

## Integrated production of pullulan and 2G ethanol from sugarcane bagasse using hydrodynamic cavitation-assisted pretreatment: process simulation and techno-economic assessment.

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### ABSTRACT

The use of fossil sources of energy and carbon results in environmental problems, which drive the interest in a transition to a sustainable economy based on renewable sources. 2G ethanol, derived from lignocellulosic raw materials, as sugarcane bagasse, is a promising alternative but still faces economic challenges, particularly due to steps as pretreatment. Hydrodynamic cavitation-assisted processes show potential for biomass pretreatment due to simplicity and mild conditions operation. Lignocellulosic biorefineries can also be economically favored by diversifying bioproduct portfolios, including high-value products alongside 2G ethanol. In this way, pullulan, an eco-friendly, biodegradable, biocompatible and non-toxic biopolymer, can be an attractive alternative. Thus, complex biorefineries can be considered, including different process options and a diversity of products. To assess biorefinery viability, conduction of software-aided process simulation can help in fundamental tasks as mass and energy balances. This study evaluated a biorefinery employing hydrodynamic cavitation-assisted alkaline pretreatment and producing pullulan alongside 2G ethanol, using the software SuperPro Designer® to aid process simulation and economic analysis.

**Keywords:** 2G ethanol. Pullulan. Hydrodynamic cavitation. Process simulation. Techno-economic assessment.

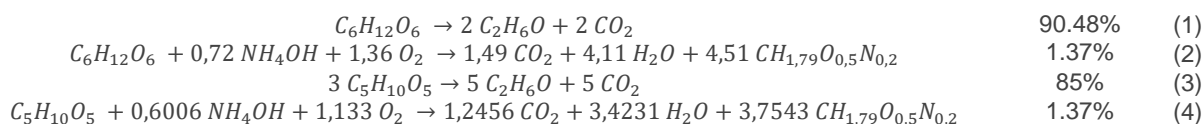
### 1 INTRODUCTION

The focus on biorefinery development stems from its utilization of renewable resources, primarily agricultural by-products, fostering a circular bioeconomy and diminishing reliance on oil.<sup>1</sup> Reducing oil dependency, especially for vital products like fuels and plastics, is imperative for a resilient future amidst the challenges posed by climate change.<sup>2</sup> Lignocellulose biomasses, owing to their wide availability and rich carbon content, are fundamental in biorefinery advancement. They are comprised mostly by cellulose, hemicellulose, and lignin fractions, and the biomasses fibers can be converted into fermentable sugars without competing with the food supply chain.<sup>3,4</sup> Second-generation ethanol (2G ethanol), for instance, is sourced from biomass, and its expansion is projected to increase by 50% the ethanol production without requiring additional cultivated area.<sup>5,6</sup> Another notable bioproduct is pullulan, an exopolysaccharide obtained through *Aureobasidium pullulans* fermentation process. It is composed by repeated maltotriose units, with applications in pharmaceuticals, food, cosmetics, and more, serving as a versatile biopolymer.<sup>7</sup>

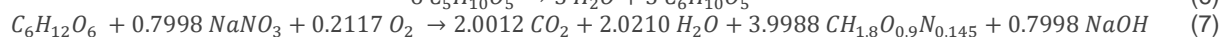
Despite their potential, lignocellulosic biomasses biorefineries encounter obstacles to economic viability. One of the main bottlenecks is the pretreatment step, essential for reducing the recalcitrance of biomasses and facilitate the access of enzymes to the carbohydrate fractions.<sup>3</sup> A promising pretreatment alternative gaining attention is hydrodynamic cavitation-assisted technique, characterized by its simplicity, mild operating conditions, absence of biological inhibitor formation, and short processing time.<sup>3</sup> Assessing the economic viability of innovative technologies like hydrodynamic cavitation on an industrial scale requires simulation tools. These tools facilitate mass and energy balances, allowing to identify process bottlenecks, and explore integration possibilities, crucial for techno-economic assessment (TEA) of biorefineries.<sup>4,8,9</sup> Diversifying product portfolios can bolster the economic sustainability of biorefineries by offering high-value specialty products alongside bulk commodities.<sup>4</sup> In this way, this study evaluated economically a biorefinery utilizing hydrodynamic cavitation-assisted pretreatment of sugarcane bagasse for 2G ethanol and pullulan production.

### 2 MATERIAL & METHODS

The process simulation utilized SuperPro Designer® v. 12.03.2101 software (Intelligen, Inc., based in Scotch Plains, United States of America). A stand-alone biorefinery processing 50 metric tons (MT) of sugarcane bagasse (SCB) per hour was considered, operating continuously throughout 330 days. The biorefinery is self-sufficiency in steam through a cogeneration system fueled by SCB. Thermodynamic calculations employed NRTL for the liquid phase and Redlich-Kwong for the vapor phase, while Raoult's Law was used for the dehydration process.<sup>8,10</sup> The biomass chemical characterization was obtained from Prado *et al.* (2013). Equations 1 to 4 presents the reactions regarding ethanol and cell formation. Other reactions were considered for other metabolites, but were not showed here.<sup>9,12</sup>



The equations added to represent the pullulan production are presented in Equations 5 to 8. The final cell and pullulan concentrations were set as 14.2 g.L<sup>-1</sup> and 32.89 g.L<sup>-1</sup>.



The economic parameters set on SuperPro Designer® for TEA are showed in Table 1.

**Table 1** Economic parameters utilized for techno-economic assessment. PC is the Purchase Cost of each equipment, TLC is the Total Labor Cost, and DFC is the Direct Fixed Cost (DC+IC+OC).

Parameter	Value	Parameter	Value
Project lifetime	25 years <sup>8</sup>	Indirect Cost (IC)	
Construction time	1.5 years <sup>8</sup>	Engineering	0.15xDC <sup>13</sup>
Start-up time	0.5 year <sup>8</sup>	Construction	0.25xDC <sup>13</sup>
Linear depreciation rate (10 years)	10% <sup>8</sup>	Other Cost (OC)	
Income tax rate	34% <sup>8</sup>	Contractor's Fee	0.04x(DC+IC) <sup>13</sup>
Minimum acceptable rate of return	12% <sup>8</sup>	Contingency	0.08x(DC+IC) <sup>13</sup>
Inflation	4.65% <sup>14</sup>	Startup Cost	
Direct Cost (DC)		Startup and Validation	0.05xDFC <sup>13</sup>
Unlisted Equipment PC	0.1xPC <sup>16</sup>	Operating Cost	
Piping	0.1xPC <sup>15,13</sup>	Maintenance	0.02xDFC <sup>15</sup>
Instrumentation	0.1xPC <sup>13</sup>	Local Taxes	0.01xDFC <sup>15</sup>
Insulation	0.03xPC <sup>16,15</sup>	Insurance	0.0004xDFC <sup>15</sup>
Electrical Facilities	0.05xPC <sup>13</sup>	Lab, quality control...	0.05x TLC*
Building	0.15xPC <sup>16,13</sup>	Bioproducts selling prices	
Yard Improvement	0.05xPC <sup>16,13</sup>	Feedstock	Price
Auxiliary Facilities	0.15xPC <sup>13</sup>	Ethanol	0.665285 US\$.Kg <sup>-1 8</sup>
		Pullulan	43.746964 US\$.Kg <sup>-1 17</sup>

\*SuperPro Designer® ethanol example.

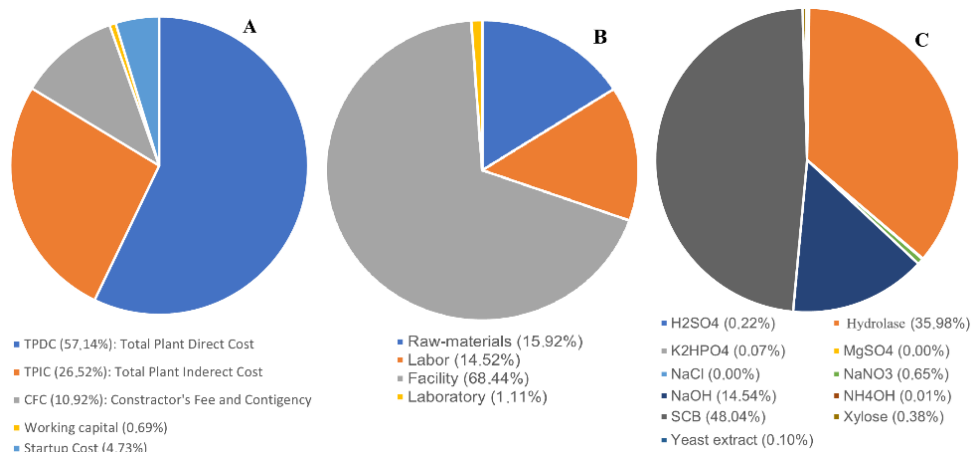
### 3 RESULTS & DISCUSSION

Results obtained for the process simulated and the TEA of the biorefinery proposed are shown in Table 3, and a cost breakdown is show in Figure 1

**Table 2** Production and Economic results obtained from the process simulation and techno-economic assessment

Parameter	Value	Parameter	Value
Anhydrous ethanol production (m <sup>3</sup> /h)	9.7862	Total Capital Investment (million US\$)	576.210
Anhydrous ethanol production (MT/h)	6.0617	Operating Cost (million US\$/year)	143.243
Surplus electricity (MWh/h)	-14.22	Return on Investment (%)	1.21
Pullulan production (Kg/h)	192.126	Net Present Value (million US\$)	-502.573
SCB for CHP system (MT/h)	50.15	Unit Ethanol Production Cost (US\$/L)	2.41
		Unit Ethanol Production Revenue (US\$/L)	1.66

From Table 1, it is possible to affirm that the biorefinery is not economically viable yet, but it shows promising results. Improvements in the current economic scenario could potentially reverse this situation, leading to positive outcomes for investors. Figure 1 highlights that raw material costs, particularly SCB, hydrolase and NaOH, significantly contribute to operational expenses, a behavior already observed in other studies.<sup>8</sup> In the future, other pretreatment mediums without NaOH will be studied, which may positively influence economic parameters since NaOH highly contributes to raw materials expenditures. Additionally, equipment purchases costs heavily impact economic sustainability. However, SuperPro Designer considers pharmaceutical equipment purchase costs; therefore, these costs will be further investigated by contacting resellers and using the CapCost spreadsheet<sup>18</sup> (facility cost is directly connected to equipment purchase cost since it was calculated based on Direct Fixed Cost). Future studies will also address other bottlenecks, such as the negative value of surplus electricity, to optimize the process. Parts of the process have high energy consumption, such as the downstream processing of pullulan, which requires significant energy for drying, and the recovery of ethanol in distillation and dehydration sections.



**Figure 1** Cost Breakdown, considering CAPEX (A), OPEX (B) and Raw-Materials (C), of the proposed biorefinery scenario.

## 4 CONCLUSION

The biorefinery examined in this study currently lacks economic viability due to several production bottlenecks, such as high raw material costs, equipment purchase prices, and energy consumption. Proposed solutions to address these issues include evaluating alternative pretreatment mediums, seeking for competitive equipment prices (influencing CAPEX and OPEX values), and optimizing pullulan downstream processes (experimental work to reduce ethanol and energy demand). These strategies are expected to positively impact economic parameters and potentially achieve economic sustainability for the standalone sugarcane bagasse biorefinery. Also, integrated 1G2G biorefinery scenarios will be evaluated.

## REFERENCES

- JIE, H., KHAN, I., ALHARTHI, M., ZAFAR, M. W., SAEED, A. 2023. Utilities Policy, 81.
- Intergovernmental Panel on Climate Change, "SYNTHESIS REPORT OF THE IPCC SIXTH ASSESSMENT REPORT (AR6)," Intergovernmental Panel on Climate Change, Geneva, 2023.
- PRADO, C. A., ANTUNES, F. F., ROCHA, T. M., MUÑOZ, S. S., BARBOSA, F. G., TERÁN-HILARES, R., CRUZ-SANTOS, M. M., ARRUDA, G. L., da SILVA, S. S., SANTOS, J. C. 2022. *Bioresour. Technol.* 345.
- SHIBUKAWA, V. P., RAMOS, L., CRUZ-SANTOS, M. M., PRADO, C. A., JOFRE, F. M., de ARRUDA, G. L., da SILVA, S. S., MUSSATTO, S. I., dos SANTOS, J. C. 2023. *Energies.* 16 (17).
- SHIBUKAWA, V., REIS, C., dos SANTOS, J., da RÓS, P. 2023. *Braz. J. Chem. Eng.*
- CHANDEL, A., ALBARELLI, A., SANTOS, D., CHUNDAWAT, S., PURI, M., MEIRELES, M. 2019. *Biofuels Bioprod. Biorefin.* 13 (4). 994-1014.
- CRUZ-SANTOS, M. M., ANTUNES, F. A. F., ARRUDA, G. L., SHIBUKAWA, V. P., PRADO, C. A., ORTIZ-SILOS, N., CASTRO-ALONSO, M. J., MARCELINO, P. R. F., SANTOS, J. C. 2023. *Bioresour. Technol.* 385.
- VASCONCELOS, M. H., MENDES, F. M., RAMOS, L., DIAS, M. O. S., BONOMI, A., JESUS, C. D. F., WATANABE, M. D. B., JUNQUEIRA, T. L., MILAGRES, A. M. F., FERRAZ, A., SANTOS, J. C. 2020. *Energy.*
- BONOMI, A., CAVALETT, O., CUNHA, M. P., LIMA, M. A. P. 2016. *Virtual Biorefinery: An Optimization Strategy for Renewable Carbon Valorization*, vol. 1, Springer Cham.
- DIAS, M. 2011. Tese de doutorado. Unicamp.
- PRADO, C. A., CUNHA, M. L. S., TERÁN-HILARES, R., ARRUDA, G. L., ANTUNES, F. A. F., PEREIRA, B., da SILVA, S. S., SANTOS, J. C. 2023. *BioEnergy Res.* 16. 2229-2241.
- DIAS, M. 2008. Dissertação de mestrado. Unicamp.
- Van RIJN, R., NIEVES, I. U., SHANMUGAM, K. T., INGRAM, L. O., VERMERRIS, W. 2018. *BioEnergy Res.* 11. 414-425.
- Banco Central do Brasil. Acess in: May 5 2023. Available in: <https://www.bcb.gov.br/>.
- OLIVEIRA, M. C. T. B., ROSENTRATER, K. A. 2021. *J. Clean. Prod.* 315.
- OLUGHU, O. O., TABIL, L. Ç., DUMONCEAUX, T., MUPONDWA, E., CREE, D., LI, X. 2023. *Results Eng.* 19.
- TERÁN-HILARES, R., RESENDE, J., ORSI, C. A., AHMED, M. A., LACERDA, T. M., da SILVA, S. S., SANTOS, J. C. 2019. *Int. J. Biol. Macromol.* 127. 169-177.
- TURTON, R., SHAEIWITZ, J. A., BHATTACHARYYA, D., WHITING, W. B. *Analysis, Synthesis, and Design of Chemical Processes*, vol. 5. Pearson.

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