin was isolated from the pretreatment liquor with relatively high purity (78%) and yield of 17.75% which could bring additional value towards more sustainable corncob valorization in biorefinery processes.

Acknowledgements
This work was supported by the Ministry of Science, Technological Development and Innovation of the Republic of Serbia (Contract No. 451-03-47/2023-01/200287 and 451-03-47/2023-01/200135) and by Alliance of International Science Organizations, project SparkGREEN (ANSO-CR-PP 2022-08).

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