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CHEMISTRY

# DEVELOPMENT OF ANALYTICAL METHODOLOGIES AND ORGANOSOLV DELIGNIFICATION PROCESSES APPLIED TO BAGASSE AND STRAW FROM SUGARCANE

Antonio Aprigio da Silva Curvelo

São Carlos Institute of Chemistry / University of São Paulo (USP)

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*Figure 1. Hot water pretreatment and delignification of sugarcane bagasse. (Vallejos ME)*

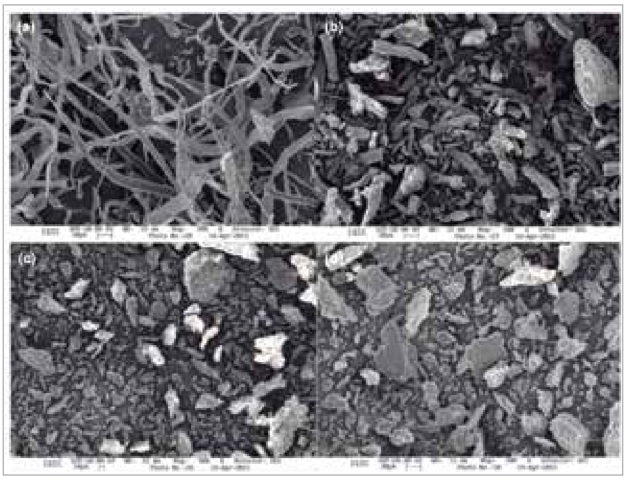

*Figure 2. SEM micrographs of (a) bagasse cellulose pulp, (b)Avicel PH101, (c) pulp hydrolyzed at 190 ºC for 80 min, (d) pulp hydrolyzed at 210oC for 40 min. (Gurgel LVA et al. 2012.* Industrial Crops and Products. **36**: *560-571)*

The proposals in this project were formulated based on scientific output and experience accumulated over 20 years dedicated to the study of characterization and production of cellulose and lignin derivatives from lignocellulosic materials, with special attention to the bagasse obtained from sugar cane processing. The proposed project is focused on the study of lignin's solvency through delignification reactions, the development of analytical methodology for the characterization of the main components of sugarcane bagasse, isolation of natural products present in the skin of the culms and the leaves of sugarcane and the study of cellulose hydrolysis in aqueous acidic media. Lignin's solvency studies include three basic processes: conventional (aqueous solutions), organosolv and organosolv assisted by sub/supercritical carbon dioxide. Considering the pretreatments steps to produce enriched cellulose samples for sugar production, it was included the study of the liquid to solid ratio in the hydrothermal and organosolv delignification. As a result of these procedures, the cellulosic pulps will be employed for the production of glucose by means of acid hydrolysis of cellulose by using mineral acids and carbon dioxide at sub/supercritical state. The technique that uses fluids at sub/supercritical state may allow the hydrolysis of cellulose without the utilization of mineral acids in an attempt to avoid the production of inhibitors for the fermentation processes. The traditional methods for the characterization of lignocellulosic materials were developed and optimized for wood and wood derivatives (pulp and paper). Due to the different characteristics of grasses and agricultural wastes (especially from crushed cane sugar industry) the modifications of existing methods and/or development of new analytical methodologies for the chemical characterization of sugarcane bagasse is of fundamental importance for both academic studies and industrial applications. The waxes present in the skin of the culms and the metabolites present in the leaves constitutes important substrates for the chemical and pharmaceutical industries and will isolated by means of organic solvent and/or supercritical carbon dioxide.

## SUMMARY OF RESULTS TO DATE AND PERSPECTIVES

The gravimetric determination of lignin by the acid treatment showed that the optimal acid concentration for the determination of the total lignin is within a defined concentration range (65 - 72%), which was different for each sugarcane bagasse fraction (pith, fiber or straw). The use of the oxidation process for the indirect determination of lignin showed that this method also needed be optimized, to be applied to samples of sugarcane bagasse. The results showed that increasing the amount of oxidizing agent improved the performance of the method, even when excess oxidant may promote oxidation of the polysaccharide present in the samples.

The hot water pretreatment of sugarcane bagasse performed at 170 °C for 60 min, with liquid to solid ratio (LSR) of 3 g/g, produced the maximum concentrations of xylose and xylan (13.76 and 36.18 g/L, respectively), equivalent to 48.29 g/L of xylan. The amount of xylan removed under these conditions was almost 57% of the xylan present in the untreated bagasse. The dissolved xylan is mainly composed of xylo-oligosaccharides (74 wt%). Glucose and glucan contents in the spent liquor were less than 1.1%, which shows that cellulose was not hydrolyzed by the hot water pretreatment. Low liquid–solid ratio (LSR) provided a simple and ambient friendly means to produce high-content xylo-oligosaccharides spend liquor with enormous potential for industrial applications.

The association of high-pressure carbon dioxide in the liquid hot water (LHW) pretreatment of sugarcane bagasse promoted a higher degree of deacetylation in comparison with LHW alone, resulting in an increase of liquor's acidity and allowed higher hemicelluloses extraction. As expected Xylan, Xylose and Furfural concentrations were strongly dependent on the reaction temperature and time. The pretreatments performed yielded operational conditions that can be useful in processes were high concentrations of xylose and/or xylan are required without the drawbacks of a process employing mineral acids and with the benefit of using reduced temperatures in comparison with LHW alone.

The kinetics of sugarcane bagasse cellulose saccharification and the decomposition of glucose under extremely low acid (ELA) conditions (0.07%, 0.14%, and 0.28% $H_2SO_4$) and at high temperatures were investigated using batch reactors. The ELA conditions were successful applied to the hydrolysis of sugarcane bagasse cellulose in batch reactors and produced glucose yields close to 70%. The residual solids obtained after the chemical saccharification of cellulose were characterized by X-ray diffraction (XRD), thermogravimetric analysis (TGA) and Scanning Electron Microscopy (SEM). The thermal, XRD and SEM studies demonstrated that the cellulose residues have thermal decomposition behavior, crystallinity index, crystallite size and particle size similar to Avicel PH-101 and can also be considered microcrystalline celluloses.

## MAIN PUBLICATIONS


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Antonio Aprigio da Silva Curvelo

Instituto de Química de São Carlos
Universidade de São Paulo (USP)
Av. Trabalhador São Carlense, 400
CEP 13566-590 – São Carlos, SP – Brasil

+55-16-3373-9938
aprigio@iqsc.usp.br