I COBBIND
I CONGRESSO BRASILEIRO DE BIOTECNOLOGIA INDUSTRIAL
XXIV SINAFERM • XV SHEB • XV ENZITEC FLORIANÓPOLIS • 2024
Creating connections between biotechnology and industrial sustainability
August 25 to 28, 2024
Costão do Santinho Resort, Florianópolis, SC, Brazil
BIORREFINERY, BIOECONOMY AND CIRCULARITY

# LIFE CYCLE ASSESSMENT OF CELLULOSE NANOCRYSTALS AND NANOFIBRILS PRODUCTION BY ENZYMATIC HYDROLYSIS IN A SUGARCANE BIOREFINERY

Gustavo Batista[1]*, Cristiane Sanchez Farinas[2,3] & Antonio José Gonçalves da Cruz[2]

*[1] Radix Engineering and Software, 20021-290, Rio de Janeiro - RJ.*
*[2] Graduate Program of Chemical Engineering, Federal University of São Carlos, 13565-905, São Carlos, SP, Brazil.*
*[3] National Nanotechnology Laboratory for Agribusiness (LNNA), Embrapa Instrumentação, Rua XV de Novembro 1452, 13560-970, São Carlos, SP, Brazil.*
** Corresponding author's email address: gustavo.batista@radixeng.com*

## ABSTRACT

The purpose of using Life Cycle Assessment (LCA) in this work was to evaluate the cellulose nanocrystals (CNCs) and cellulose nanofibrils (CNFs) production by enzymatic hydrolysis in a sugarcane biorefinery, identifying hotspots that can direct to process design changes to reduce environmental footprint. Modeling and simulation of a unit for CNCs / CNFs production from sugarcane bagasse (the main residue from the sugarcane industry) was carried out. In order to proceed the LCA, an inventory of raw-materials, products and emissions was made. The analysis employed the cradle-to-gate approach. The Global Warming Potential (GWP) metric was estimated using the SimaPro® software and using the EcoInvent v.3.3 database. LCA results showed that daily production of 5.2 ton of CNCs occurred with accumulated GWP of 25.0 tons of $CO_2$ equivalents. An estimated GWP of 0.25 kg of $CO_2$ equiv. per kg of dry equiv. CNCs (or 14.36 g of $CO_2$ equiv. / MJ of process outputs) were accounted after energetic allocation. In other impact categories aside from GWP, the environmental impacts of ethanol and $H_2O_2$ were generally the most relevant.

**Keywords:** Life Cycle Analysis. Enzymatic Hydrolysis. Cellulose Nanocrystals and Nanofibrils. Sugarcane Biorefineries. Global Warming Potential (GWP).

## 1 INTRODUCTION

Growing environmental concerns on a global scale make the development of environmentally sustainable processes a priority. With the implementation of the carbon credits market, the quantification of the Global Warming Potential (GWP) and other metrics of environmental impacts have also a stronger impact on investment decision-making[1]. Life Cycle Assessment (LCA) is a standardized tool to quantify the environmental sustainability performance of emerging technology products along all phases of their life cycles, allowing the comparison of different process designs[2,3]. If the methodology is used during a new product development phase, especially during the process methodology planning, it can indicate the process stages or technologies with the highest environmental impacts, and thus provide a guide for improvements in the implementation of the technology[4]. ISO 14040:2006 and ISO 14044:2006 established a methodological framework for conducting LCA studies.

The energetic efficiency and the use of agricultural residues are key performance indicators in a low carbon society. The biomass-based processes, such as biorefineries, use residues such as sugarcane bagasse to produce energy, ethanol, and different molecules of higher added-value. Nanocellulose is an example of an emerging, still under development material for which a reduced environmental impact is expected when comparing to other existing materials[5,6]. Cellulose nanocrystals (CNCs) are crystalline and highly ordered materials of small diameter, elongated length, and high surface area whose main applications are as reinforcement in polymeric materials and the applications in biomedicine. Consisting in a high added-value renewable biocomposite, but still in limited availability and presenting low yields of obtainment and isolation, the nanocellulose market is in continuous and strong growth.

To the best of our knowledge, the technical-environmental analysis of the production of CNCs and CNFs from sugarcane biorefinery residues in a high scale is a topic not yet well investigated in literature. Thereby, the purpose of using LCA in this work was to simulate the CNCs / CNFs production in sugarcane biorefineries by enzymatic hydrolysis, and to quantify the GWP of this nanocellulose unit in a 100-year horizon through LCA, identifying hotspots that can direct to process design changes to reduce the environmental footprint.

## 2 MATERIAL & METHODS

The simulated methodology of production proposed in this work employed sugarcane bagasse as feedstock. The process started with hydrothermal pretreatment (195°C, 10 min, water input as 3.33 x dry mass of bagasse) of the bagasse followed by organosolv delignification (190 °C, 2h, 1:1 vethanol/vwater, 1:10 dry mass / volume of solution) with ethanol recycle by flashing and distillation. After that, a purification with diluted peroxide (50 °C, 1 h, $H_2O_2$ 7% vol, NaOH 5% vol, 10:1 m/m relative to input) was used to maximize the cellulose content before the hydrolysis. The enzymatic hydrolysis was carried out in the following conditions: 50 °C, 48 h, water input of 6.66 x dry mass, enzyme cocktail input of 10 FPU / g of biomass, and enzyme activity of 205 FPU / ml of enzyme – measured in lab for *Cellic Ctec-3* enzyme cocktail fabricated by Novozymes®). After washing and filtering of the produced CNCs and CNFs, the downstream process then proceeded with dialysis, sonication, and drying of the material to purity of 95% in a spray-dryer. The annual sugarcane bagasse utilization as feedstock was set at 72,000 tons per year. The mass and energy balances for discontinuous equipment were discretized, i.e., the input and output streams had mass and energy contents distributed over the time of the equipment usage cycles.

Hydrothermal pretreatment is an environmentally friendly, very effective way of removing hemicelluloses and reducing the initial recalcitrance of biomasses[7]. Organosolv pretreatment with ethanol was selected over other treatment options because it provides high rates of removal of lignins and residual hemicelluloses, whilst being environmentally less aggressive than the chemical processes[8]. In its turn, complementary alkaline delignification was selected for its high effectiveness in removing residual lignin content, generating biomasses with high-purity cellulose. Enzymatic hydrolysis is an alternative to the state-of-the art acid hydrolysis with $H_2SO_4$ to the nanocelluloses generation, and produces C6 sugars as by-product that can be filtered and then exported to the sugarcane biorefinery for ethanol generation. As enzymatic hydrolysis does not degrade all amorphous cellulose fractions present in the hydrolyzed matrix, both CNCs as CNFs are formed as products.

Experimental input parameters were based on data obtained in the LNNA laboratory at *Embrapa Instrumentação* with experimental methodologies that were already published in previous works by the research group[9,10]. Mass and energy balances were performed on Microsoft Excel® electronic spreadsheets. In the energy balances, the thermodynamic calculations for the equipment were performed using ThermoSolver® software and the results were transposed to the electronic spreadsheets. The NRTL thermodynamic model was used to represent the non-idealities of liquid phase mixtures in each analyzed system. Figure 1 shows a box diagram that represents the simulated process.

In order to proceed the LCA, an inventory of raw-materials, products and emissions were made based on the process modeling stage. The analysis employed the cradle-to-gate approach, and the functional unit was considered as 1 kg of cellulose nanomaterials produced (CNCs + CNFs). The GWP coefficient quantified the Greenhouse Gas Emissions (GHG) as grams of equivalent $CO_2$ emitted per each produced kg of CNCs + CNFs for 100 years of operation. The carbon intensity of residues from any process stage was equaled to zero in the cradle-to-gate approach. For the allocation of environmental impacts to the products (CNCs and CNFs) and the by-products from the process (lignin and C5 / C6 sugars), energetic allocation was carried out as the impact's distribution factor. In addition to the GWP metric, other environmental assessment categories were also evaluated, as the *CML-IA Baseline v3.04 2000* method was selected in *SimaPro® 9.0.0.35 PhD* software and using the *EcoInvent® v.3.3* database.

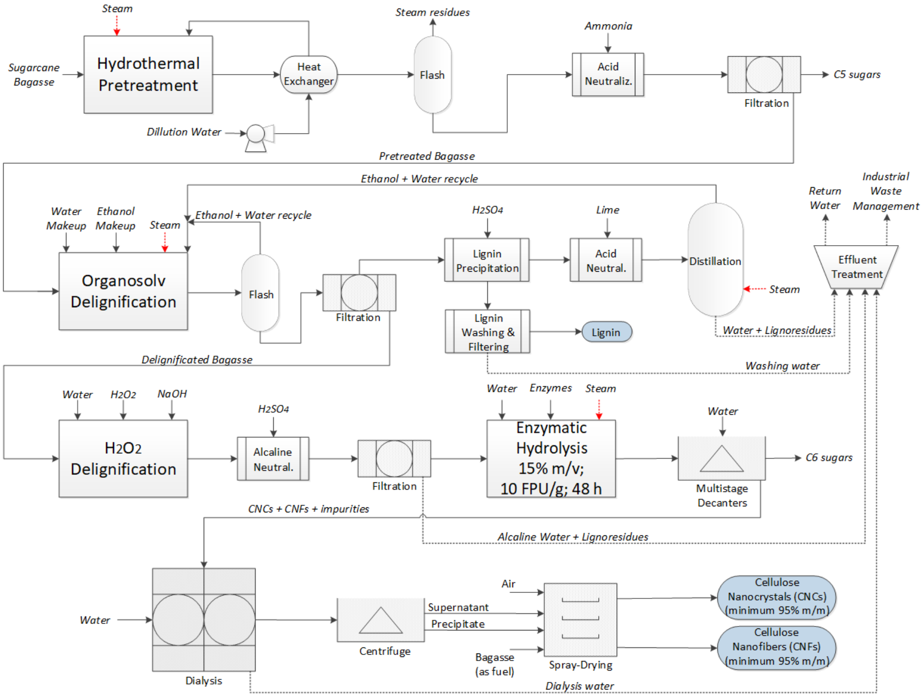

**Figure 1** Block diagram for the CNCs production methodology proposed in this work.

## 3 RESULTS & DISCUSSION

Modeling and simulation results showed that the nanocelluloses production from sugarcane bagasse by enzymatic hydrolysis was water-use intensive, as 281 $m^3$ of water / ton CNCs were consumed. LCA results showed that daily production of 5.2 tons of CNCs + CNFs (along with by-products) occurred with accumulated GWP of 25.0 tons of $CO_2$ equivalents. Ethanol from organosolv pretreatment (25.7%), $H_2O_2$ from purification (19.5%), and sugarcane bagasse transport and burning for steam and energy generation for the process (19.3%) were the main contribution inputs for GWP.

An estimated GWP of 0.25 kg of $CO_2$ equiv. per kg of dry equiv. nanocelluloses were accounted after energetic allocation. This result corresponds to 14.36 g of $CO_2$ equiv. / MJ of process outputs. In some other impact categories aside from GWP, the environmental impacts of ethanol and $H_2O_2$ were generally the most relevant, especially the $H_2O_2$ marine aquatic ecotoxicity (78.7% of the total 44.7 * $10^6$ kg of 1,4-DB equiv. per day of production), as seen in Figure 2. On the other hand, sugarcane bagasse was identified as generating high environmental impacts of terrestrial ecotoxicity, soil acidification and water eutrophication (60% of the total), possibly due to the fertilizers and pesticides used on tillage.

Although CNCs are generally non-toxic and are produced from renewable resources, the environmental impacts of their production routes have not been studied extensively yet[11]. Life Cycle Assessments for the production of nanocellulose varieties by hydrolysis are scarce in literature, but GWP values obtained in this work are in the same order of magnitude of that found on some other works that evaluated nanocelulose production by other routes, e.g., ALBARELLI et al.[12] (0.870 kg of $CO_2$ equiv. / kg of cellulose nanomaterials by sulfuric acid hydrolysis of sugarcane bagasse pretreated with SO2-catalized steam explosion). Comparing the relatively low GWP values found in this work with the ones of processes that use derivatives of fossil fuels (and even other biochemicals[2]) indicates that the nanocelluloses production by enzymatic hydrolysis from sugarcane bagasse is an option of interest for industries in the sector that aim to expand their portfolio with a high added-value product while reducing the emission of environmental impacts. LCA is a useful tool to identify hotspots in environmental sustainability profiles of bio-based chemicals.

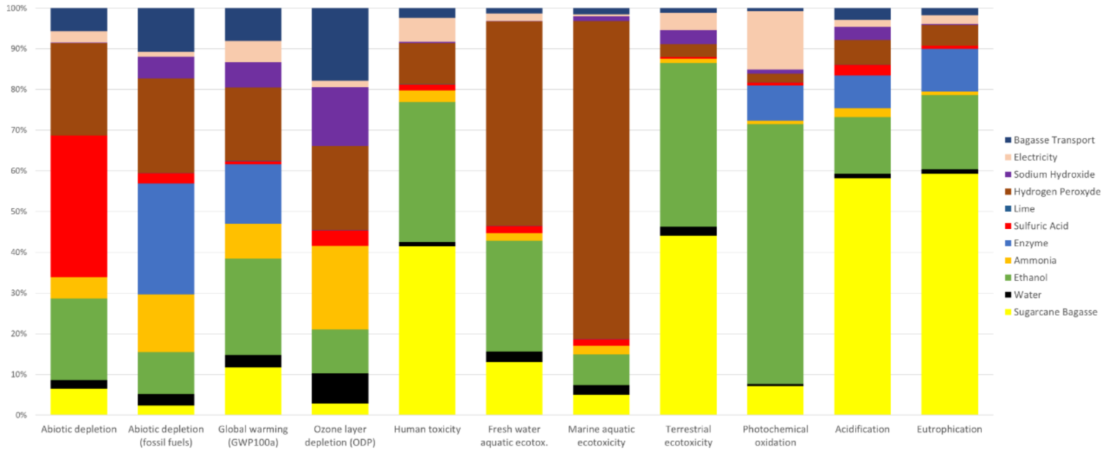

**Figure 2** Relative environmental impacts of each process input obtained thorough Life Cycle Analysis (SimaPro® software).

# 4 CONCLUSION

A LCA of an industrial nanocellulose production unit by enzymatic hydrolysis and from sugarcane bagasse was performed. The results showed that the GWP potential of the proposed process is concentrated in specific steps (ethanol from organosolv pretreatment and $H_2O_2$ from purification are highlighted). The identification of these steps can orientate researchers in identifying hotspots that can direct to process design changes, aiming to obtain production routes that can be environmentally friendly withal economically competitive. The implementation of a strong national production base for this biopolymer may generate jobs of different levels of qualification and make the country a reference for the nanomaterials productive sector, given the competitive potential of the existing biomass industry in Brazil.

# REFERENCES

[1] ÖGMUNDARSON, O. SUKUMARA, S. HERRGÅRD, M. J. FANTKE, P. 2020. Trends in Biotechnology, v. 38. 1203-1214.
[2] ÖGMUNDARSON, O. HERRGÅRD, M. J. FORSTER, J. HAUSCHILD, M. Z. FANTKE, P. 2020. Nature Sustainability, v. 3. 167–174.
[3] FOROUGHI, F. GHOMI, E. R. DEHAGHI, F. M. BORAYEK, R. RAMAKRISHNA, S. 2021. Materials, v. 14. 714-736.
[4] IBICT - Instituto Brasileiro de Informação em Ciência e Tecnologia. 2014. CNI. Brasília, 38 p.
[5] ARVIDSSON, R. NGUYENAND, D. SVANSTRÖM, M. 2015. Environmental Science and technology, v. 49. 6881-6890.
[6] PICCINNO, F. HISCHIER, R. SEEGER, S. SOM, C. 2018. Journal of Cleaner Production, v. 174. 283-295.
[7] BATISTA, G. SOUZA, R.B.A. PRATTO, B. SANTOS-ROCHA, M.S.R. CRUZ, A.J.G. 2019. Bioresource Technology, v. 275, 321-327.
[8] NASCIMENTO, D. M. DIAS, A. F. ARAÚJO JUNIOR, M. F. FIGUEIRÊDO, M. C. B. 2016. Industrial Crops and Products, v. 93. 58-65.
[9] BONDANCIA, T. J. AGUIAR, J. BATISTA, G. CRUZ, A. J. G. MARCONCINI, J. M. MATTOSO, L. H. C. FARINAS, C. S. 2020. Industrial & Engineering Chemistry Research, v. 59, 11505-11516.
[10] BONDANCIA T.J. & BATISTA G., AGUIAR J., LOREVICE M.V., CRUZ A.J.G., MARCONCINI J.M., MATTOSO L.H.C., FARINAS C.S. 2022. ACS Sustainable Chemistry & Engineering, v. 10. 4660-4676.
[11] VANDERFLEET, O. M. CRANSTON, E. D. 2021. Nature Reviews Materials, v. 6, 124-144.
[12] ALBARELLI, J. BLÖSCH-PAIDOSH, A. T. MARÉCHAL, F. MEIRELES, M. A. A. 2016. Chemical Engineering Transactions, v.47, 49-54.

# ACKNOWLEDGEMENTS

The authors would like to thank the Brazilian research funding agencies São Paulo Research Foundation - FAPESP (Grants 2016/10636-8 and 2019/25261-8) and National Council for Scientific and Technological Development - CNPq (Grant 140761/2017-9). This study was financed in part by Coordination of Improvement of Higher Education Personnel − CAPES, Brazil (Finance Code 001) with Grant 88887.364443/2019-00.