

Lignocellulosic crop residues – characterization as raw materials for bio-based production chain

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Introduction

Lignocellulosic crop residues (LCR) represent a large biomass category generated by agricultural harvesting activities and are regarded as crop wastes. Cereal straws, in particular of wheat and corn stalks are ubiquitous in the temperate climate zone due to their large amount and availability (Giannoccaro et al., 2017; Jain et al., 2022).

LCR are made up mostly by biopolymers (polysaccharides and lignin) resulted from biosynthesis process. This is giving LCR the character of renewability (Klemm et al., 1998). The main polysaccharides, making up about 60-70% of the chemical composition, are cellulose and hemicelluloses. (Ren and Sun, 2010, Kopetz, 2013).

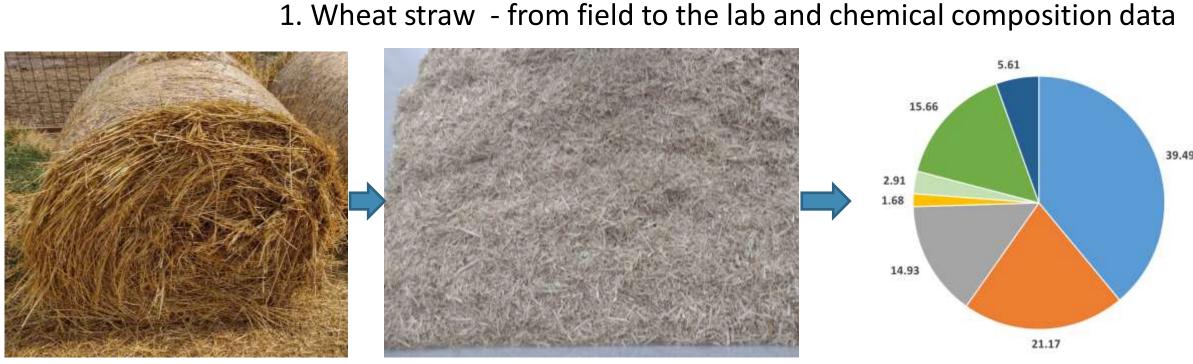
The main objective of the current work is to emphasize the potential of LCR by revealing the important chemical components' contents. Preliminary results of laboratory trials on the extraction of hemicelluloses and insights of their chemical structure elucidation are presented. Extraction of hemicelluloses and their characterization is an important step in the light of their further use as biopolymers with direct application.

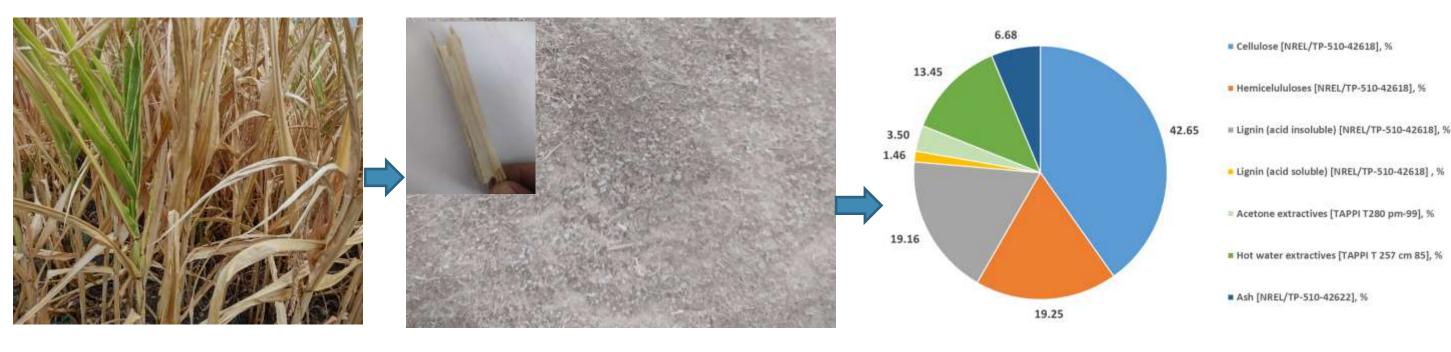
Materials

Wheat straws (mixture of three varieties in equal ratios) collected from Romanian farms (harvest of summer 2022) were further grinded and analyzed for cellulose, hemicelluloses, lignin as well as minor components such as ash, acetone and water extractives.

Corn stalks (harvest of autumn 2021) was also kindly supplied by local farmers and analyzed in similar manner as wheat straw.

Subsequent to the analysis hemicellulose extraction by alkaline treatment (NaOH -5% w/w) was performed. Hemicelluloses were ethanol precipitated, recovered by centrifugation oven dried and analyzed.







From left to right – the initial immersing of raw materials in NaOH solution prior to thermal treatment; the Duran shots after thermal treatment at 100°C for 60 minutes; precipitation tests at various pH-values sample image of separated hemicelluloses before drying and finally hemicelluloses preparations from wheat straw and corn stalks.

The obtained hemicellulose were subjected to complete hydrolysis in H_2SO_4 solution (4%) for 1 h at 121°C in closed reaction vessels. The resulted hydrolysate containing degradation sugars were subjected to HPLC analysis for sugar identification and quantification.

Thus, it was found out that both hemicelluloses separated from wheat straw (HCWS) and corn stalks (HCCS) were xylan backboned - 70% xylose of total sugars in case of HCWS and 77% xylose in case of HCCS.

Results, discussions & important remarks

2. Corn stalks- from field to the lab and chemical composition data

3. Hemicelluloses separation by alkaline extraction

As previously noted (Li et al., 2017; Puitel et al., 2022), the main branching sugar anhydro-unit was found to be that of arabinose. In the case of the present study arabinan content showed up a 22,3% in case of HCWS and 19.2% in case of HCCS. In previous work, spectral analysis by 1H-NMR in deuterium oxide showed up the presence of some other xylan substituents such as α glucuronic and β -glucose. Further perspectives of work include the improvement of extraction yields of xylan based hemicelluloses

Cellulose [NREL/TP-510-42618], %

Hemicelululoses [NREL/TP-510-42618], %

Lignin (acid insoluble) [NREL/TP-510-42618], %

Lignin (acid soluble) [NREL/TP-510-42618], %

Acetone extractives [TAPPI T280 pm-99], %

Hot water extractives [TAPPI T 257 cm 85], %

Ash [NREL/TP-510-42622], %

(2017); (2010);

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Acknowledgments



- ✓ Biomass generated as a result of agricultural activities;
- ✓ Lignocellulosic agricultural waste biomass residues with content of pollysacharides and lignin, mainly resulted as wastes from cultivated crops: straws & stalks -high availability at low price;
- ✓ Adequate chemical composition for pulping to papermaking fibers and other ways of valorisation (ethanol production);
- ICR are made up mostly by biopolymers (polysaccharides and lignin) resulted from biosynthesis process
- ✓ High volumes and low density –problems regarding suitable storage.
- It is to emphasize the presented work is to emphasize the potential of LCR by revealing the important chemical components' contents.
- Yereliminary results of laboratory trials on the extraction of hemicelluloses and insights of their chemical structure elucidation are presented.
- ✓ Extraction of hemicelluloses and their characterization is an important step in the light of their further use as biopolymers with direct application.
- **RESIDUES PROCESSING TOWARDS CIRCULAR ECONOMY INTEGRATION (SUSTECLCR)".**



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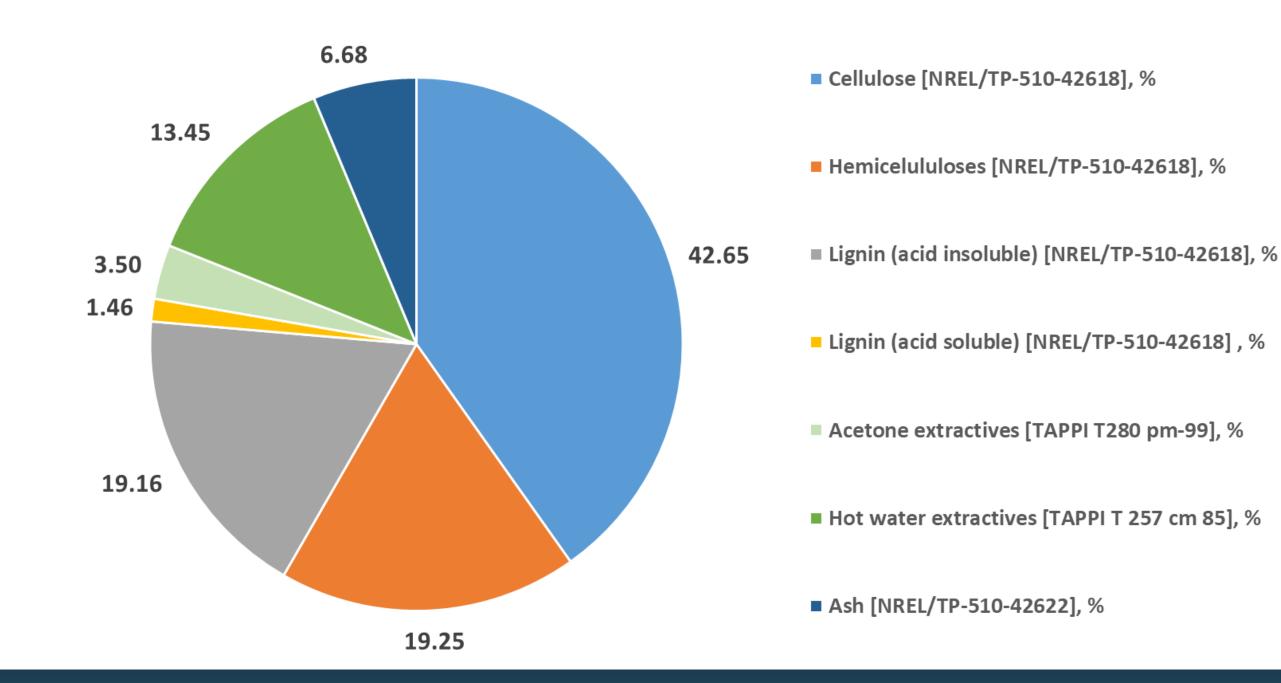
Raw materials and their chemical composition



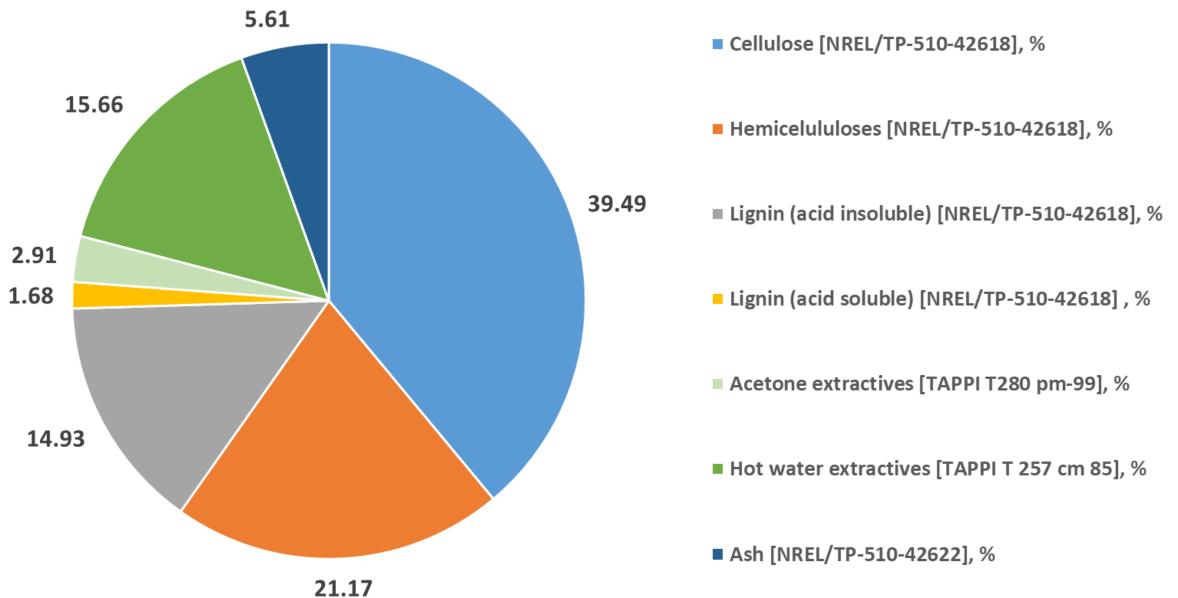
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Separation and characterization of hemicelluloses

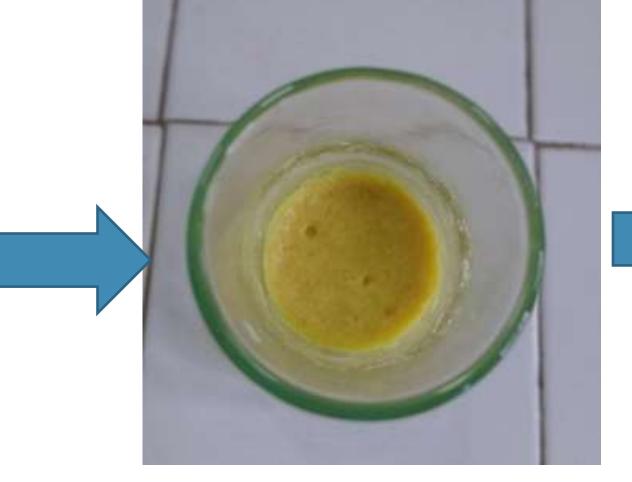


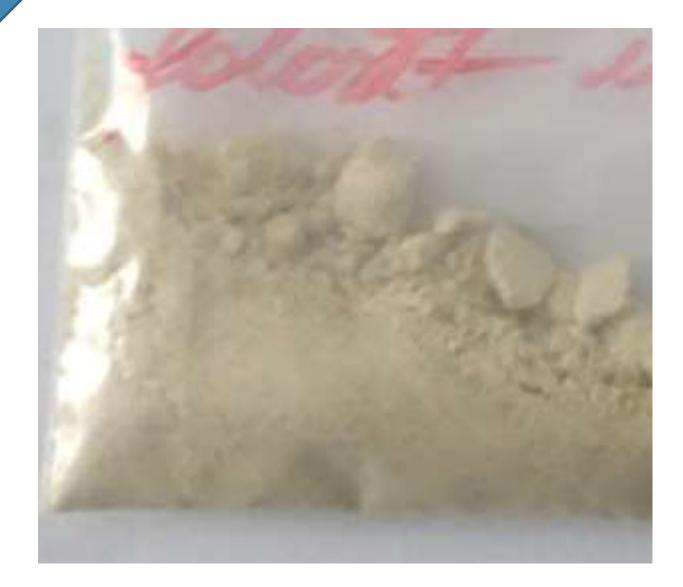


• The obtained hemicellulose were subjected to complete hydrolysis in H₂SO₄ solution (4%) for 1 h at 121°C in closed reaction vessels. The resulted hydrolysate containing degradation sugars were subjected to HPLC analysis for sugar identification and quantification.









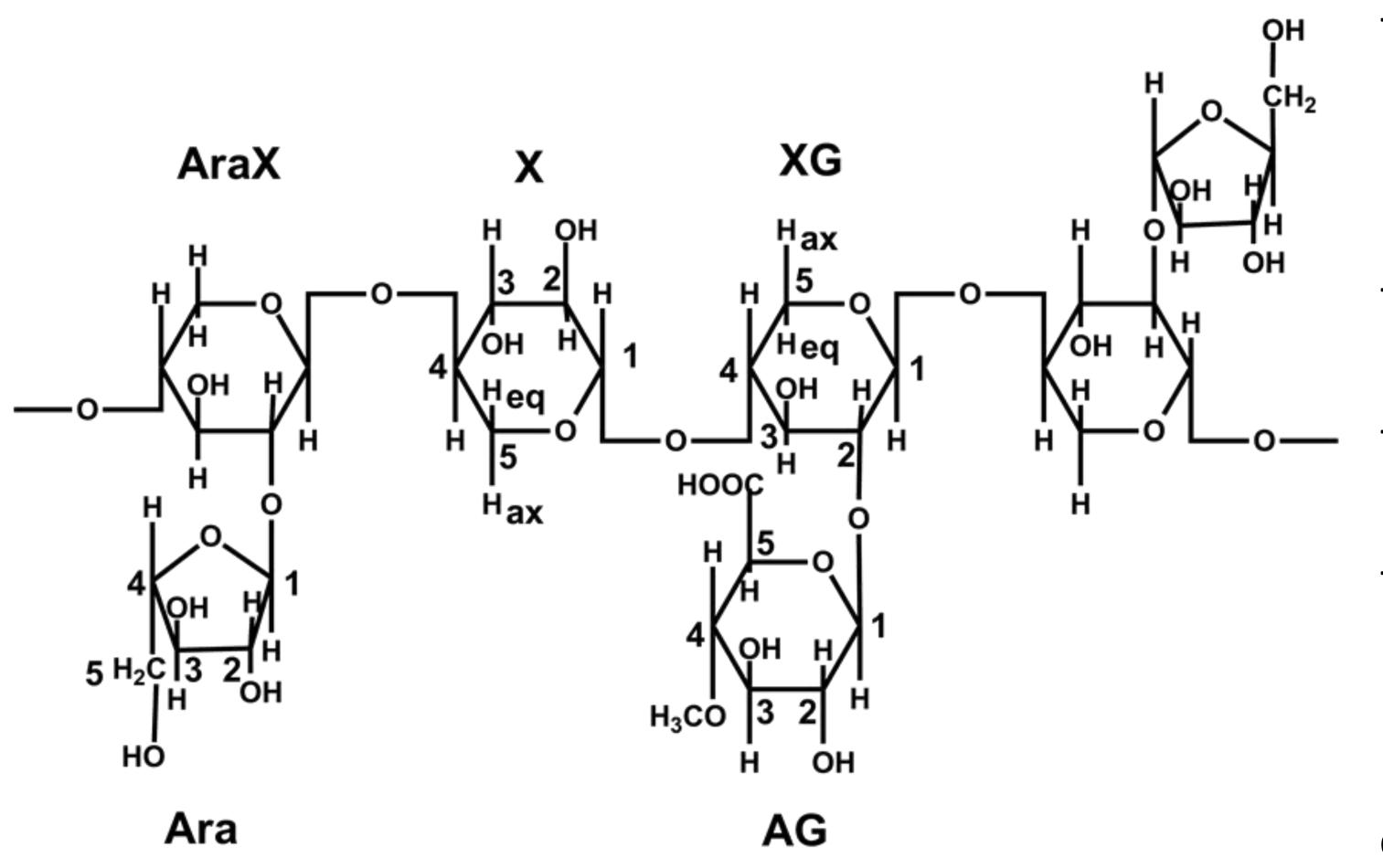
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Extracted hemicelluloses structure

- hemicelluloses separated from wheat straw (HCWS) and corn stalks (HCCS) were xylan backboned - 70% xylose of total sugars in case of HCWS and 77% xylose in case of HCCS:
- the main branching sugar anhydro-unit was found to be that of arabinose.
- arabinan content showed up a 22,3% in case of HCWS and 19.2% in case of HCCS.
- In previous work, spectral analysis by 1H-NMR in deuterium oxide showed up the presence of some other xylan substituents such as α -glucuronic and β -glucose.

Further perspectives of work include the improvement of extraction yields of xylan based hemicelluloses

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