



Universidade Federal de São Carlos
Centro de Ciências Exatas e de Tecnologia
Programa de Pós-Graduação em Engenharia Química



Gustavo Batista

**ANÁLISE TÉCNICO-ECONÔMICA-
AMBIENTAL DA PRODUÇÃO DE
NANOCELULOSE EM BIORREFINARIAS
DE CANA-DE-AÇÚCAR**

***TECHNO-ECONOMIC-ENVIRONMENTAL ANALYSIS OF
NANOCELLULOSE PRODUCTION IN SUGARCANE
BIOREFINERIES***

São Carlos – SP
31 de agosto de 2021



Universidade Federal de São Carlos
Centro de Ciências Exatas e de Tecnologia
Programa de Pós-Graduação em Engenharia Química



Gustavo Batista

Análise Técnico-Econômica-Ambiental da Produção de Nanocelulose em Biorrefinarias de Cana-de-Açúcar

*Techno-Economic-Environmental Analysis of Nanocellulose
Production in Sugarcane Biorefineries*

Tese apresentada ao Programa de Pós-Graduação em Engenharia Química da Universidade Federal de São Carlos como requisito para a obtenção do Título de Doutor em Engenharia Química na área de concentração de Pesquisa e Desenvolvimento de Processos Químicos.

Orientador: Prof. Dr. Antonio José Gonçalves da Cruz

Coorientadora: Prof^a. Dra. Cristiane Sanchez Farinas

São Carlos – SP

31 de agosto de 2021



UNIVERSIDADE FEDERAL DE SÃO CARLOS

Centro de Ciências Exatas e de Tecnologia
Programa de Pós-Graduação em Engenharia Química

Folha de Aprovação

Defesa de Tese de Doutorado do candidato Gustavo Batista, realizada em 31/08/2021.

Comissão Julgadora:

Prof. Dr. Antonio Jose Gonçalves da Cruz (UFSCar)

Profa. Dra. Cristiane Sanchez Farinas (EMBRAPA)

Prof. Dr. Stanley Endrigo Bilatto Rodrigues (EMBRAPA)

Prof. Dr. Felipe Fernando Furlan (UFSCar)

Prof. Dr. Luiz Antonio Magalhães Pontes (UFBA)

O presente trabalho foi realizado com apoio da Coordenação de Aperfeiçoamento de Pessoal de Nível Superior - Brasil (CAPES) - Código de Financiamento 001.

O Relatório de Defesa assinado pelos membros da Comissão Julgadora encontra-se arquivado junto ao Programa de Pós-Graduação em Engenharia Química.

AGRADECIMENTOS

Em primeiro lugar, agradeço a Deus por ter me guiado e por ter me possibilitado vivenciar incontáveis experiências durante este Curso de Doutorado.

Aos meus pais e familiares pelo incentivo e perseverança em momentos importantes. À minha namorada, Ana Carolina Borges Silva, por me entender tão bem e por me propiciar tanto apoio e companheirismo nas horas mais difíceis.

Agradecimento especial ao orientador deste trabalho, Prof. Dr. Antonio José Gonçalves da Cruz, pela compreensão, atenção e cortesia sempre presentes, sendo exemplo de pesquisador por excelência a seus orientados. Agradecimento especial também à coorientadora deste trabalho, Prof. Dra. Cristiane Sanchez Farinas, por todas as contribuições e pelo constante incentivo ao espírito investigativo e persistente que se espera de todo bom pesquisador. Aos professores Dr. Ronalds Gonzalez e Dr. Hasan Jameel pela disponibilidade e por tantos conhecimentos adquiridos durante o Doutorado Sanduíche na NCSU - EUA.

Aos membros da Banca de Avaliação, Dr. Stanley Bilatto e Prof. Dr. Felipe Furlan, que deram contribuições importantes a este trabalho desde as etapas iniciais. Ao Prof. Dr. Luiz Pontes por ter gentilmente aceitado o convite à Banca de Avaliação.

A todos os colegas do laboratório *Kyatera* (Simone Miyoshi, Guilhermina Schultz, Erich Potrich, Brenda Gomes, Andreza Longati, Andrew Milli, Harishikan Reddy, Ediane Alves e Fabrício Menezes) pelo apoio e pelos ensinamentos, além de tantos momentos de alegria vivenciados juntos.

Aos colegas Ivan Veloso, Heitor Altino, Gustavo Sipp, Matusalém Carmo, Paula Squinca, Thalita Bondancia, Emanuela Queiroz, Mayara Santos, Erick Takayama, Kaio Rodrigues, Matheus Esperança, Camila Fávaro, Amarílis Souza, Ariane Sbrice, Juliana Freitas, Mariana Brondi, Rauber Pereira, Cássia Santana, Ricardo Arbach, Ana Vieira, Juliana Sandri, Carolina Perez, Raíssa Silva, Gabriel Luz, Bruna Pratto, Rajnish Kumar, Franklin Zambrano, Juliana Jardim e Yali Li por terem partilhado seus tempos e me auxiliado em vários momentos no desenvolvimento deste trabalho em diferentes contextos.

Ao Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) pelo financiamento através da Bolsa de Pesquisa nº 140761/2017-9. À Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES) pelo financiamento através da Bolsa de Pesquisa no Exterior CAPES-PRINT nº 88887.364443/2019-00 (Código de Financiamento 001). À Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP) pelo financiamento do Projeto Temático nº 2016/10636-8 (“Da fábrica celular à biorrefinaria integrada Biodiesel-Bioetanol: uma abordagem sistêmica aplicada a problemas complexos em micro e macroescalas”).

Aos professores e funcionários do Programa de Pós-Graduação em Engenharia Química da UFSCar pelos ensinamentos e assistência durante todo o período. E a todos que, mesmo aqui não citados, contribuíram direta ou indiretamente para a realização deste trabalho.

“Todas as riquezas do mundo não valem um bom amigo”

Voltaire

“Eu não sei que quero ser, mas sei muito bem o que não quero me tornar”

Friedrich Nietzsche

Este trabalho é dedicado a você, Dolly.

RESUMO DO PROJETO

A produção de etanol, açúcar e energia nas biorrefinarias de cana-de-açúcar brasileiras gera uma grande quantidade de resíduos, como o bagaço e a palha. Uma alternativa é o reaproveitamento destes resíduos como matérias-primas para a obtenção de nanocelulose, biomaterial de alto valor agregado com aplicações inovadoras em diversos setores e para os quais há projeção de grande crescimento de mercado para os próximos anos. No entanto, o potencial econômico e ambiental das tecnologias de produção de nanocelulose a partir dos resíduos da cana-de-açúcar ainda precisam ser avaliados para melhor subsidiar os investimentos neste setor. Assim, este trabalho se propôs a avaliar as viabilidades técnica, econômica e ambiental de diferentes rotas de processo de obtenção de nanocelulose em unidades anexas à biorrefinaria de cana-de-açúcar. Para isto foram aplicadas ferramentas de modelagem e análise de processos, utilizando dados prévios obtidos na literatura e informações de *experts* da área. Foram desenvolvidos balanços de massa e de energia para diferentes estudos de caso. A avaliação da viabilidade econômica destes cenários foi realizada através do cálculo do preço mínimo de comercialização da nanocelulose (MPSP, do inglês *Minimum Product Selling Price*) de forma a satisfazer a taxa mínima de atratividade arbitrada para o investimento. Já a Análise de ciclo de vida destes processos indicou as tecnologias com menores impactos ambientais. Almeja-se que este trabalho possa gerar resultados que indiquem oportunidades de investimento para usinas de cana-de-açúcar que queiram diversificar seu portfólio de produtos. Ademais, pesquisadores poderão utilizar os resultados a fim de concentrar esforços na otimização das rotas de maior viabilidade para aumento do potencial produtivo da indústria de nanocelulose.

Palavras-chave: *Nanocelulose, Nanocristais de Celulose, Nanofibras de Celulose, Biorrefinarias de Cana-de-Açúcar, Etanol de Segunda Geração, Análise Econômica, Análise de Sensibilidade Paramétrica, Análise de Ciclo de Vida Ambiental.*

SUMMARY

The production of ethanol, sugar and energy in Brazilian sugarcane biorefineries generates a large number of residues, such as bagasse and straw. An alternative is the reuse of these residues as feedstock for obtaining cellulose nanomaterials, high value-added biomaterials with innovative applications in several sectors and projection of great market growth in the coming years. However, the economic and environmental potential of nanocellulose production technologies from sugarcane residues still need to be evaluated to subsidize investments in this sector. Thus, this work aims to evaluate the technical, economic and environmental feasibilities of different process routes for obtaining cellulose nanomaterials in a process unit attached to a sugarcane biorefinery. For this, process modeling and analysis tools were applied, using previous data obtained in literature and field experts' information. Mass and energy balances were developed for different Case Studies. The economic feasibility of these scenarios was evaluated by calculating the MPSP (Minimum Product Selling Price) of nanocellulose that reaches the Minimum Acceptable Rate of Return (MARR) arbitrated for the investment. In turn, the Life Cycle Analysis of the processes indicated the technologies with the lower environmental impacts. It is expected that this work generates results that indicate investment opportunities for sugarcane biorefineries that plan to diversify their product portfolio. Furthermore, researchers will be able to use the results to focus efforts on optimizing the most viable routes towards increasing the productive potential of the nanocellulose industry.

Keywords: *Nanocellulose, Cellulose Nanocrystals, Cellulose Nanofibers, Sugarcane Biorefineries, Second-Generation Ethanol, Economic Analysis, Parametric Sensitivity Analysis, Environmental Life Cycle Analysis.*

LIST OF FIGURES

Figure 1 – Value-adding in the sugarcane biorefineries (Source: MANDEGARI et al., 2017).	6
Figure 2 – World scenario for fuel ethanol production (Source: adapted from U.S. GRAINS COUNCIL, 2021).....	7
Figure 3 – (a) Locations in Brazil with the largest sugarcane crop areas; (b) illustrative scheme with the approximate mass and energy fractions of products and residues generated from sugarcane (Source: adapted from UNICA, 2021).	8
Figure 4 – Morphological structure of lignocellulosic biomass materials. Cellulose is highlighted for the production of cellulose nanocrystals (Source: adapted from REVISTA PESQUISA FAPESP, 2018).....	9
Figure 5– Internal structure of cellulose fibers, highlighting the crystalline and the amorphous domains of the elementary fibrils (Source: adapted from NG et al., 2015).....	10
Figure 6 – Comparison of size scales between various organic / mineral materials and cellulose nanocrystals (CNCs) and cellulose nanofibrils (CNFs) (Source: NELSON et al., 2016).	10
Figure 7 – Cellulose nanofibrils (CNFs) internal structure scheme. Approximated size scales are given for each macro/micro components of the biomass (Source: adapted from LIN & DUFRESNE, 2014).	12
Figure 8 – (a) Cellulose microstructure highlighting crystalline and disordered (amorphous) regions of the biomass; (b) Cellulose nanocrystals (CNCs) isolated from the cellulose microstructure (Source: adapted from XIE et al., 2018).....	13
Figure 9 – Some cellulose nanomaterials applications areas by material types (Source: TAN et al., 2019).	15
Figure 10 – Timeline of R&D milestones of CNCs production (VANDERFLEET & CRANSTON, 2021).	17
Figure 11 – Diversification of cellulose-based products by technology development. Cellulose nanomaterials are highlighted as a 5 th generation, emerging technology (Source: ARANTES et al., 2020).	17
Figure 12 – Pilot and industrial-scale plants identified worldwide for the production of cellulose nanocrystals (CNCs) (Source: VANDERFLEET & CRANSTON, 2021).	18
Figure 13 – Cellulose Lab [®] main products price table for 2020 year (adapted from the CELLULOSE LAB website, 2021).	19
Figure 14 – (a) Growth forecast for the nanocellulose materials market by global region (in US\$ million) (Source: adapted from MARKETS AND MARKETS, 2021); (b) Market share by application in 2020 for the global nanocellulose market (Source: adapted from EXPERT MARKET RESEARCH, 2021).	20
Figure 15 – Scientific publications related to CNCs and CNFs between 2010 and 2020 (Source: generated with SciFinder [®]).	21
Figure 16 – CNCs obtained from sugarcane bagasse by using steam explosion (SEB) and hydrothermal (LHW) pretreatments (Source: CAMARGO et al., 2016).	22

Figure 17 – Block diagram of a CNMs production unit by chemical methods attached to an E1G/E2G ethanol biorefinery. Sugarcane bagasse generated in the enzymatic hydrolysis step of the E2G process can be used as feedstock to obtain CNMs.	22
Figure 18 – Physical appearance of sugarcane bagasse untreated fiber (a), steam-exploded fiber (b), enzymatically treated fiber (c), and alkaline treated fiber (d) (Source: LAM et al., 2017).	25
Figure 19 – Schematic representation of nanocelluloses production by (a) enzymatic and (b) chemical routes (Source: adapted from ARANTES et al., 2020).	26
Figure 20 – (a) The simplified laboratory method to produce CNCs with H ₂ SO ₄ hydrolysis; (b) The levelling off degree of polymerization of cellulose chains during sulfuric acid hydrolysis (Source: adapted from VANDERFLEET & CRANSTON (2021).	27
Figure 21 – (a) Enzyme synergism is the enzymatic hydrolysis of biomasses (Source: adapted from ZHANG, 2006); (b) Comparison of CNMs dimensions for different types of biomass processing (Source: YANG et al., 2018).	29
Figure 22 – (a) Comparison of CNCs and CNFs as aqueous slurries and submitted to freeze-drying or spray-drying (Source: adapted from PROCESS DEVELOPMENT CENTER - UNIVERSITY OF MAINE, 2021); (b) Mechanism of spray-drying process for CNCs suspensions (Source: NG et al., 2015).	31
Figure 23 – The EMSO [®] Virtual Sugarcane Biorefinery from LaDaBio research group (Source: ELIAS et al., 2019).	33
Figure 24 – Time-cumulative Cash Flow Analysis for a typical industrial enterprise (Source: adapted from TURTON et al., 2009).	36
Figure 25 – LCA stages according to ISO 14040:2006 (Source: ISO 14040:2006).	38
Figure 26 – A typical LCA roadmap for nanobiopolymers (Source: YANG et al., 2018).	39
Figure 27 - Block diagram for the CNCs production methodology proposed in Case Study C2.	59
Figure 28 - Block diagram for the CNCs / CNFs production methodology proposed in Case Study C6.	63
Figure 29 - Block diagram for the CNCs / CNFs production methodology proposed in Case Study C8.	65
Figure 30 – Capital expenditure (CAPEX) estimated for Case Studies C1 to C8.	88
Figure 31 – Operational expenditure (US\$ per dry ton of produced CNMs) estimated for Case Studies C1 to C8.	92
Figure 32 – Operational expenditure (US\$ million per year) estimated for Case Studies C1 to C8.	93
Figure 33 - Tornado-shaped graph results for the Sensitivity Analysis of Parameters on MPSP. Process inputs, utilities and by-products (\pm 25% variations) (top) and main process parameters and financial assumptions (bottom) were analyzed for Case Studies C1 (left) and C2 (right). Blue bars refer to decreasing values, while red bars refer to increasing values of parameters.	101
Figure 34 - Tornado-shaped graph results for the Sensitivity Analysis of Parameters on MPSP. Process inputs, utilities and by-products (\pm 25% variations) (top) and main process parameters and financial assumptions (bottom) were analyzed for Case Studies C6 (left) and C8 (right). Blue bars refer to decreasing values, while red bars refer to increasing values of parameters.	102

Figure 35 - Probabilistic Risk Assessment of Parameters by Monte-Carlo simulation for Case Study C2. Regions of the graph in blue denote ranges for which the MPSP can be expected with 95% statistical confidence.	104
Figure 36 - Global Warming Potential (as ton of CO ₂ equiv. accumulated per day) by unit sectors of C2, C4, C6 and C8 Case Studies (not allocated).	106
Figure 37 – Energy allocated Global Warming Potential (as ton of CO ₂ equiv. accumulated per kg of process products and by-products) for the C2, C4, C6 and C8 Case Studies.	108
Figure A1 - Block diagram for the CNCs production methodology proposed in Case Study C1. II	
Figure A2 - Block diagram for the LCNCs production methodology proposed in Case Study C3.	III
Figure A3 - Block diagram for the CNCs production methodology proposed in Case Study C4.	IV
Figure A4 - Block diagram for the CNCs suspensions production methodology proposed in Case Study C5.	V
Figure A5 - Block diagram for the CNCs / CNFs production methodology proposed in Case Study C7. .VI	
Figure A6 - Probabilistic Risk Assessment of Parameters by Monte-Carlo simulation for Case Study C1. Regions of the graph in blue denote ranges for which the MPSP can be expected with 95% statistical confidence.	VII
Figure A7 - Probabilistic Risk Assessment of Parameters by Monte-Carlo simulation for Case Study C3. Regions of the graph in blue denote ranges for which the MPSP can be expected with 95% statistical confidence.	VIII
Figure A8 - Probabilistic Risk Assessment of Parameters by Monte-Carlo simulation for Case Study C4. Regions of the graph in blue denote ranges for which the MPSP can be expected with 95% statistical confidence.	IX
Figure A9 - Probabilistic Risk Assessment of Parameters by Monte-Carlo simulation for Case Study C5. Regions of the graph in blue denote ranges for which the MPSP can be expected with 95% statistical confidence.	X
Figure A10 - Probabilistic Risk Assessment of Parameters by Monte-Carlo simulation for Case Study C6. Regions of the graph in blue denote ranges for which the MPSP can be expected with 95% statistical confidence.	XI
Figure A11 - Probabilistic Risk Assessment of Parameters by Monte-Carlo simulation for Case Study C7. Regions of the graph in blue denote ranges for which the MPSP can be expected with 95% statistical confidence.	XII
Figure A12 - Probabilistic Risk Assessment of Parameters by Monte-Carlo simulation for Case Study C8. Regions of the graph in blue denote ranges for which the MPSP can be expected with 95% statistical confidence.	XIII
Figure A13 - Relative environmental impacts of each process input for Case Study C2 obtained through Life Cycle Assessment (CML-IA Baseline v3.04 2000 method, SimaPro [®] software). The absolute values for each impact category are also shown.	XIV
Figure A14 - Relative environmental impacts of each process input for Case Study C4 obtained through Life Cycle Assessment (CML-IA Baseline v3.04 2000 method, SimaPro [®] software). The absolute values for each impact category are also shown.	XV

Figure A15 - Relative environmental impacts of each process input for Case Study C6 obtained through Life Cycle Assessment (CML-IA Baseline v3.04 2000 method, SimaPro® software). The absolute values for each impact category are also shown.XVI

Figure A16 - Relative environmental impacts of each process input for Case Study C8 obtained through Life Cycle Assessment (CML-IA Baseline v3.04 2000 method, SimaPro® software). The absolute values for each impact category are also shown. XVII

LIST OF TABLES

Table 1 – Cellulose nanomaterials and cellulose micromaterials main physical properties and structure characteristics (ISO TS 20477:2017; SHEN et al., 2020).	11
Table 2 – Some nanocellulose applications (by category) documented in literature.....	16
Table 3 – Chemical composition of lignocellulosic materials of different sources.	23
Table 4 – Main types, methods and key characteristics of biomass pretreatments.....	24
Table 5 - Classification of industrial cost estimate types.	35
Table 6 – Some other works that explored the production of CNMs from sugarcane bagasse.	43
Table 7 - Mass compositions % (on a dry basis) of raw bagasse and E2G bagasse that were used as feedstocks in the Case Studies of this work.....	51
Table 8 - Comparison between the main process characteristics of each Case Study analyzed in this work. LCNCs refers to cellulose nanocrystals with lignin content in the composition.	53
Table 9 - Main specification inputs used in the process modeling of Case Study C1.	56
Table 10 - Main specification inputs used in the modeling of Case Study C2.	58
Table 11 - Main specification inputs used in the modeling of Case Study C6.	62
Table 12 - Main specification inputs used in the modeling of Case Study C8.	64
Table 13 - Estimated costs for inputs and utilities and selling prices for by-products of the Case Studies.	67
Table 14 – Types of costs for the tropicalization of industrial equipment.	69
Table 15 - Methodology for obtaining direct and indirect costs of equipment deployment (adapted from PETERS et al., 2003; TOWLER & SINNOTT, 2009) and arbitrated equipment tropicalization factor. ...	69
Table 16 - Methodology for calculating project execution costs (PEC) from total equipment deployment cost (adapted from PETERS et al., 2003; TOWLER and SINNOTT, 2009).....	70
Table 17 - Input parameters for the Cash Flow Analysis of Case Studies analyzed in this work.....	71
Table 18 - GWP data obtained on SimaPro® software for inputs and outputs of the Case Studies analyzed in this work.....	75
Table 19 – Main results obtained in modeling and mass / energy balances for the Case Studies C1 and C2.	77
Table 20 – Main results obtained in modeling and mass / energy balances for the Case Study C8.	81
Table 21 - Main results obtained in the modeling and mass and energy balances for Case Studies C6 and C7.	83
Table 22 - Main results obtained in the modeling and mass and energy balances for Case Study C3.	84

Table 23 – Main results obtained in modeling and mass and energy balances for Case Study C4.	85
Table 24 – Equipment deployment costs for Case Study C2.....	86
Table 25 – Main results of the Cash Flow Analysis for the Case Studies C1 to C8. Values are in US\$ millions when not explicitly mentioned.	98
Table 26 – Worst-case and best-case scenarios (95% confidence) for MPSP values in a Monte-Carlo Probabilistic Risk Assessment for each Case Study of this work.....	103
Table 27 – Water usage for the methodologies proposed in Case Studies C2, C4, C6 and C8.	105

LIST OF ACRONYMS

ACF	– Annual Cash Flow
AVAP	– American Value-Added Pulping method
CAGR	– Compound Annual Growth Rate
CAPEX	– Capital Expenditure
CEPCI	– Chemical Engineering Plant Cost Index
CFA	– Cash Flow Analysis
CNCs	– Cellulose Nanocrystals
CNFs	– Cellulose Nanofibrils
CNMs	– Cellulose Nanomaterials
DC	– Direct Costs of Equipment Deployment
E1G	– First-Generation Bioethanol
E2G	– Second-Generation Bioethanol
E2G Bagasse	– Solid portion of sugarcane bagasse that results from enzymatic hydrolysis of E2G process
EC	– Total Single Equipment Deployment Cost
EMSO®	– Environment for Modeling, Simulation and Optimization
FOB	– Free on Board cost
GHG	– Greenhouse Gas Emissions
GWP	– Global Warming Potential
IC	– Indirect Costs of Equipment Deployment
IRR	– Internal Rate of Return
LaDABio	– Bioprocess Development and Automation Laboratory (UFSCar)
LCA	– Life-Cycle Assessment
LCNCs	– Cellulose Nanocrystals with Lignin Content in the Composition
LCNMs	– Cellulose Nanomaterials with Lignin Content in the Composition
L/W	– Cellulose Nanomaterial Aspect Ratio – Length per width
MARR	– Minimum Acceptable Rate of Return
MCC	– Microcrystalline Cellulose
MFC	– Microfibrillated Cellulose
MPSP	– Minimum Selling Price of the main Product
NPV	– Net Present Value
OPEX	– Operational Expenditure
PEC	– Project Execution Costs
PSE	– Process Systems Engineering
Raw Bagasse	– Sugarcane bagasse generated after the milling stage of E1G production
R&D	– Research & Development of Processes
TC	– Total Cost of Equipment Deployment
TEA	– Techno-Economic Analysis
TEMPO	– 2,2,6,6-tetramethylpiperidinyloxyl oxidation method
TF	– Tropicalization Factor for Equipment from US Gulf Coast to central-south Brazil
TR	– Time of Return for the Investment
USDA	– United States Department of Agriculture

SUMMARY

CHAPTER 1 – CONTEXTUALIZATION AND MOTIVATION	1
CHAPTER 2 – OBJECTIVES	4
CHAPTER 3 – LITERATURE REVIEW	5
3.1 Biorefineries and Sugarcane Biorefineries	5
3.1.1 Ethanol	6
3.1.2 Second-Generation Ethanol	7
3.1.3 Lignocellulosic Biomasses	8
3.2 Cellulose Nanomaterials	10
3.2.1 Cellulose Nanofibrils (CNFs)	12
3.2.2 Cellulose Nanocrystals (CNCs)	13
3.2.3 Lignin-Containing Cellulose Nanomaterials (LCNMs)	13
3.2.4 Applications of Cellulose Nanomaterials	14
3.2.5 Cellulose Nanomaterials Global Production, Price and Market Forecast	16
3.3 Nanocellulose Production in Sugarcane Biorefineries	21
3.3.1 Biomass Pretreatments	23
3.3.2 Biomass Hydrolysis	25
3.3.2.1 Acid Hydrolysis with Mineral Acids	26
3.3.2.2 Acid Hydrolysis with Organic Acids	27
3.3.2.3 Enzymatic Hydrolysis	28
3.3.3 Downstream processes	29
3.4 Process Systems Engineering	31
3.4.1 Mathematical Modeling of Processes	32
3.4.1.1 The Virtual Sugarcane Biorefinery	32
3.4.2 Techno-Economic Analysis of Processes (TEA)	33
3.4.2.1 CAPEX, OPEX and Cash Flow Analysis	34
3.4.3 Analysis of Environmental Impacts of Processes	37
3.4.3.1 Life Cycle Assessment (LCA)	37
CHAPTER 4 – STATE OF ART	40
4.1 Technical Feasibility of CNMs from sugarcane bagasse	40
4.2 Economic Analysis of Cellulose Nanomaterials Production	44
4.3 Life Cycle Analysis of Cellulose Nanomaterials Production	46
CHAPTER 5 – METHODOLOGY	49
5.1 The Virtual Sugarcane Biorefinery	49
5.2 The Case Studies	51
5.2.1 Case Study C1	54

5.2.2 Case Study C2.....	57
5.2.3 Case Study C3.....	60
5.2.4 Case Study C4.....	60
5.2.5 Case Study C5.....	61
5.2.6 Case Study C6.....	61
5.2.7 Case Study C7.....	62
5.2.8 Case Study C8	64
5.3 Techno-Economic Analysis (TEA)	66
5.3.1 TEA Premises	66
5.3.2 Costs of Inputs and Utilities and By-Products Selling Prices	66
5.3.3 Unit Deployment Costs.....	67
5.3.4 Project Execution Costs.....	69
5.3.5 Cash Flow Analysis	70
5.4 Sensitivity Analysis of Parameters	72
5.5 Probabilistic Risk Assessment of Parameters	73
5.6 Life-Cycle Assessment (LCA).....	73
CHAPTER 6 – RESULTS AND DISCUSSION	76
6.1 Modeling CNM production routes - Technical Analysis.....	76
6.1.1 Acid hydrolysis using different feedstocks - Case Studies C1 and C2.....	77
6.1.2 Enzymatic Hydrolysis - Case Study C8.....	81
6.1.3 Citric Acid Hydrolysis - C6 and C7 Case Studies	82
6.1.4 No alkaline delignification – Case Study C3.....	84
6.1.5 No sulfuric acid recovery – Case Study C4.....	84
6.1.6 No spray-drying section – Case Study C5	85
6.2 Techno-Economic Analysis (TEA)	86
6.2.1 Capital Expenditure (CAPEX).....	86
6.2.2 Operational Expenditure (OPEX)	90
6.2.3 Cash Flow Analysis (CFA).....	94
6.2.4 Sensitivity Analysis of Parameters.....	99
6.2.5 Probabilistic Risk Assessment of Parameters.....	103
6.3 Life-Cycle Assessment	105
CHAPTER 7 – CONCLUSIONS AND OUTLOOK	110
7.1 Future works suggestions	111
CHAPTER 8 – REFERENCES	112
ANNEXES.....	I

CHAPTER 1 – CONTEXTUALIZATION AND MOTIVATION

The concept of biorefinery is broad and subject to constant changes. However, in a general definition, biorefineries are facilities that integrate processes for converting biomass into bioenergy, biofuels, chemicals, and bio-based materials, with the objective of consciously use natural resources, minimize effluents and obtain higher value-added products (KAMM & KAMM, 2004). This type of project can be carried out, for example, when adding value to a waste that would previously be discarded. Within this definition, sugarcane processing plants have a high potential for expand its portfolio of products, improving its economics and sustainability.

Fuel ethanol is the most relevant biofuel today in the world in energy, environmental, economic and technological terms (PEREIRA *et al.*, 2015). Ethanol is produced on a large scale from feedstocks such as corn, in the United States, and sugarcane, in Brazil. It is also produced from sugarcane and other biomasses in countries like India and China and in the European Union. Sugarcane processing generates a large number of agricultural residues. Each ton of processed sugarcane generates approximately 140 kg of bagasse (CONAB, 2018) and 140 kg of straw (SAAD *et al.*, 2008), both on a dry basis. The bagasse and straw fractions contain, respectively, ~36% and ~32% of the total energy content of sugarcane (UNICA, 2021). If until the early 1990s these biomasses were seen as “wastes” in sugar and ethanol mills, the economic use of these biomasses has gained great visibility more recently (CORRÊA, 2016). A very interesting approach is to use these residues to complement the production at the mills and generate value-added products that enhance the profitability of the biorefineries (FURLAN, 2012), since they have low cost and high availability (RESENDE *et al.*, 2014).

Sugarcane bagasse and straw are residual lignocellulosic biomasses whose carbohydrates can be transformed into fermentable sugars. However, this processing is hampered by the biomass structure complexity, requiring pretreatment and hydrolysis steps of cellulosic fractions before the fermentation of sugars. This processing allows the production of the second-generation ethanol (E2G), also known as cellulosic ethanol. However, the use of these biomasses for the E2G production has restrictions imposed by the energy demands of the sugarcane processing plant, as their typical use is as fuel for

biorefinery boilers, generating self-sufficient steam and extra electricity as by-product that is sold to the grid (DIAS *et al.*, 2011; FURLAN, 2013; CARPIO & SOUZA, 2017). These residues (mainly sugarcane straw) can also be left in the fields for nutrient recycling (LONGATI *et al.*, 2019).

The analysis of innovative bioproducts production is important in the current biorefinery scenario, since the consolidation of the industrial production of second-generation ethanol (E2G) is based on the economic improvement of the process (MONTAÑO, 2013) and depends on the variation of domestic and international demands for biofuels and bioelectricity (DIAS *et al.*, 2011). Another interesting alternative is the use of the sugarcane biomass residues to also obtain nanocellulose. Cellulose nanomaterials (CNMs) are high value-added products with different applications in several industrial sectors.

CNMs are highly ordered materials of small diameter, high length per width (L/W) ratio, and high surface area, which can be obtained from a wide variety of natural resources. Cellulose nanocrystals (CNCs) and cellulose nanofibrils (CNFs) are both known as types of nanocellulose. These nanomaterials are derived from renewable sources and are light and biodegradable, which gives them an environmental advantage over synthetic materials usually derived from petroleum by-products. According to ZION RESEARCH® (2016), the global nanocellulose market in 2015 was US\$ 65 million. According to AMECO RESEARCH® (2020), the global nanocellulose market grew in 2019 to almost US\$ 400 million, and the estimation is that it will reach the values of US\$ 530 million by the end of 2021, US\$ 661.3 million by the end of 2023 and US\$ 1.094 billion by the end of 2027, at a Compound Annual Growing Rate (CAGR) of 15.3% in the period between 2020 and 2027.

The addition of new products to the biorefinery portfolio aims to increase its competitive potential, generating options with return of investment and low environmental impacts when compared to other production technologies, given that the partial substitution of petroleum products is a trend for the coming years. Among the several application fields of nanocellulose materials, their use as mechanical reinforcements in polymers stands out, resulting in significant increases in the mechanical and thermal resistance properties of materials (LI *et al.* 2018; WANG *et al.*, 2018). Applications in biomedicine are also noteworthy (NSOR-ATINDANA *et al.*, 2018; XIAO *et al.*, 2018). However, despite the diversity of application areas, a major challenge

that still exists in the use of CNMs for commercial purposes is the limited availability and high costs in an incipient market, in addition to the low process yields in hydrolysis and isolation (CAMARGO *et al.*, 2016; FERREIRA *et al.*, 2018).

Some Brazilian companies have been investing in R&D in the cellulose nanomaterials area by acquiring stakes in foreign companies to assimilate technologies. *Granbio*[®], one of the Brazilian companies with technology to produce E2G from sugarcane bagasse, acquired 25% of *American Process Inc.* (API) in 2013. In 2015, API announced a new low-cost technology to extract CNMs from biomass and started pre-commercial production. *Granbio*[®] disclosed in 2018 that had been investing in cellulose nanomaterials R&D for four years (at that time) and that operates a plant in the United States through its affiliate API. In 2016, *Fibria*[®], a Brazilian company that is the global leader in commercial pulp sales became a shareholder in *CelluForce*[®], a leading Canadian company in the production of cellulose nanocrystals. *Fibria*[®] has the production rights for cellulose nanocrystals in Brazil and the distribution rights throughout Latin America, being owner of a pilot plant for the production of microfibrillated nanocellulose at the Aracruz unit (PESQUISA FAPESP magazine, 2018).

To the best of our knowledge, the evaluation of the potential of nanocellulose production technologies from sugarcane residues is still necessary in different methodology scenarios. There are still few industrial plants producing E2G, two of them in Brazil – one by *GranBio*[®] and one by *Raízen*[®]. Moreover, the economic feasibility analysis and the environmental analysis of industrial nanocellulose production methodologies, using lignocellulosic residues from sugarcane biorefineries as feedstock, are topics not yet well investigated in literature that could support future investments in this sector. In this context, Process Systems Engineering (PSE) is presented as a less costly and faster alternative than the construction of pilot plants. The use of PSE tools can generate a wide range of useful information about of the process by using a data framework of experimental and market inputs. Such results could be useful both for the field researchers, who could direct efforts to optimize the most promising routes for the production of nanocellulose, and also for investors of the sugarcane sector, as potential alternatives for investment and expansion of the product portfolio of sugarcane biorefineries could be indicated.

CHAPTER 2 – OBJECTIVES

This work aims to investigate the technical, economic feasibility and environmental impacts of nanocellulose production in a sugarcane biorefinery by using data sources for modeling and simulation in software. The specific objectives of the project are listed below:

- Use literature references and information from specialists in the field regarding the technical feasibility of producing nanocellulose varieties in sugarcane biorefineries by different process routes;
- Study flowchart analysis of nanocellulose production methodologies (including process modeling and mass & energy balances) for biorefinery production, using lignocellulosic residues such as sugarcane bagasse as feedstock;
- Evaluate the economic feasibility analysis in the commercial market (through CAPEX & OPEX estimations and Cash-Flow Analysis) for the proposed methodologies, aiming to indicate potential investment alternatives for the sugar and alcohol industrial sector;
- Perform sensitivity analysis of the main process input parameters and uncertainty analysis of nanocellulose MPSPs, in order to assess possible effects of R&D process optimizations and market costs variations in the time horizon of the analyzed scenarios;
- Assess the potential environmental impacts of methodologies through Life Cycle Assessment (LCA) to compare the environmental performance of process routes on an industrial scale and indicate the main emission sources for R&D optimization.

3.1 Biorefineries and Sugarcane Biorefineries

Global energy policies are nowadays leaning towards increasing the share of renewable energies in their matrix. Increasing concerns about climate change and energy security have motivated the search for alternative forms of energy. There is a scientific consensus that carbon dioxide (CO₂) and other greenhouse gases (GHGs) emissions are responsible for environmental damage. Over the last 50 years, about 90% of world's energy demands have been extracted from fossil fuels, generating approximately 1.5×10^{10} Mg of CO₂ emissions per year to the planet atmosphere (PIRES *et al.*, 2019). Engineering research has been dedicating great efforts to enable a more sustainable, less oil/fossil-based energetic matrix to humankind (FURLAN *et al.*, 2012). Biorefineries combine the necessary technologies between biological raw materials and industrial intermediates and final products (KAMM & KAMM, 2004).

Among the potential large-scale industrial biorefineries, the lignocellulosic biorefinery will most probably reach the highest success. The raw material situation is optimal, with many types of source biomasses, and the conversion products have a good position to compete within both the traditional petrochemical and the innovative product markets. The high availability of the biomass combined with appropriate technology / know-how provides many opportunities for biorefineries to convert the negative impact and cost of agricultural or industrial “wastes” into bioenergy and new value-added biomaterials and bioproducts (MARCONDES *et al.*, 2020). Besides these benefits, biomass-based energy generation can use agricultural residues, avoiding competition with food crops (PIRES *et al.*, 2019).

In this context, Brazil is notable as a country that has made considerable progress towards replacing fossil fuels by renewable energy sources. Sugarcane is one of the major cultures of the world, being cultivated in more than 100 countries, but Brazil and India together generate slightly more than half of all sugarcane produced in the world. Moreover, Brazil and the United States lead the global production of bioethanol. In the 2020/21 harvest, it is estimated that more than 605 million tons of sugarcane were processed by the Brazilian sugar-ethanol mills, resulting in ethanol production of 30.37

billion liters (9.69 billion liters of anhydrous ethanol and 20.68 billion liters of hydrous ethanol) and sugar production of 38.46 million tons. 53.9% of the processed sugarcane was used for the biofuel production. The estimated harvested area in the country was 7.77 million hectares, with an average yield of 77.9 tons of sugarcane per cultivated hectare (UNICA, 2021).

In the harvest of sugarcane, residues such as sugarcane bagasse and sugarcane straw are produced on a considerable scale. In the 2020/21 harvest, approximately 180 million tons of bagasse and about 108 million tons of straw were produced (UNICA, 2021). An important aspect related to the overall sustainability of biorefineries is the needing for process development to enable the use of the whole biomass, especially for the production of high-value products (Figure 1). Reuse is one of the main components of Circular Economy concept, which consists in the use of a preprocessed material as a raw material for a diversity of processes (MALLUCELLI *et al.*, 2017).

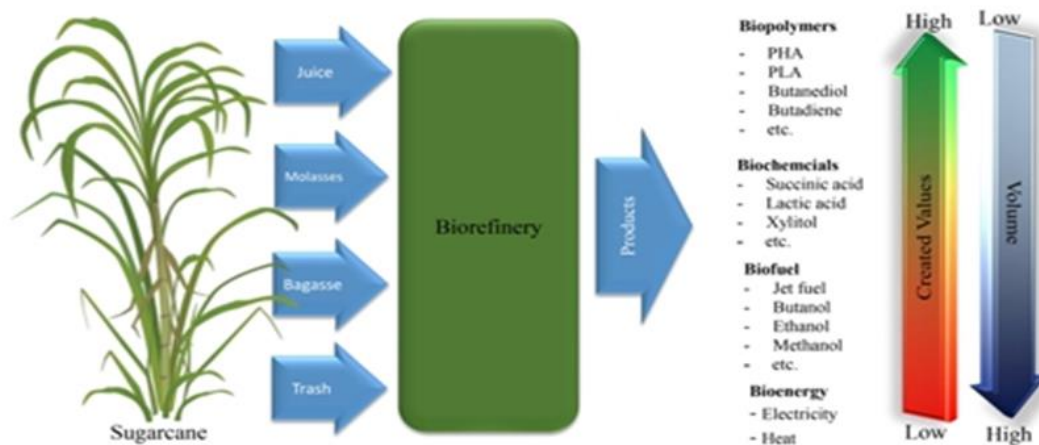


Figure 1 – Value-adding in the sugarcane biorefineries (Source: MANDEGARI *et al.*, 2017).

3.1.1 Ethanol

Ethanol is, fundamentally, the most globally relevant biofuel in energy, environmental, economic and technological aspects today (Figure 2). Ethanol can be produced from any biomass that contains significant amounts of starch (such as wheat and corn) or fermentable sugars (such as sugar beet and sugarcane). The processing of first-generation ethanol (E1G) from sugarcane involves steps such as juice concentration, sugar fermentation and product recovery by distillation. Meanwhile, the use of starch feedstocks, as extensively done in countries like the United States, requires an extra enzymatic step to convert starch to short-chain sugars (LIMAYEM & RICKE, 2012).

Brazil stands out for its pioneering use of sugarcane for the production of fuel ethanol since the creation of the *ProÁlcool Program* after the first oil crisis in 1973. This biofuel can be used in mixtures or as a substitute for gasoline in cars whose engines are adapted to its properties. Since the 2000s, the sale of flex fuel cars (which accept mixtures of ethanol and gasoline in any proportion as fuel) has become popular in the country. The success of fuel ethanol reaffirmed sugarcane as a well-established crop in Brazil, especially in the central-north of the state of São Paulo (Figure 3a) that accounts for more than 60% of national production (BIOETANOL, 2008; PEREIRA *et al.*, 2015).

World Fuel Ethanol Production in Million Liters

Region	2015	2016	2017	2018	2019
USA	55,970	58,261	60,238	60,824	59,633
Brazil	27,216	25,553	25,250	30,278	32,395
EU	5,243	5,205	5,292	5,405	5,443
China	3,077	3,099	3,255	3,975	4,315
Canada	1,648	1,648	1,777	1,814	1,890
India	737	1,040	794	1,512	2,003
Thailand	1,263	1,217	1,399	1,474	1,588
Argentina	798	998	1,096	1,096	1,096
Rest of World	1,478	1,852	1,565	2,075	2,268
Total	97,426	98,968	1,00,661	1,08,448	1,09,718

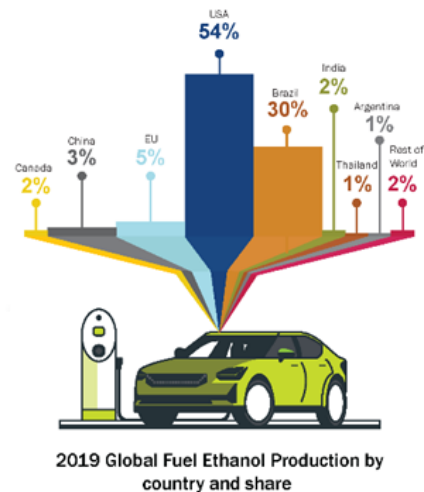


Figure 2 – World scenario for fuel ethanol production (Source: adapted from U.S. GRAINS COUNCIL, 2021).

3.1.2 Second-Generation Ethanol

The ethanol production process in sugarcane plants generates many residues and by-products, not only in the harvest and separation phase (such as sugarcane bagasse and straw) but also in the pre-processing phases, reaction and fuel downstream (such as vinasse). Once sugarcane bagasse and straw residues contain a significant part of the mass and energy content of the harvested sugarcane (Figure 3b), a biorefinery alternative is the reutilization of these in the production of the second-generation ethanol (E2G) (MUKTHAM *et al.*, 2016).

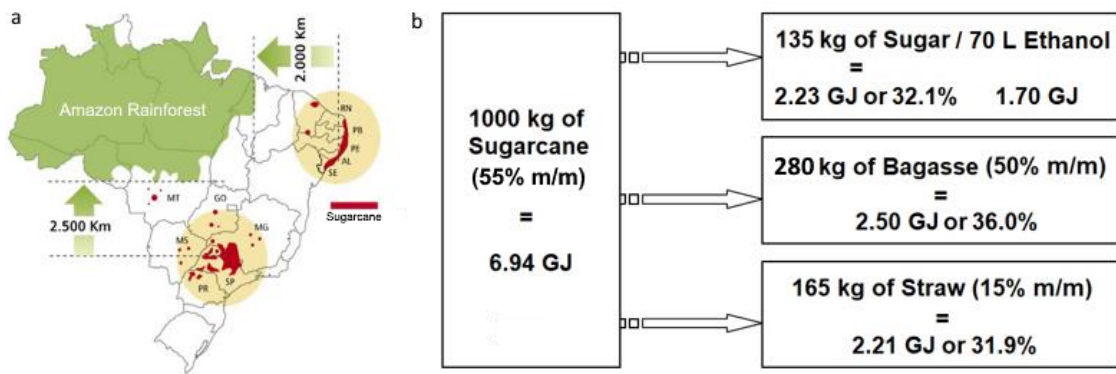


Figure 3 – (a) Locations in Brazil with the largest sugarcane crop areas; (b) illustrative scheme with the approximate mass and energy fractions of products and residues generated from sugarcane (Source: adapted from UNICA, 2021).

E2G has the same properties of E1G ethanol, but a more complex raw material processing is necessary due to the recalcitrance of the lignocellulosic materials. The production of ethanol from these materials does not compete with food production and also contributes to the reduction of greenhouse gas emissions by using residues of the plant as feedstocks (LIMAYEM AND RICKE, 2012). The world effort to turn E2G economically viable has been intense during the last decade (FURLAN *et al.*, 2015; MENDES *et al.*, 2017; ÖZÜDOĞRU *et al.*, 2019). Biochemical routes for the production of E2G basically involve four main stages: pre-treatment of the biomass, for removal of hemicellulose and lignin contents; acidic and / or enzymatic hydrolysis of polysaccharides to monomeric sugars; fermentation of sugars; and distillation / recovery of bioethanol (MUKTHAM *et al.*, 2016). It is important to point out that the E2G units share process facilities with the E1G plant in order to integrate mass and energy streams, this way minimizing costs and increasing productivity, such as can be seen in the arrangements proposed by DIAS *et al.* (2012) and FURLAN *et al.* (2012).

3.1.3 Lignocellulosic Biomasses

Biomasses can be defined as renewable resources from organic matter (of animal or vegetable origin) that have bioenergy and can be processed to generate more elaborated bioenergetics that are suitable for final use (KAMM & KAMM, 2004). In this context, lignocellulosic biomass materials such as sugarcane bagasse and straw have a complex morphological structure, consisting essentially from three polymers: hemicellulose (20 to 40%), lignin (10 to 20%) and cellulose (35 to 50% by mass) (Figure 4). Hemicellulose can be easily hydrolyzed to pentoses such as xylose and arabinose due to its amorphous

structure and higher solubility. On the other hand, lignin is formed by a complex branched structure of amorphous polymers and has hydrophobic behavior, providing support and rigidity to the lignocellulosic matrix. It is not possible to generate fermentable sugars from lignin, and this compound still creates a physical barrier that hinders hydrolysis processes, especially to the enzymatic type (MOOD *et al.*, 2013), making the previous removal of lignin highly desirable.

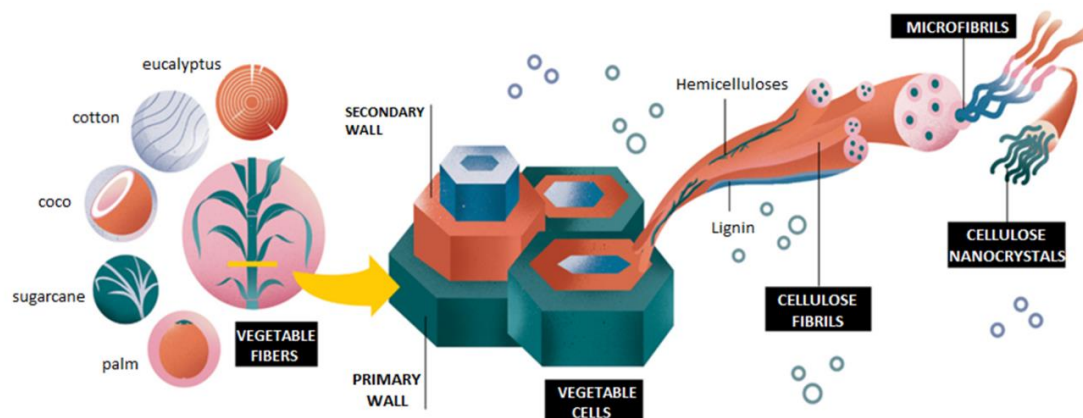


Figure 4 – Morphological structure of lignocellulosic biomass materials. Cellulose is highlighted for the production of cellulose nanocrystals (Source: adapted from REVISTA PESQUISA FAPESP, 2018).

In cellulose, most of the structures are highly organized in fibers, fibrils and microfibrils, being called crystalline regions - by crystalline, one should understand solid structures where its ions, molecules, or atoms are in an ordered, three-dimensional arrangement. Other structures, chaotically interconnected, are called amorphous regions - solid structures where its ions, molecules, or atoms are oriented randomly, lacking any order (ISO TS 20477:2017) (Figure 5). The lower the degree of crystallinity, the lower the organization of the cellular structure, making it more susceptible to hydrolysis and the consequent formation of monomeric sugars (such as glucose) for later fermentation and E2G generation (ZHANG and LYND, 2004; LAM *et al.*, 2016).

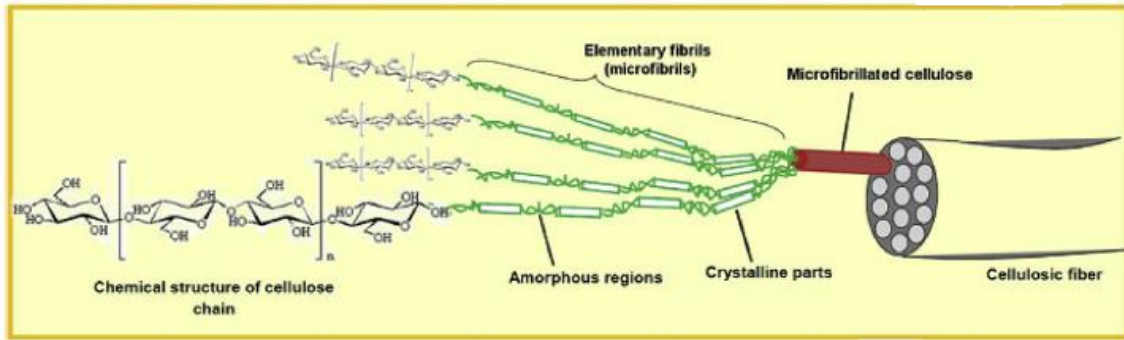


Figure 5– Internal structure of cellulose fibers, highlighting the crystalline and the amorphous domains of the elementary fibrils (Source: adapted from NG *et al.*, 2015).

3.2 Cellulose Nanomaterials

Cellulose nanomaterials (CNMs) are biopolymers composed from molecules of high crystallinity of cellulose (MARIANO *et al.*, 2014), encompassing all types of cellulosic substrate on a nanoscale range (1-100 nm) (HABIBI, 2010; ISO TS 20477:2017) (Figure 6). Given the structural variations in the original matrices, different vegetable fibers (algae is another potential source – ROSS *et al.*, 2021) and feedstock processing methodologies enable the obtaining of different types of nanocellulose, such as cellulose nanofibers (CNFs), cellulose nanocrystals (also reported in literature as cellulose whiskers and nanowhiskers) (CNCs), bacterial nanocellulose (GEORGE *et al.*, 2011; LIN and DUFRESNE, 2014; ROVERA *et al.*, 2018; ZHONG, 2020), tunicate CNCs and algal celluloses (FOSTER *et al.*, 2018).

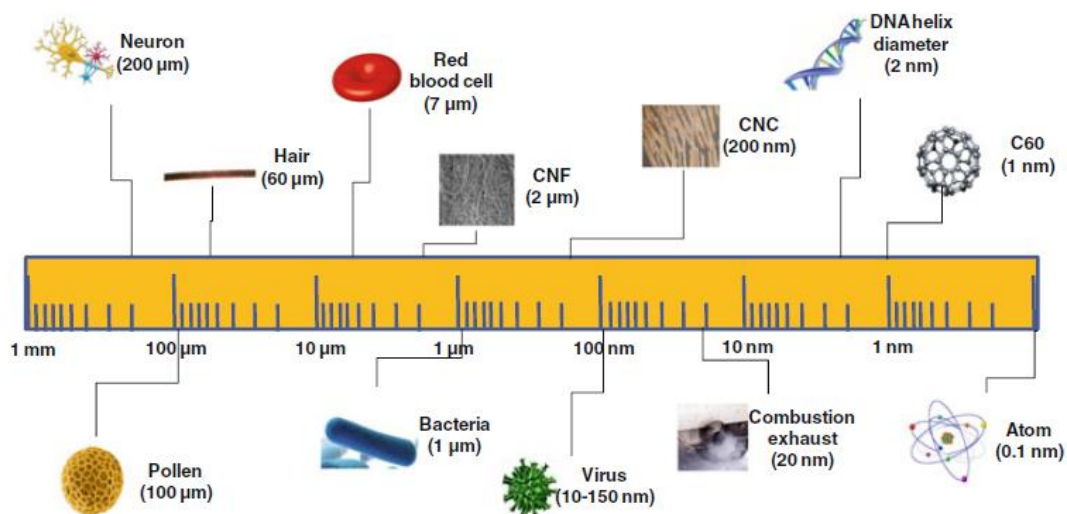


Figure 6 – Comparison of size scales between various organic / mineral materials and cellulose nanocrystals (CNCs) and cellulose nanofibrils (CNFs) (Source: NELSON *et al.*, 2016).

Whether CNMs are separated by industrial processes or produced directly by organisms, they all contain a common structural component that is called elementary fibril (Figure 5). This common component provides a way to describe CNMs from all manufacturing methods and cellulose sources (ISO TS 20477:2017). The unique physical and chemical characteristics of nanocellulose are related to its nanoscale size, fibril morphology and large surface area per volume (LIN and DUFRESNE, 2014). The interest in the development of CNMs is due to the fact that such materials generally behave differently from those on the metric scale. On a nanometric scale, for example, materials can be stronger and maximize the conduction of heat or electricity, opening up opportunities for newer technologies and the modernization of equipment (DUFRESNE, 2012; VANDERFLEET & CRANSTON, 2021).

Other cellulose materials that have been reported for several applications are microfibrillated cellulose (MFC) (LAVOINE *et al.*, 2012) and microcrystalline cellulose (MCC) (VANHATALO *et al.*, 2014) (Table 1). MFCs are generally produced by mechanical treatments with or without chemical or enzymatic pretreatment. These materials consist of long and thin fibers, interconnected with each other, which form a three-dimensional network with crystalline and amorphous regions. MFCs have high viscosity and yield stress, shear thinning and also have high water holding capacity. The size distribution of these fibers is wide, and even if some fibers have diameters in nanoscale, they are a lot of bigger than the nanofibrils (up to 0.2 mm). Strictly speaking, MFCs and MCCs shouldn't really be considered as types of nanocellulose, as they are orders of magnitude bigger and not close to the nano size. The production of MFCs and MCCs will not be evaluated in this work since the analysis of nanomaterial-scale materials manufacturing from sugarcane residues was prioritized.

Table 1 – Cellulose nanomaterials and cellulose micromaterials main physical properties and structure characteristics (ISO TS 20477:2017; SHEN *et al.*, 2020).

Particle Type	Length (μm)	Width (nm)	Aspect Ratio (L/W)	Structure Form
CNC	0.10 – 0.35	3 – 50	5 – 50	Pure crystalline structure
CNF	up to 100	3 – 100	> 50	Contains both crystalline and amorphous regions

MFC	50 – 100	10 – 100	> 50	Contains multiple elementary fibrils with both crystalline and amorphous regions
MCC	10 – 50	10 – 50 (μm)	< 2	Manufactured by partially depolymerizing high purity cellulose

3.2.1 Cellulose Nanofibrils (CNFs)

Cellulose nanofibrils (CNFs) are elongated and flexible materials, with lengths typically up to 100 μm and diameters between 3 and 100 nm (FOSTER *et al.*, 2018; ISO TS 20477:2017). The CNFs preparation consists in the removing of the external amorphous phase of the cellulose, resulting in portions of crystalline cellulose still interconnected by a residual, yet present amorphous fraction, generating intertwined networks with a fibrous aspect (Figure 7) (SONG *et al.*, 2014; LI *et al.*, 2021). CNFs main characteristics are the high aspect ratio (L/D) and high Young Modulus (i.e., high stiffness), with the main application fields being in the reinforcement of composites (BESBES *et al.*, 2011) and in the nanocellulose films obtaining (WANG *et al.*, 2013). CNFs can be obtained by chemical, mechanical and enzymatic treatments, or by association of these processes (HUBBE *et al.*, 2008; FENG *et al.*, 2018; HONGRATTANAVICHIT & AHT-ONG, 2020). Despite being energy intensive procedures, the use of mechanical production methods is presented in literature as a cleaner alternative to chemical methods due to the absence in the use of reagents (BUFALINO, 2014).

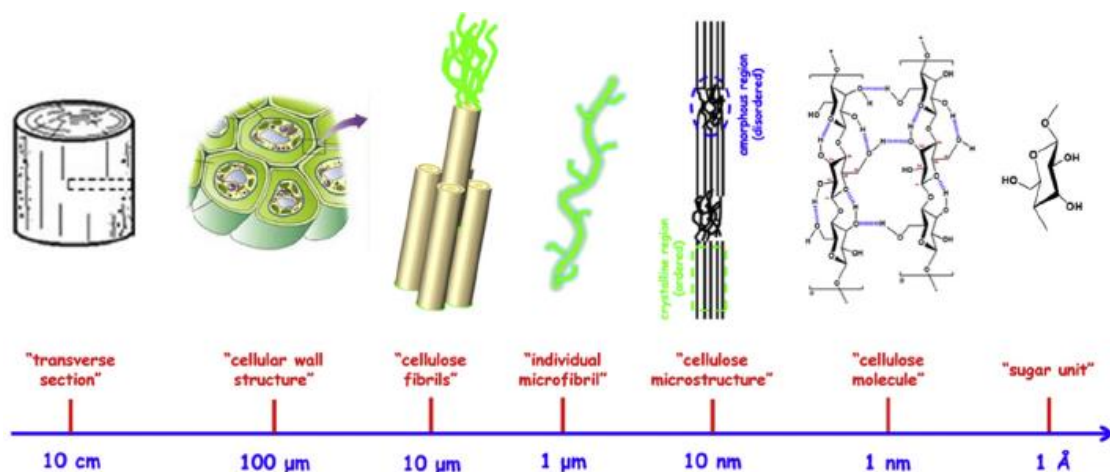


Figure 7 – Cellulose nanofibrils (CNFs) internal structure scheme. Approximated size scales are given for each macro/micro components of the biomass (Source: adapted from LIN & DUFRESNE, 2014).

3.2.2 Cellulose Nanocrystals (CNCs)

Cellulose nanocrystals (CNCs) are characterized as needle-shaped and crystalline structures, widely ordered, with lengths between 50 and 350 nm and diameters between 3 and 50 nm, not exhibiting longitudinal splits, inter-particle entanglement, or network-like structures (FOSTER *et al.*, 2018; ISO TS 20477:2017). Unlike cellulose nanofibers, CNCs are generated from the hydrolysis of the amorphous binding segments of cellulose, since these segments do not stabilize in short side chains by intramolecular hydrogen bonds. In this way, they are available for hydrogen bonds with water molecules, releasing cellulose nanocrystals free in suspension (NG *et al.*, 2015) (Figure 8). CNCs have high rigidity, high mechanical strength (modulus of 110–220 GPa - higher specific modulus (modulus/density) than those of steel, concrete, glass, and aluminum), low density (1.6 g/cm³) and high aspect ratio (L/W), characteristics that increase the mechanical holding capacity of the nanomaterial by allowing higher surface interaction between the particles. (SIQUEIRA, BRAS and DUFRESNE, 2009).

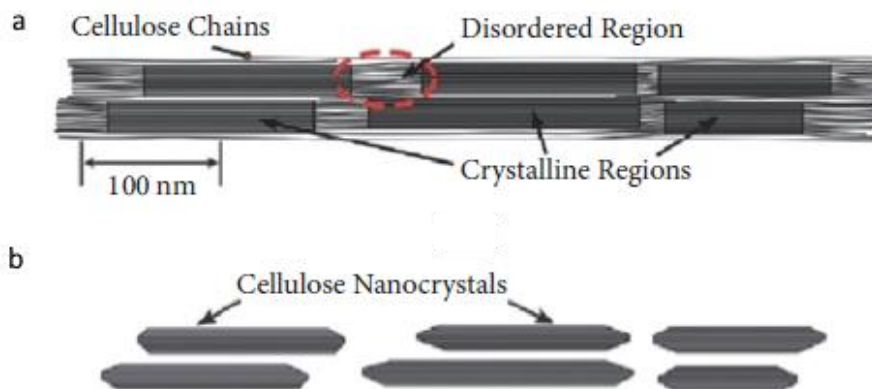


Figure 8 – (a) Cellulose microstructure highlighting crystalline and disordered (amorphous) regions of the biomass; (b) Cellulose nanocrystals (CNCs) isolated from the cellulose microstructure (Source: adapted from XIE *et al.*, 2018).

3.2.3 Lignin-Containing Cellulose Nanomaterials (LCNMs)

The CNMs processing mostly involves pretreatments of the biomasses to remove lignin and hemicellulose, which reduces the yields of CNMs obtaining. Due to the complex nature of lignin, various pretreatments have been proposed for depolymerization of biomasses. Since the lignocellulosic components are tightly embedded in the plant cell wall (Figure 4), the access of the reagents required for efficient separation is generally

hindered (EWULONU *et al.*, 2018). Thereby, lignin-containing cellulose nanomaterials (LCNMs) are receiving attention as alternative cellulose nanomaterials (TROVAGUNTA *et al.*, 2021).

LCNMs are produced by avoiding the conventional pretreatment processes or only applying mild treatments to the hydrolysable biomass. These processing conditions retain some lignin components in the final nanomaterials, and also lower upstream costs and environmental impacts with the absent (or mild) pretreatments (ROJO *et al.*, 2015). It has been demonstrated that the presence of residual lignin in cellulose nanocrystals and nanofibers can improve the chemical compatibility and the physical and mechanical properties of these materials, hence extending their range of applications (BILATTO *et al.*, 2020). Lignin-containing cellulose nanocrystals (LCNCs) and lignin-containing cellulose nanofibrils are two alternative CNMs with lignin contents. LCNCs, for example, have higher hydrophobicity, higher roughness, and higher thermal stability than CNC-lignin free counterparts (AGARWAL *et al.*, 2018; EWULONU *et al.*, 2018; BILATTO *et al.*, 2020). For some applications, these physical-chemical properties are challenges that still need to be addressed in the CNMs technology. Numerous studies have reported that the presence of residual lignin also improves the fibrillation of cellulosic fibers (TROVAGUNTA *et al.*, 2021).

3.2.4 Applications of Cellulose Nanomaterials

Cellulose nanomaterials, either as cellulose nanofibrils (CNF) or cellulose nanocrystals (CNC), have a wide range of potential applications in different industrial sectors due to their renewable nature and remarkable properties (Figure 9). Owing to the high level of structural organization, nanocellulose became an attractive additive for several sectors related to Materials Engineering. Small amounts (about 1%) of these CNMs are enough for big improvements in some products (BIBBO *et al.*, 2019).

Among the different applications of this nanometric biopolymer, the use as mechanical reinforcement in polymeric materials (ethylene polyoxide, polyvinyl acetate, polyethylene, polypropylene, polyurethane, etc.) stands out, resulting in significant increases in the mechanical and thermal resistance properties of the added materials (SIQUEIRA *et al.*, 2009; LI *et al.*, 2018; WANG *et al.*, 2018). The crystalline properties of CNCs, for example, give rigidity to the modified polymeric matrix. It also creates an

impermeable crystal structure that hinders the infiltration and diffusion of molecules such as water, allowing the generation of barrier properties (selective permeability) in polymers (NG *et al.*, 2015). In this case, thermal stability is a property of interest for CNCs, once initial degradation temperatures are expected due to the high temperatures required in the processing of polymeric materials (DUFRESNE, 2012).

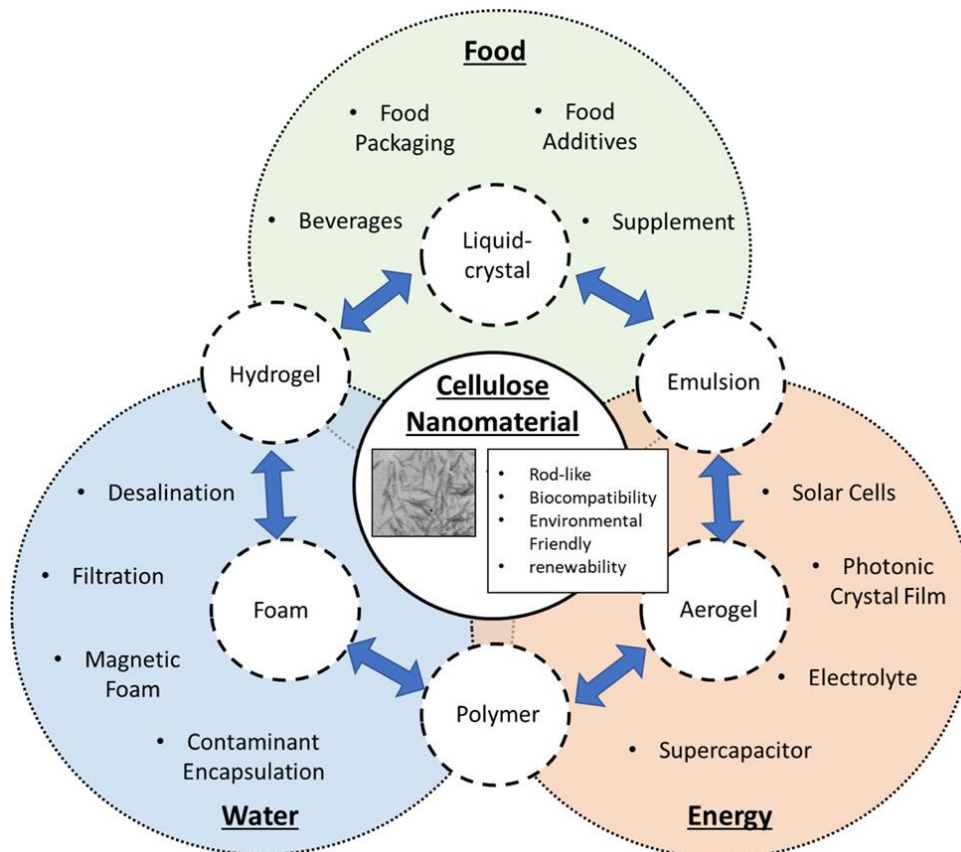


Figure 9 – Some cellulose nanomaterials applications areas by material types (Source: TAN *et al.*, 2019).

Another promising field for nanocellulose applications is the packaging sector (FERRER *et al.*, 2017; GOND & GUPTA, 2020). Regulatory agencies in several countries have tightened laws to reduce applications of non-biodegradable materials in this industry, mainly due to the increase in the use of disposable materials which has resulted in an increase in greenhouse gas emissions (GHGs). CNMs have excellent characteristics that make them suitable for use in this sector, such as biodegradability, non-toxicity, antimicrobial properties, flexibility and transparency. These materials can help to extend the shelf-life of food in several ways, including preventing microbial growth (AZEREDO *et al.*, 2017). Applications in the fields of biomedicine (NSOR-ATINDANA *et al.*, 2018; XIAO *et al.*, 2018), paints and coatings (CATALDI *et al.*,

2017), adhesives, oil and gas industry, electronics, agriculture (mainly as agrochemicals additives) and filtration are also well reported in literature (Table 2).

Table 2 – Some nanocellulose applications (by category) documented in literature.

High Volume Applications	Low Volume Applications	Novel and Emerging Applications
Cement	Wallboard facing	Sensors in biomedical, environmental and industrial areas
Automotive parts	Insulation	Reinforcement fiber – construction
Paper & packaging coatings	Aerospace applications	Air & water filtration
Paper & packaging Fillers	Aerogels for oil and gas industry	Viscosity modifiers
Replacement-plastic packaging	Paint additives	Cosmetics additive
Plastic films replacement		Flexible electronics
Hygiene and absorbent products		3D printing
Textiles for clothing		Photovoltaic cells

Sources: SAMIR *et al.*, 2005; LIN & DUFRESNE, 2014; SHATKIN *et al.*, 2014; AZEREDO *et al.*, 2017; CATALDI *et al.*, 2017; FERRER *et al.*, 2017; LI *et al.*, 2018; WANG *et al.*, 2018; XIAO *et al.*, 2018.

3.2.5 Cellulose Nanomaterials Global Production, Price and Market Forecast

Cellulose nanocrystals (CNCs) were first produced in 1947 by Nickerson and Habrle by sulfuric acid hydrolysis. Despite this early report, there was such a 40-year “gap” in the R&D area before scientific interest in CNCs aroused again in the 1990s years. CNMs are now produced industrially in tonnes-per-day quantities and, in such scale, are already suitable for high-volume, commercial applications (VANDERFLEET & CRANSTON, 2021) (Figure 10).

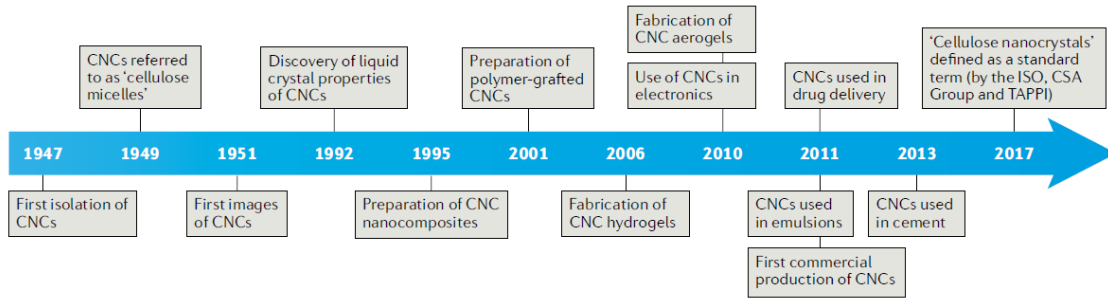


Figure 10 – Timeline of R&D milestones of CNCs production (VANDERFLEET & CRANSTON, 2021).

The production of nanocellulose varieties characterizes the 5th generation of technology development from cellulosic compounds, enabling the R&D of a wide range of innovative products from biomasses (Figure 11). Industrial production of CNMs is on the upswing and multiple suppliers are crucial for market growth (LINDSTRÖM & AULIN, 2014). Different CNMs material grades are evolving, including performance and premium grades (for food, medical, cosmetic and personal care). Commercial products already do exist, and many more are close to deployment. Some companies have a focus application area for their production (*Anomera*[®] in cosmetics and *Blue Goose Biorefineries*[®] in cement reinforcement, for example) (VANDERFLEET & CRANSTON, 2021).

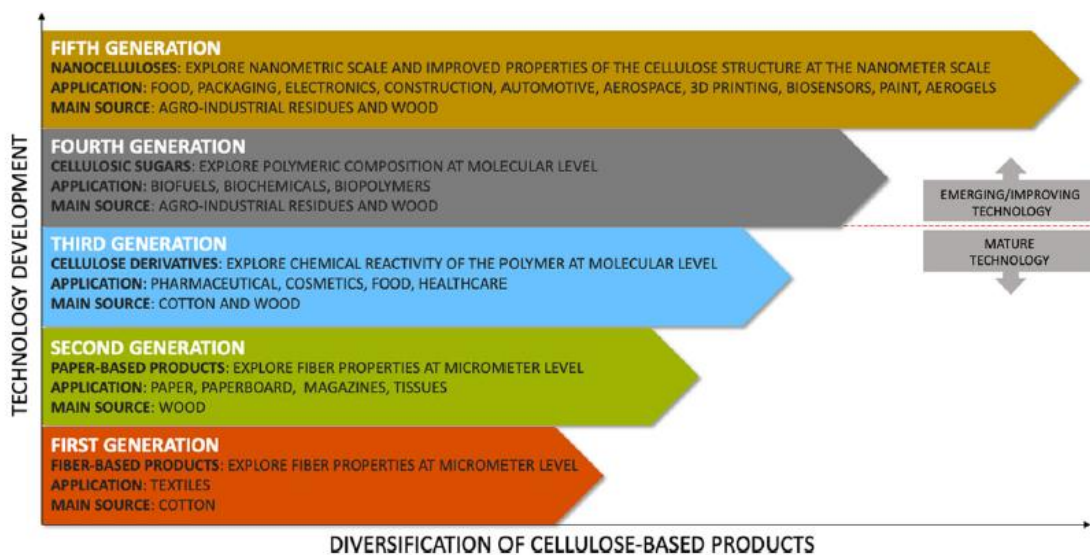


Figure 11 – Diversification of cellulose-based products by technology development. Cellulose nanomaterials are highlighted as a 5th generation, emerging technology (Source: ARANTES *et al.*, 2020).

The use of cellulose nanomaterials has aroused the interest of several institutions and several countries. Canada, Finland and United States corporations have been investing heavily in the area. There are some companies already producing this

nanomaterial at scale, such as *Celluforce*[®] (Canada), Alberta-Pacific Forests Industries[®] (Canada) and *Granbio*[®] (USA / Brazilian owned) (Figure 12). In 2020, the *Nippon Paper Industries*[®] unit located at the Ishinomaki plant (Japan) was the world's leader in large-scale producing of nanocellulose. Production started in 2017 and the installed capacity is 500 ton / year of CNFs. The unit deployment cost was 1.6 billion yen (US\$ 14.5 million). According to *Nippon*[®], the plant produces CNF from wood pulp chemically treated by (2,2,6,6-Tetramethylpiperidin-1-yl)oxyl (also known as *TEMPO*) catalytic oxidation method. This process easily defibrates the pulp and enables the obtaining of nanofibers with uniform width (NIPPON PAPER GROUP, 2020).

Company	Location	Biomass sources	Production volume	CNC surface chemistry	Production route
Alberta-Pacific Forest Industries Inc.	Alberta, Canada	Hardwood or softwood kraft pulp and dissolving pulp	500 kg per day	Sulfated	Sulfuric acid hydrolysis (continuous process)
Anomera Inc.	Ontario, Canada	Softwood pulp	30kg per day (current); 1 tonne per day (projected 2020)	Carboxylated	Dilute hydrogen peroxide oxidation
Blue Goose Biorefineries Inc.	Saskatchewan, Canada	Viscose grade dissolving pulp	10kg per day	Carboxylated	Transition metal-catalysed oxidation
CelluForce Inc. (can also be procured from University of Maine)	Quebec, Canada	Bleached softwood kraft pulp	1 tonne per day (since 2012)	Sulfated	Sulfuric acid hydrolysis (batch process)
Cellulose Lab	New Brunswick, Canada	Dissolving or commercial pulp, cotton, sisal, tunicate	10kg per day	Sulfated (plus surface modifications)	Sulfuric acid hydrolysis (batch process)
GranBio (formerly American Process Inc.)	Georgia, USA (Brazilian owned)	Woodchips (eucalyptus), agricultural residues, energy crops	500 kg per day	Unmodified (plus grade containing lignin coating)	AVAP [®] patented process with ethanol and SO ₂ (continuous process)
FPInnovations	Quebec, Canada	Bleached chemical wood pulp	1.5 kg per day	Sulfated or phosphated	Sulfuric or phosphoric acid hydrolysis (batch process)
InnoTech Alberta	Alberta, Canada	Various bleached hardwood or softwood pulps	2kg per day	Sulfated	Sulfuric acid hydrolysis (batch and continuous process)
Melodea Ltd	Rehovot, Israel	Various bleached hardwood or softwood pulps	>10 tonnes per year (projected 2020)	Sulfated	Sulfuric acid hydrolysis (batch process)
USDA Forest Products Laboratory	Wisconsin, USA	Dissolving pulp	10kg per day	Sulfated	Sulfuric acid hydrolysis (batch process)

Figure 12 – Pilot and industrial-scale plants identified worldwide for the production of cellulose nanocrystals (CNCs) (Source: VANDERFLEET & CRANSTON, 2021).

Several pilot-scale startups and research institutes around the world also sell / provide CNCs, CNFs and bacterial nanocelluloses produced with the use of different technologies. However, the nanocelluloses prices offered by these institutions are considerably high since the producers are aiming at the development of technologies and not the large-scale commercialization at first. In 2020, the price catalog of Canadian *Cellulose Lab*[®] reported *free on board* (FOB) costs between US\$ 2 and US\$ 50 per gram of nanocellulose according to the different processing methodologies (Figure 13). *Nanografi Nanotechnology*[®] (a Turkish company) was selling dry CNCs and CNFs

respectively at € 765 / kg and € 794 / kg in 2021, while *Blue Goose Biorefineries*[®] (a Canadian company) was selling CNCs (in 8% v/v solution) at US\$ 1000 / dry kg.

2020 Cellulose Lab Nanocellulose Products Price

www.CelluloseLab.com



Product Series	Cellulose Lab Catalog Number	Product	Fiber Dimension, surface group	Form	Large Package Order		Extra Large Order
					Size (oven-dry weight basis)	Cost, USD per gram (oven-dry weight)	
Commercial Grade Cellulose Nanofibrils	CNF-COM-Regular	Commercial Grade Cellulose Nanofibrils prepared by high pressure homogenizer	Width: nominal width 30-300 nm; Length: 3-30 um Surface Group: Hydroxyl Hydrophilic	1-10% solids in water			Please contact us
	CNF-COM-Extra	Commercial Grade Cellulose Nanofibrils prepared by high pressure homogenizer with extra treatment	Width: nominal width 10-100 nm; Length: 1-10 um Surface Group: Hydroxyl Hydrophilic	1-10% solids in water			
NFC series (Cellulose Nanofibrils or nanofibrillated cellulose) or MFC series (micro fibrillated cellulose)	CNF-FD	Cellulose Nanofibrils Freeze-dried	Width: nominal width 30-80 nm; Length: up to several hundred micron Surface Group: Hydroxyl Hydrophilic	Dry	201 g – 2 kg	\$6.00	Please contact us
	CNF-TEMPO-FD	TEMPO (Anionic type) Cellulose Nanofibrils Powder	Average width: 50 nm; Length: 0.5um - 80um Surface Group: Carboxyl Hydrophilic	Dry	51 g – 1 kg	\$20.00	
	CNF-PO	Cellulose Nanofibrils, Periodate oxidated; Ordered upon request	Width: 10-50 nm; Length: 800-1500 nm Surface Group: dialdehyde Hydrophilic	0.3-1% in water	51 g – 1 kg	\$20.00	
	CNF-Hydrophobic	Hydrophobic CNF, Organic acid hydrolysis; Ordered upon request	Width: 10-50 nm; Length: 800-1500 nm Surface Group: Ester group Hydrophobic	0.5-1% in DMAC	51 g – 1 kg	\$25.00	
	CNF-Lignin	Lignin coated CNF slurry at DMAC; Ordered upon request	Width: 10-50 nm; Length: 800-1500 nm Surface Group: Ester group, lignin Hydrophobic	0.5-1% in DMAC	51 g – 1 kg	\$35.00	
	CNF-PO	Cellulose Nanofibrils, Periodate oxidated; Ordered upon request	Width: 10-50 nm; Length: 800-1500 nm Surface Group: dialdehyde Hydrophilic	0.3-1% in water	51 g – 1 kg	\$20.00	
	CNF-Hydrophobic	Hydrophobic CNF, Organic acid hydrolysis; Ordered upon request	Width: 10-50 nm; Length: 800-1500 nm Surface Group: Ester group Hydrophobic	0.5-1% in DMAC	51 g – 1 kg	\$25.00	
	CNF-Lignin	Lignin coated CNF slurry at DMAC; Ordered upon request	Width: 10-50 nm; Length: 800-1500 nm Surface Group: Ester group, lignin Hydrophobic	0.5-1% in DMAC	51 g – 1 kg	\$35.00	
NCC (or CNC) series (Nanocrystalline Cellulose or Cellulose Nanocrystals)	CNC-Slurry	Cellulose Nanocrystals, Sulfuric acid hydrolysis	Width: 5-20 nm; Length: 100-250 nm Surface Group: Hydroxyl, sulfonic group, Hydrophilic	0.5 - 6% solids in water	501 g – 5 kg	\$2.50	
	CNC-Slurry-HS	Cellulose Nanocrystals, Sulfuric acid hydrolysis, high sulfonic group content	Width: 5-20 nm; Length: 100-250 nm Surface Group: Hydroxyl, sulfonic group, Hydrophilic	0.5 - 10% solids in water	501 g – 5 kg	\$3.00	
	CNC-FD	Cellulose Nanocrystals Freeze-dried	Width: 5-20 nm; Length: 100-250 nm Surface Group: Hydroxyl, sulfonic group Hydrophilic	Dry	201 g – 1 kg	\$7.00	
	CNC-SD	Cellulose Nanocrystals Spray-dried	Width: 5-20 nm; Length: 140-200 nm Surface Group: Hydroxyl, sulfonic group Hydrophilic	Dry	201 g – 1 kg	\$5.50	
	CNC-Cationic	Cationic type Cellulose Nanocrystals; Ordered upon request	Width: 5-20 nm; Length: 140-200 nm Surface Group: Quaternary ammonium, hydroxyl Hydrophilic	0.5% - 2% in water	51 g – 1 kg	\$40.00	
	CNC-TEMPO-Low	Cellulose Nanocrystals, TEMPO (anionic type) modified, at different carboxyl group content (0.15 - 0.6 mmol/g); Ordered upon request	Width: 5-20 nm; Length: 140-200 nm Surface Group: Carboxyl group, hydroxyl Hydrophilic	0.5% - 2% in water	51 g – 1 kg	\$20.00	
	CNC-OA	Cellulose Nanocrystals, Organic acid hydrolysis; Ordered upon request	Width: less than 100 nm; Length: less than 100 nm Surface Group: Ester group, hydroxyl Hydrophobic	0.5 - 1%, in DMAC or water	51 g – 1 kg	\$35.00	
Bacterial Cellulose	BC-Sheet	Bacterial Cellulose Slurry, sheet form	Width: 50 - 100 nm; Length: ≥ 30 um Surface Group: Hydroxyl Hydrophilic	5.5% in water	250 g – 1 kg	\$8.00	
	BC-FD	Bacterial Cellulose Slurry, freeze-dried powder	Width: 50 - 100 nm; Length: ≥ 30 um Surface Group: Hydroxyl Hydrophilic	Dry	51 g – 1 kg	\$40.00	

Customer is responsible for the shipping cost and customs clearance.

Cost is by weight, dry basis, exclusive of shipping charges. S/H will be added.

Orders will be shipped via DHL, Fed Ex or UPS Express delivery, unless otherwise instructed - subject to available inventory.

Figure 13 – Cellulose Lab[®] main products price table for 2020 year (adapted from the CELLULOSE LAB website, 2021).

It is difficult to find information on media regarding the cost of CNMs on larger (i.e., industrial) scales, primarily because companies keep prices under market confidentiality, but also because these prices depend of the process, the scale, the feedstock treatment, and the application type, and also change over time. Despite that, the commercial selling price of cellulose nanocrystals was estimated by *TAPPI*[®] in the range of US\$20 to US\$ 120/kg of CNCs for dissolving pulp hydrolyzed by sulfuric acid (NELSON *et al.* 2016). ARANTES *et al.* (2020) reported an estimated selling price of US\$ 50 / kg of CNCs (for larger scales) by communication with *Celluforce*[®], and this last employs a sulfuric acid hydrolysis of Northern Bleached Softwood Kraft Pulp (NBSK) in the production.

It is also not simple to find precise information about the nanocellulose materials production and selling market, as several companies sell these strategic data to entities of interest. Furthermore, it is difficult to measure and predict the behavior of an incipient market, and therefore the estimates given by specialized companies are not coincident. However, it can be said that the nanocellulose market has already surpassed US\$ 200 million and that CAGR rates between 15 and 25% are expected for the period of the next 4 to 7 years (Figure 14a) (AMECO RESEARCH, 2020; MARKETS AND MARKETS, 2021; MARKET FORECAST DATE, 2021). The applications market share is still highly concentrated in composites and packaging, and in the pulp and paper sectors. However, the expansion in the number of applications and the R&D popularization of the CNMs benefits (Figure 15) should increase the market potential of CNMs for applications such as biomedicine and food and beverages (Figure 14b) (EXPERT MARKET RESEARCH, 2021).

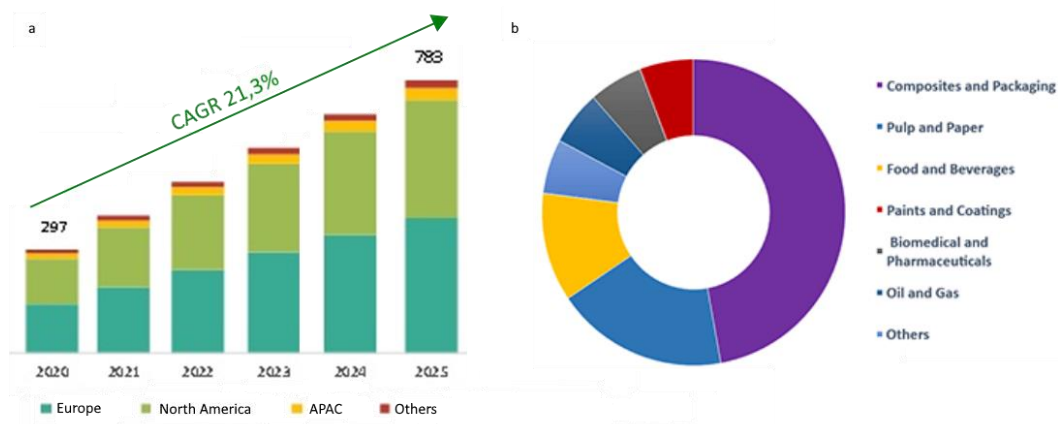


Figure 14 – (a) Growth forecast for the nanocellulose materials market by global region (in US\$ million) (Source: adapted from MARKETS AND MARKETS, 2021); (b) Market share by application in 2020 for the global nanocellulose market (Source: adapted from EXPERT MARKET RESEARCH, 2021).

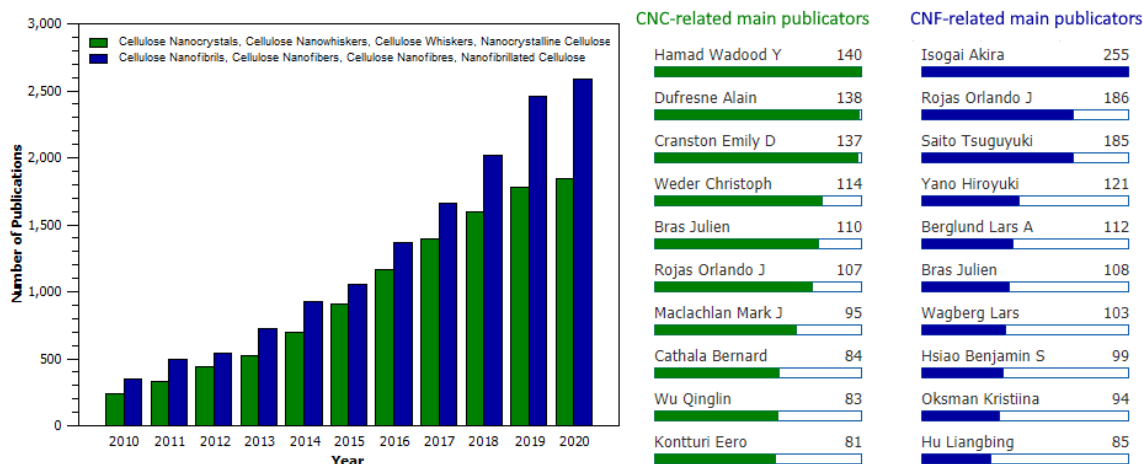


Figure 15 – Scientific publications related to CNCs and CNFs between 2010 and 2020 (Source: generated with *SciFinder*[®]).

3.3 Nanocellulose Production in Sugarcane Biorefineries

A solid fibrous residue containing highly crystalline cellulose is generated at the end of the hydrolysis enzymatic step of the E2G processing. An interesting alternative for the use of this residue would be to use it as feedstock for nanocellulose production. This solid was previously processed through the E2G enzymatic hydrolysis step, in which the majority of the amorphous fractions of cellulose are primarily degraded to fermentable sugars for the E2G biorefinery (CAMARGO *et al.*, 2016). Thus, cellulose with a higher degree of crystallinity (an ideal characteristic for the production of CNMs) is found in this biomass residual fraction.

The work of CAMARGO *et al.* (2016) determined that the CNCs obtained from the residual solid phase of the E2G enzymatic hydrolysis (Figure 16) have appropriate physical, chemical and thermal characteristics for different applications. Thus, the use of this residual material looks promising for adding value to the sugarcane biorefinery sector. Other works highlighted the properties of CNFs (PINTO *et al.*, 2019; ZHANG *et al.*, 2020) and CNCs obtained from raw sugarcane bagasse processing, as the works of TEIXEIRA *et al.* (2011), MANDAL & CHAKRABARTY (2011), KUMAR *et al.* (2014), GHAZY *et al.* (2016), OLIVEIRA *et al.* (2016), MEESUPHONG *et al.* (2021), PEREIRA & ARANTES (2020), and DE AGUIAR *et al.* (2020). The block diagram illustrated in Figure 17 exemplifies a process route model for the generation of CNMs from sugarcane lignocellulosic residues in the context of a E1G + E2G production biorefinery (FARINAS *et al.*, 2017). The nanocellulose production units can be attached

to the primary biorefinery and, therefore, share process facilities (including mass and energy integrations) in order to minimize costs and increase competitiveness (DIAS *et al.*, 2012; FURLAN *et al.*, 2015; RESHMY *et al.*, 2021). The production of CNMs from the bagasse or from the solid residue of the E2G enzymatic process requires treatments for previous removal of residual lignin and hemicellulose fractions.

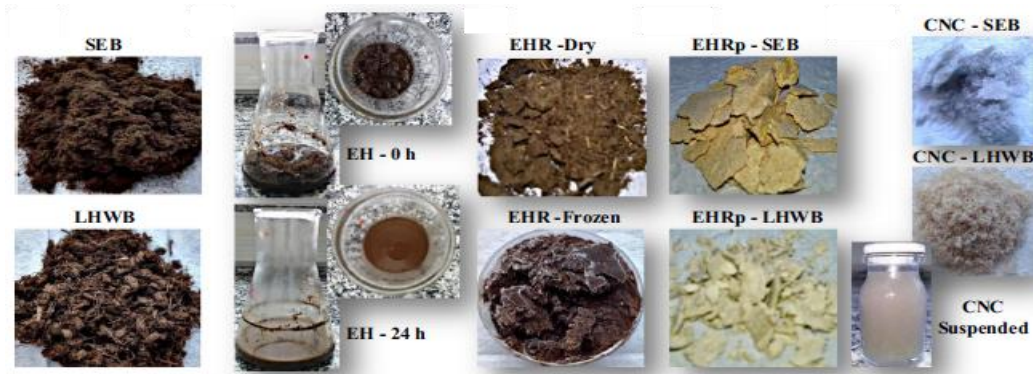


Figure 16 – CNCs obtained from sugarcane bagasse by using steam explosion (SEB) and hydrothermal (LHW) pretreatments (Source: CAMARGO *et al.*, 2016).

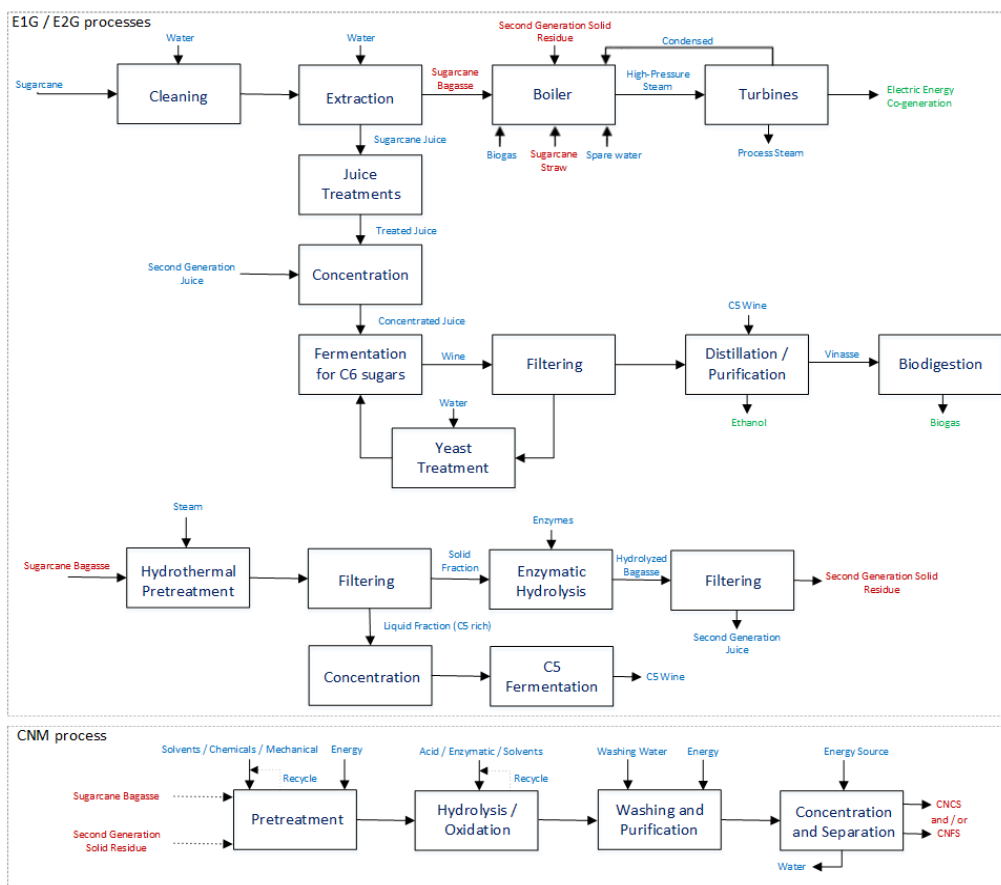


Figure 17 – Block diagram of a CNMs production unit by chemical methods attached to an E1G/E2G ethanol biorefinery. Sugarcane bagasse generated in the enzymatic hydrolysis step of the E2G process can be used as feedstock to obtain CNMs.

3.3.1 Biomass Pretreatments

Sugarcane bagasse is a lignocellulosic biomass and so has in its composition hemicellulose and lignin contents in addition to the cellulosic fraction (CAMARGO *et al.*, 2016; OLIVEIRA *et al.*, 2016) (Table 3). The biomass pretreatment methods aim to disassemble the lignocellulosic structure, remove lignin and hemicellulose contents, increase the surface area of the biomass, and decrease the degree of polymerization of the cellulose, all to obtain higher purity levels of cellulose with greater accessibility to hydrolysis (WYMAN *et al.*, 2005). This process can be carried out by physical methods (such as mechanical grinding) (LIU *et al.*, 2018; SOFLA *et al.*, 2019), chemical methods (using acids such as sulfuric, phosphoric and nitric, or alkaline solutions of ammonia, NaOH, etc.), and biological methods. The use of less environment-aggressive treatments such as organosolv (with solvents such as methanol, ethanol, ethylene glycol and other alcohols) (AGNIHOTRI *et al.*, 2015; LI *et al.*, 2016a; BORAND & KARAOSMANOĞLU, 2018), steam explosion (ROCHA *et al.*, 2012) and hydrothermal (ROCHA *et al.*, 2017; BATISTA *et al.*, 2018; SANTO *et al.*, 2018) pretreatments is also proposed for biomass upstream processing (Table 4). Given the high recalcitrance of sugarcane biomass, there are cases in which combinations between these pretreatments are used to obtain cellulose with higher levels of purity (XIE *et al.*, 2018). Generally, higher severity pretreatments form degradation products, which have a negative effect during the subsequent hydrolysis (PRATTO, 2015).

Table 3 – Chemical composition of lignocellulosic materials of different sources.

Source	Cellulose (%)	Hemicellulose (%)	Lignin (%)	Extracts, pectin and waxes (%)
Hardwood	43-47	25-35	16-24	2-8
Softwood	40-44	25-29	25-31	1-5
Cotton Stalk	48-52	25-27	24-26	2-4
Corn cob	28-34	39-47	21-29	5-12
Wheat Straw	37-43	31-37	18-22	2-14
Sugarcane Bagasse	42-47	27-32	20-22	3-5

Source: adapted from MALUCELLI *et al.*, 2017.

Table 4 – Main types, methods and key characteristics of biomass pretreatments.

Type	Method	Key Characteristics	
		Favorable	Unfavorable
Mechanical	Milling	- Low initial investment - Low wastes generation	- High energy consumption - Low yield of fermentable sugars
	Acid Pretreatment (diluted / concentrated)	- Practical and simple, does not require thermal energy - Effective hemicellulose removal - High yield in fermentable sugars	- Generates toxic inhibitors - Requires acid recovery (or neutralization) steps
Chemical	Alkaline Pretreatment	- Effective lignin removal - High increase in biomass specific surface	- Long pretreatment residence time - Neutralization of slurry
	Oxidative Delignification	- Very effective lignin removal - Reduced toxic inhibitors	- Low hydrolysis of oligomers - High costs of oxygen and catalyst
	Ozonolysis	- Very effective lignin removal - Reduced toxic inhibitors	- High costs of ozone - Very expensive process
	Ammonia Fiber Expansion (AFEX)	- Low waste generation - Low inhibitors generation	- Higher temperature and pressure conditions - Not effective in lignin removal - Requires ammonia recovery
	Ionic Liquids	- Very effective on biomass increasing specific surface - Low inhibitors generation	- High costs of ionic liquids
Solvent	Organosolv	- Effective on lignin and hemicellulose removal - Lower environmental impacts	- Formation of toxic inhibitors - Organic solvent recycling - High initial investment
	Hydrothermal	- Effective on hemicellulose removal - No chemicals used - Lower environmental impacts	- Not effective on lignin removal - High inhibitors generation - High initial investment
	Steam Explosion	- Very effective on hemicellulose removal - High yield of fermentable sugars	- Incomplete disruption of lignin-carbohydrate matrix - Formation of inhibitors
	Enzymatic Pretreatment	- Low use of chemicals and energy - Lower environmental impacts	- Lower delignification yields - High costs of enzymes - Slow bioconversion

Source: adapted from LIMAYEM & RICKE (2012), MOOD *et al.* (2013), KARP *et al.* (2013), and PIRES *et al.* (2019).

Some pretreatment methods are especially effective in removing higher lignin contents and are then called delignification methods (Figure 18) (also known as purification or bleaching - names derived from the Kraft process used in the paper and cellulose industries) (WYMAN *et al.*, 2005; ARNI, 2018). Several low-cost compounds have been tested for the delignification of lignocellulosic materials. Examples include sodium hypochlorite (NaOCl), which is an oxidizing agent, and hydrogen peroxide (H₂O₂) (HIGA *et al.*, 2012), which acts in breaking the bonds between the amorphous compounds present in the material composition.

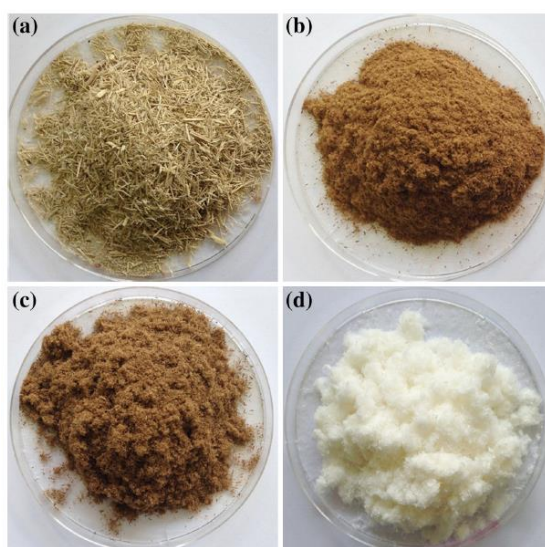


Figure 18 – Physical appearance of sugarcane bagasse untreated fiber (a), steam-exploded fiber (b), enzymatically treated fiber (c), and alkaline treated fiber (d) (Source: LAM *et al.*, 2017).

3.3.2 Biomass Hydrolysis

The most conventional methods of nanocellulose extraction from sugarcane bagasse include acid hydrolysis, mechanical treatments, enzymatic hydrolysis, and oxidation routes using APS (ammonium persulfate), TEMPO, peroxide, and metal-catalyzed oxidation. These processes aim the removing of the amorphous cellulose phase, either partially to obtain cellulose nanofibrils (CNFs), or completely to obtain cellulose nanocrystals (CNCs) (DUFRESNE, 2012; BONDANCIA *et al.*, 2020).

In the process of generating cellulose nanocrystals, that are highly crystalline structures, the hydrolysis is the most common method, used subsequently to the biomass pretreatment (PHANTHONG *et al.*, 2018). Hydrolysis is necessary for the degradation

of the amorphous binders of the cellulosic structure. It can be catalyzed by acids or cellulolytic enzymes (Figure 19). Acid hydrolysis, although cheaper and generally efficient – it favors the achievement of higher crystallinity indices for nanocellulose in shorter reaction times - has some drawbacks such as the need to recovery the acid (SUN and CHENG, 2002). On the other hand, enzymatic hydrolysis has high specificity and occurs under milder conditions of temperature and pH, but the lower yields, higher reaction times (CARVALHO *et al.*, 2013; ANGARITA *et al.*, 2015) and the high cost of enzymes are still technological bottlenecks that need to be assessed (HIMMEL *et al.*, 2007; ROSALES-CALDERON *et al.*, 2021).

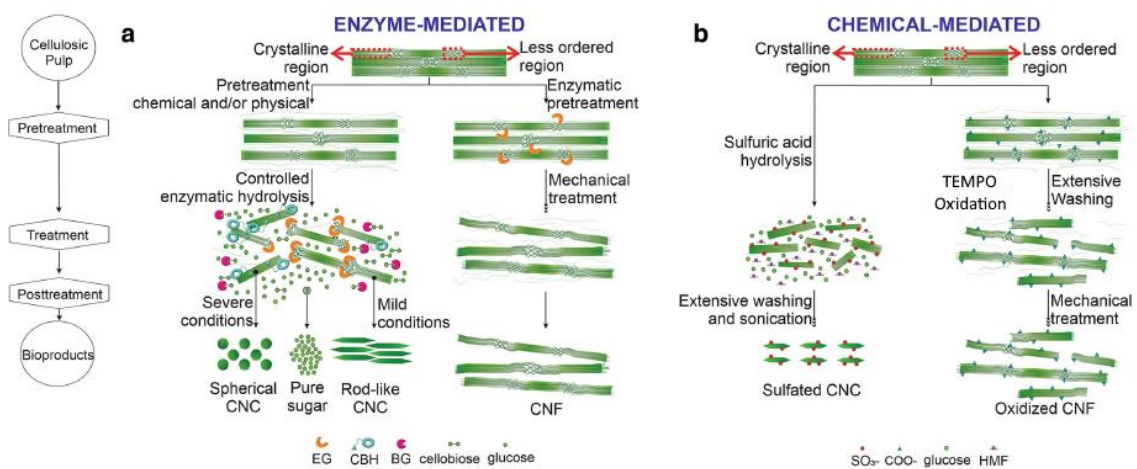


Figure 19 – Schematic representation of nanocelluloses production by (a) enzymatic and (b) chemical routes (Source: adapted from ARANTES *et al.*, 2020).

3.3.2.1 Acid Hydrolysis with Mineral Acids

The most common method for biomass hydrolyzing towards CNMs production is the acid hydrolysis with mineral acids. It can use different acids (most commonly sulfuric and hydrochloric), in different proportions, and usually with process recycling (VÁRNAI *et al.*, 2020). Prior delignification provides better efficiency in the contact between cellulose and acid (LI *et al.*, 2016a). The properties of the obtained nanocrystals are strongly related to the reaction time, temperature and type of acid used in the process (HUNTLEY *et al.*, 2015). When hydrolysis is carried out with HCl, nanocrystals tend to aggregate due to the absence of charges involved, generating agglomeration and precipitation. However, when H₂SO₄ is used, the formation of ester-sulfates in solution generates negative charges that favor electrostatic repulsion and the consequent

dispersion in water, generating suspensions with a colloidal aspect (SAMIR, ALLOIN AND DUFRESNE, 2005). High colloidal stability is essential to produce uniform dispersions with predictable and consistent performance (VANDERFLEET & CRANSTON, 2021). It should be noted that acid hydrolysis processes, as a more aggressive approach than the enzymatic one, favor the obtaining of lower degrees of polymerization of cellulose (Figure 20) and higher levels of crystallinity for produced CNMs in shorter reaction times (WANG *et al.*, 2014; XIE *et al.*, 2018).

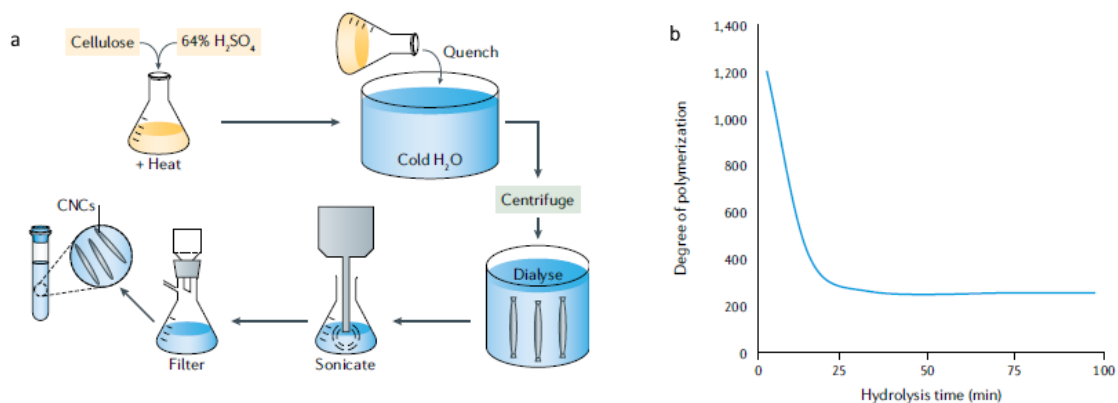


Figure 20 – (a) The simplified laboratory method to produce CNCs with H_2SO_4 hydrolysis; (b) The levelling off degree of polymerization of cellulose chains during sulfuric acid hydrolysis (Source: adapted from VANDERFLEET & CRANSTON (2021)).

3.3.2.2 Acid Hydrolysis with Organic Acids

Although maximizing CNMs yield in hydrolysis is often very important, CNMs applicable performance is equally as important. In general, harsher hydrolyses (longer, hotter or with more concentrated acids) in fact produce CNCs with smaller sizes and more surface charge groups (AGUAYO *et al.*, 2018). If the hydrolysis is not harsh enough, disordered regions remain unhydrolyzed and only a few CNCs will be produced, while the rest of the initial cellulose mass will be recovered as solid residue. Nevertheless, highly harsher hydrolysis processes can begin to degrade the crystalline regions, reducing both the yield and the degree of crystallinity of the nanomaterials (VANDERFLEET & CRANSTON, 2021). Besides, with the introduction of sulfate groups from sulfuric acid hydrolysis, the obtained CNCs have a relatively low thermal stability and also are hardly functionalized further (JI *et al.*, 2019). Therefore, it is important to investigate CNMs production using other hydrolysis agents, such as organic acids.

The study of CNCs isolation using organic acids mainly focuses the advantages of natural occurrence, availability and non-toxicity. Acids containing more than one acidic group can introduce negatively charged carboxyl groups that lead to improved stability in aqueous suspensions (JIANG *et al.*, 2021). Citric acid is an innocuous acid for CNCs production with less experimental risks than other acids (JI *et al.*, 2019; YU *et al.*, 2019). The hydrolysis of cellulosic feedstocks with this organic acid is generally conducted at high acid concentrations (60–80%) and temperatures (80–140 °C) for several hours (BONDANCIA *et al.*, 2020; JI *et al.*, 2019). Even though citric acid is a weaker acid ($pK_a = 3.13$), the crystallinity indexes that can be achieved are generally in the same order as that of CNCs obtained with mineral acids (up to 83%, according to BONDANCIA *et al.*, 2020). Compared to mineral acids, it also avoids over-hydrolysis of cellulose, but unfavorably reduces the CNC yield, generating CNFs by partial hydrolysis in the process (JI *et al.*, 2019; BONDANCIA *et al.*, 2020). Esterification reactions between the organic acid and surface hydroxyl groups of cellulose can also happen, especially in the presence of a catalytic amount of strong mineral acids (such as hydrochloric acid and sulfuric acid) (JIANG *et al.*, 2021).

3.3.2.3 Enzymatic Hydrolysis

Another methodology to obtain nanocellulose in biorefineries is the enzymatic hydrolysis, which uses a pool of highly specific cellulases for the degradation of the amorphous phases of cellulose (HENRIKSSON *et al.*, 2007; CAMARGO *et al.*, 2016; RIBEIRO *et al.*, 2019; SQUINCA *et al.* 2020). In the enzymatic hydrolysis a synergism between three types of enzymes generally occurs: endoglucanases, which attack regions of low crystallinity and release oligosaccharides; exoglucanases, which degrade oligomers to cellobiose, and β -glucosidases, which hydrolyze cellobiose to glucose (Figure 21a) (ZHANG & LYND, 2004; TAHERZADEH *et al.*, 2007). Factors such as the type, concentration and crystallinity of the substrate, presence of inhibitors, enzyme concentration and thermostability, temperature, pH, and agitation rate can influence the process (PRATTO *et al.*, 2015; BONDANCIA *et al.*, 2018). Many of these factors are correlated, so it is difficult to quantify the influence of each one individually (MAEDA *et al.*, 2011).

CNMs obtained by enzymatic hydrolysis generally have superior thermal properties when compared to that obtained by acid hydrolysis due to the presence of ester-

sulfates originated in the latter (GEORGE *et al.*, 2011), and even suitable nanomaterial dimensions (Figure 21b). Still, at this stage of R&D, CNCs produced with enzymatic hydrolyses are colloiddally unstable, with nanoscale dimensions that are not consistently achieved, and have low crystallinities (VANDERFLEET & CRANSTON, 2021). However, the high cost of the enzymes in the enzymatic process is still the main technological bottleneck, but there is perspective that the evolution of researches in the area of genetic engineering may reduce the impact of this adverse factor on the final cost of production (RIBEIRO *et al.*, 2019; ROSALES-CALDERON *et al.*, 2021).

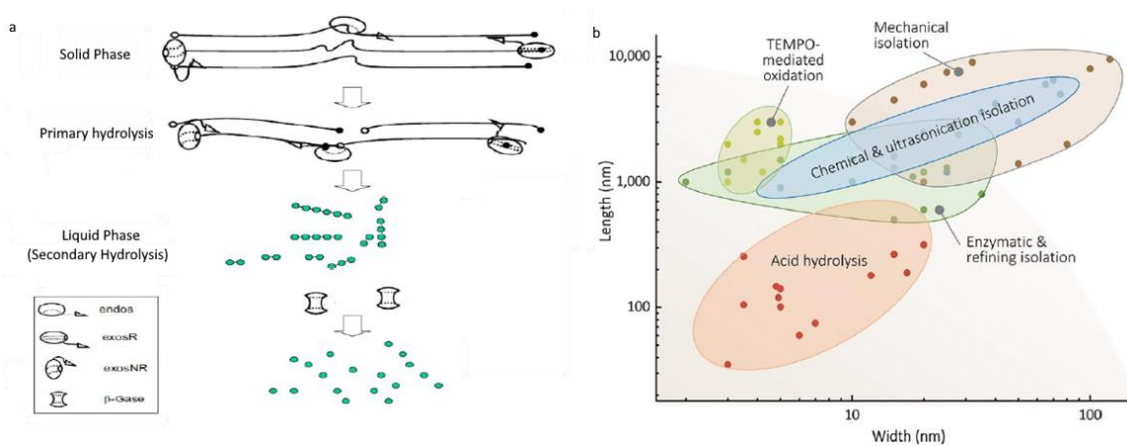


Figure 21 – (a) Enzyme synergism is the enzymatic hydrolysis of biomasses (Source: adapted from ZHANG, 2006); (b) Comparison of CNMs dimensions for different types of biomass processing (Source: YANG *et al.*, 2018).

3.3.3 Downstream processes

After hydrolysis, some steps are required to neutralize (or remove) the acid contents (if acid hydrolysis was employed) and increase the purity of the nanocellulose. Decantation and filtration (or centrifugation) followed by neutralization and dialysis are commonly used in these steps. In the end of processing, CNCs and CNFs can be dried by equipment such as spray-drying and freeze-drying to obtain high purity conditions and facilitate the transport of the material (ASSIS *et al.*, 2017).

A typical CNMs extraction method after hydrolysis involves the use of centrifugation, with the purpose of removing acid and the not-hydrolyzed biomass. After hydrolysis, the reaction is diluted with an excess of water with the objective of quenching the reaction (MALUCELLI *et al.*, 2017). A series of 4500 g centrifuges and washing stages, herein called multistage decanters, are presented as an effective way of separating

CNMs from hydrolysis output streams. The purpose of this step is to wash the CNCs suspension from acid and sugars formed in hydrolysis step, and to separate the suspended CNCs particles from the liquid phase (ASSIS *et al.*, 2017). After centrifugation, CNCs are usually obtained from the turbid liquid supernatant in form of bigger cellulosic material fractions, but some impurities or acid still remain in the solid precipitate. To recover the thermal stability of CNCs, the acid sulfate groups are necessary to be removed by alkali neutralization and dialysis (NG *et al.*, 2015).

The alkali used in the neutralization step should be able to produce a water-soluble salt to avoid any undesired contamination on the produced samples. NaOH is an ideal candidate since it can form water-soluble sodium sulfate salt (NG *et al.*, 2015). In the dialysis step, CNMs precipitates obtained from multistage decanters are re-suspended in water and subjected to dialysis in ultra-pure water using regenerated dialysis membranes (or tubes) until neutral pH is reached. In addition to removing the non-reactive sulfate groups, dialysis also can remove residual salts and soluble sugars. To attain a constant pH, the dialysis could be lasting from several days to 2 weeks (NG *et al.*, 2015; MALLUCELLI *et al.*, 2017).

After removal of the sugars and impurities, nanoparticles can be isolated by their type (CNCs and CNFs) using centrifugation at lower rotation speeds (BONDANCIA *et al.*, 2020). These nanomaterials can be sold as suspensions or can also be dried (Figure 22a). An extra drying step allows cost savings in material transport and also ease the use in industrial applications. This step, however, must be well defined, as this process can irreversibly damage the structure and stability of the crystals, in addition to leading to sample dispersion problems. There are industrial applications of CNMs that are feasible only in the case of the use of aqueous slurries, but there are others where to dehydrate aqueous CNMs suspensions is especially important, for example, the thermoplastic composite processing with extrusion or injection molding involving thermal melting processes. In this regard, a robust dehydration method to dry CNMs suspensions while maintaining inherent nano-scale dimensions is imperative (NG *et al.*, 2015).

Freeze-drying shows great potential in the CNMs drying as it allows fast freezing and water evaporation, without over affecting nanocellulose structure. Nevertheless, this method is known to be very expensive, making it unlikely to be used on larger scales (MALUCELLI *et al.*, 2017). Spray-drying has been proposed since it is a suitable and scalable continuous process to dry CNMs suspensions (Figure 22b), as its lower labor and maintenance costs established it as a standard industrial dehydration method. Apart from

that, strong hydrogen bonding due to the high polarity of CNMs can promote re-aggregation during spray-drying procedures (NG *et al.*, 2015; MALUCELLI *et al.*, 2017).

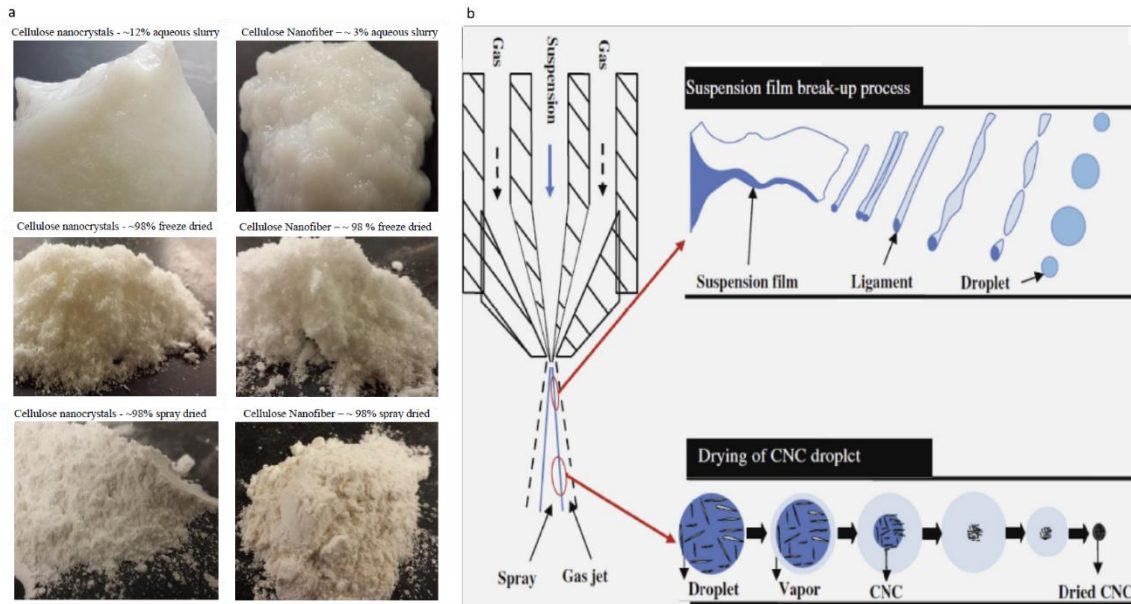


Figure 22 – (a) Comparison of CNCs and CNFs as aqueous slurries and submitted to freeze-drying or spray-drying (Source: adapted from PROCESS DEVELOPMENT CENTER - UNIVERSITY OF MAINE, 2021); (b) Mechanism of spray-drying process for CNCs suspensions (Source: NG *et al.*, 2015).

3.4 Process Systems Engineering

Process Systems Engineering is a broad category of engineering that deals with the process design for the purpose of converting raw goods to usable end products and including energy. It is based on mathematical modelling, simulation and optimization applied to the design of processes and products, but also to the planning, scheduling, operation and control. It is a creative activity based in solid mathematical and programming knowledge, where tools are used to assess the best flowsheet for a given set of products and raw materials, once provided an adequate objective function (FURLAN *et al.*, 2016). The practical result is the improvement in the economic profitability and in the reliability, safety and sustainability of chemical processes. Process Systems Engineering tools can be very useful, especially when coupled with detailed economic analyses. These tools can be used to explore the influence of process parameters on the economic feasibility of processes and set minimum performances to be achieved experimentally for several process metrics (ÖGMUNDARSON *et al.*, 2020a).

3.4.1 Mathematical Modeling of Processes

Mathematical models and process simulations are useful in the design, optimization and control phases of industrial equipment. The use of these techniques may generate results in a less costly, less risky and faster way than the construction of pilot plants. Such representations are especially useful when combined with process mass and energy balances and descriptive economic analyses (FURLAN *et al.*, 2016). A mathematical modeling must incorporate useful information for the understanding of the system in different situations, but it should not be so complex (e.g., try to represent all the phenomena involved) because some of the phenomena may have minimal influence on the results (SANTOS-ROCHA *et al.*, 2017). A suitable mathematical model is one that minimizes the framework complexity while still managing to describe the process with a reasonable accuracy (KADAM *et al.*, 2004).

3.4.1.1 The Virtual Sugarcane Biorefinery

EMSO[®] (*Environment for Modeling, Simulation and Optimization*) is an equation-oriented computational environment that allows obtaining results for dynamic and / or stationary simulation processes, data and process optimization, solution of algebraic and differential-algebraic systems, among others. The research group of the *Laboratory for the Development and Automation of Bioprocesses (LaDABio)*, from the Chemical Engineering Department of Universidade Federal de São Carlos (DEQ/UFSCar), has previously developed on this platform a compilation of models that can simulate a biorefinery for the production of E1G and E2G, including juice extraction and treatment, sucrose / glucose concentration and fermentation, ethanol purification, combined heat and power generation, E2G hydrothermal pretreatment and E2G hydrolysis, along with other process enhancements (Figure 23) (FURLAN *et al.*, 2016; LONGATI *et al.*, 2018; LONGATI *et al.*, 2019; ELIAS *et al.*, 2019; POTRICH *et al.*, 2020; PINTO *et al.*, 2021). Many of these models are based on typical yield relationships of the processes, and their association generates a complex optimization problem involving a system of non-linear equations that are subject to constraints (FURLAN, 2012; ANGARITA *et al.*, 2015).

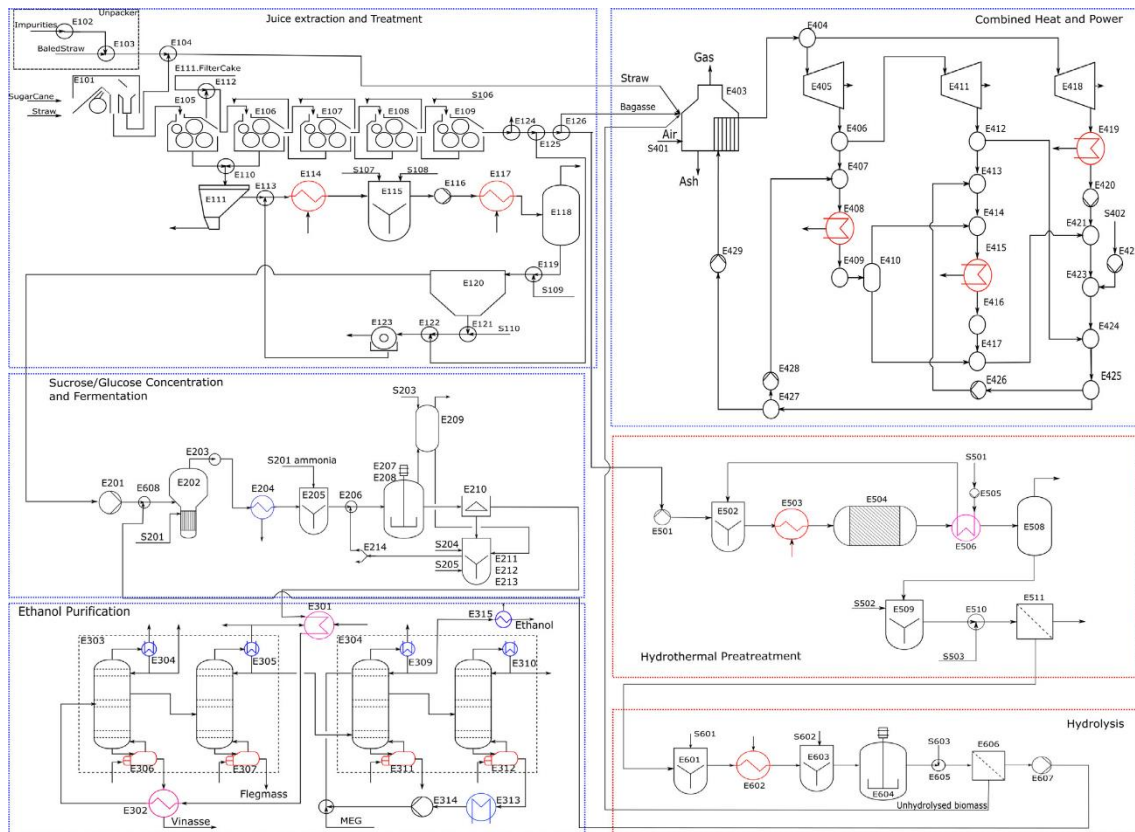


Figure 23 – The EMSO® Virtual Sugarcane Biorefinery from *LaDaBio* research group (Source: ELIAS *et al.*, 2019).

3.4.2 Techno-Economic Analysis of Processes (TEA)

Techno-economic Analysis (TEA) is a useful tool to assess the biomass-to-product yield, energy efficiency, and production costs of processes. Such studies typically investigate (and can optimize) the production costs of a biorefinery process in a bottom-up model, including detailed descriptions of process equipment and material and energy balances (ZETTERHOLM *et al.*, 2020). This tool is capable of generating a wide range of useful information using a framework of experimental and market inputs that is being constantly renewed in literature and other propagation media (BONDANCIA *et al.*, 2020; ROSALES-CALDERÓN *et al.*, 2021).

The methods used for modeling the industrial-level performance of a biorefinery concept are dependent on the technical maturity of the specific technology. Models of commercially available production processes, or processes that have been thoroughly investigated by R&D (sulfuric acid hydrolysis for CNCs production is an example) can be validated against existing operating data. In turn, for *ex-ante* assessments of new biorefinery concepts, modeling becomes a more complex issue, and simulation models

accounting for reaction kinetics or thermodynamic restrictions can be used. Yet, this approach often deviates substantially from experimental data, but it is, however, common in areas as gasification modeling, mainly due to a lack of better alternatives (ZETTERHOLM *et al.*, 2020).

Plant-level models can be used for estimating the process capital costs (CAPEX) and operating costs (OPEX) of processes. Biorefineries typically benefit from scale factors, i.e., specific CAPEX costs decrease with increasing plant size. TEA has great importance in the investment decision making as it identifies the possible financial return to be generated by a product and arouses investor interest in the industrial project. Such tool can also be used to quantify the influence of process parameters on the economic feasibility of the process, identifying the best routes for obtaining a certain product, and to define minimum performances for various operating metrics (CHANG *et al.*, 2018). TEA is one of the different levels of cost estimation depending on the maturity (percent complete by definition) of an industrial project (Table 5). The main TEA uses include comparing different process layouts, assessing the effects of local variables on the global process responses (sensitivity analyses) and assessing the effect of process optimization on the plant feasibility (FURLAN *et al.*, 2016).

3.4.2.1 CAPEX, OPEX and Cash Flow Analysis

A typical TEA considers two main classes of costs for a project analysis: CAPEX (Capital Expenditure) and OPEX (Operational Expenditure). CAPEX is defined as the investment in capital goods, i.e., the amount of resources invested in the acquisition or improvement of assets aiming the adequate operation of the enterprise. OPEX, in its turn, is the set of expenses with operational resources, i.e., the resources spent for the proper operation of business activities (PETERS and TIMMERHAUS, 2002; TURTON *et al.*, 2009; TOWLER & SINNOTT, 2009; ZETTERHOLM *et al.*, 2020).

Table 5 - Classification of industrial cost estimate types.

TEA Class	Maturity level of the project	Final use	Methodology	Accuracy (min / max deviation)
Class 5	0% to 2%	Conceptual selection	Analogies, capacity data, simple models	-20% to -50% +30% to +100%
Class 4	1% to 15%	Feasibility analysis	Equipment data, parametric models	-15% to -30% +20% to +50%
Class 3	10% to 40%	Authorization / control of expenses	Semi-detailed units, detailed items per set	-10% to -20% +10% to +30%
Class 2	30% to 75%	Control / bidding	Detailed units, user-defined details	-5% to -15% +5% to +20%
Class 1	65% to 100%	Bidding checking	Very detailed units, measured and checked details	-3% to -10% +3% to +15%

Source: adapted from *AACE*, International Recommended Practice No. 18R-97, 2011.

There are several metrics to assess the potential return of an industrial project. Some of the most used are the Net Present Value (NPV), the Internal Rate of Return (IRR) and the Time of Return for the Investment (TR). The Minimum Acceptable Rate of Return (MARR) is a set value that represents the minimum return that the investor expects to obtain by year if adopting the investment option. MARR is usually based in the investment returns paid by the high security, fixed income investments, such as federal treasury bonds. NPV is obtained after bringing to zero date all the cashflows of an investment project and adding them to the value spent in the initial investment, using MARR as the discount rate. IRR, in turn, measures the profitability for which the capital is being remunerated in a given period of time, and represents the discount rate that equals the total cash inflows and outflows while considering the value of money in time. Thus, to determine the economic feasibility of an investment in a given market environment, the IRR must exceed or be equal to the MARR (Figure 24). Another important project economic indicator is the Time of Return for the Investment (TR), that indicates the time for the accumulated profits (corrected over time) pay the plant, i.e., equal the initial investment for the implementation of the industrial unit (PETERS and TIMMERHAUS, 2002; TURTON *et al.*, 2009; TOWLER & SINNOTT, 2009).

NPV and IRR are well-established, very useful metrics for the Cash Flow Analysis (CFA) of projects - one example is in the assessment of the economic feasibility of E2G biorefineries. However, when the final product(s) of the evaluated project is (are)

innovative one(s), in an incipient market, and not yet having consolidated market value(s) (as in the case of CNMs production in this work), an additional metric for comparing the economic feasibility can be utilized: The Minimum Selling Price of the main Product (MPSP) (DE ASSIS *et al.*, 2017; BONDANCIA *et al.*, 2020; Liu *et al.*, 2021; BLAIR & MABEE, 2021). MPSP indicates the lowest selling value of a product that still allows the enterprise to present net profitability above zero in a time horizon. The numerical value of MPSP is that which equals the IRR to the MARR and, therefore, generates a zero-value NPV for the investment. Selling prices lower than MPSP result in lower returns than MARR, although do not necessarily implying that the investment leads to financial losses.

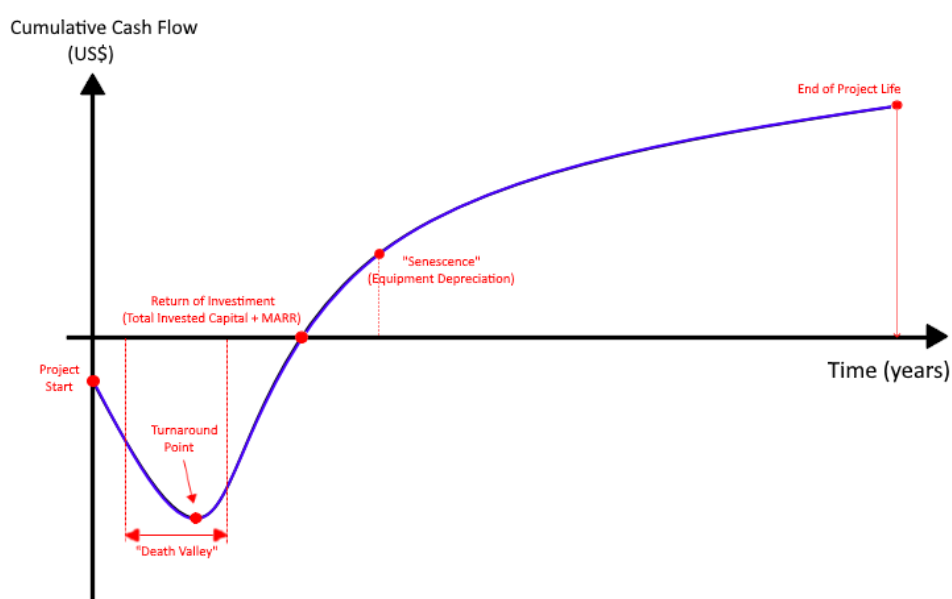


Figure 24 – Time-cumulative Cash Flow Analysis for a typical industrial enterprise (Source: adapted from TURTON *et al.*, 2009).

Although TEA of processes has great importance, its isolated approach should no longer be used as the only indicator of product viability and to assess different process designs. Growing attention in support of the global sustainable development agenda and a viable bioeconomy became environmental analysis of processes increasingly important in the development of biochemicals. It is expected that, in the near future, the results of TEA and LCA may be combined to assess the environmental and economic sustainability of the processes simultaneously (ÖGMUNDARSON *et al.*, 2020).

3.4.3 Analysis of Environmental Impacts of Processes

Growing environmental concerns on a global scale make the development of environmentally sustainable processes a priority. At the *21st Conference of the Parties of the United Nations Framework Convention on Climate Change* in 2015, a new agreement was proposed to strengthen the fight against climate change, the *Paris Agreement*. This aims to limit the increase in the global average temperature to 2 °C by 2100, but with a greater effort for the world temperature to rise by only 1.5 °C in this period. If no action was taken, the forecast is that by 2100 the world average temperature will rise around 4.5 °C (UNITED NATIONS DEVELOPMENT PROGRAMME, 2021).

Producing biochemicals from renewable resources is a key driver for moving towards a sustainable society where energetic efficiency and the use of agricultural residues are performance indicators (ÖGMUNDARSON *et al.*, 2020b). The new production technologies must be evaluated in the early stages of their development regarding to the consumption of chemicals, energy and water (LEÃO *et al.*, 2017).

3.4.3.1 Life Cycle Assessment (LCA)

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 (ÖGMUNDARSON *et al.*, 2020a; ÖGMUNDARSON *et al.*, 2020b; FOROUGHİ *et al.*, 2021). A complete cycle analysis starts from the extraction of the material and goes through production, use, possibilities for recycling and reusing, and final disposal phases, when there is return to the environment. 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 (IBICT, 2014).

ISO 14040:2006 and ISO 14044:2006 established a methodological framework for conducting LCA studies. LCA is a method structured and standardized by international guidelines, consisting of four different phases that are normally interdependent (Figure 25): (1) definition of objective and scope, including the boundaries of the decision system and the functional unit; (2) inventory analysis, with

input and output data collection; (3) evaluation of impacts – in this phase, information about emissions and inventory analysis results are translated into indicators that reflect potential impacts for a product system throughout its life cycle; and (4) interpretation of results, where the values obtained are summarized and discussed as a basis for conclusions, recommendations and decision making in accordance with the goal and scope definition (ISO 14040:2006; ISO 14044:2006).

With the implementation of the carbon credits market, the quantification of the Global Warming Potential (GWP) and of other metrics of environmental impacts have now also a strong impact on investment decision-making, once high environmental impact production methodologies will be neglected due to environmental and economic aspects as well (ÖGMUNDARSON *et al.*, 2020a). On the basis of data analysis, meaningful insights and decisions can be made to minimize the environment impact of products and processes (LI *et al.*, 2013).

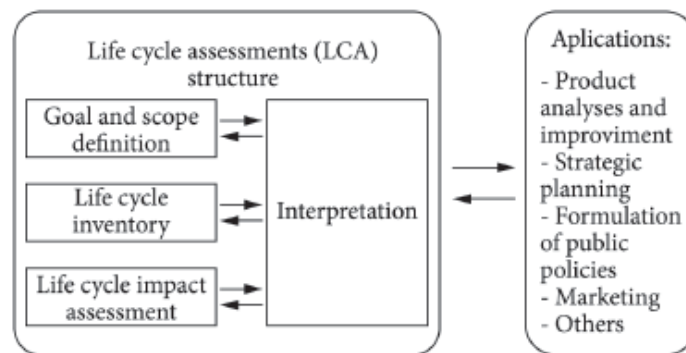


Figure 25 – LCA stages according to ISO 14040:2006 (Source: ISO 14040:2006).

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 (ARVIDSSON *et al.*, 2015; PICCINNO *et al.*, 2018). Due to some challenges such as data unavailability and limitations related to the end-of-life applicability and the solvent recycle treatments in lab-scale processes, there are only a few LCA studies related to nanocellulose products (LI *et al.*, 2013; ARVIDSSON *et al.*, 2015; HERVY *et al.*, 2015; NASCIMENTO *et al.*, 2016; YANG *et al.*, 2018; TURK *et al.*, 2020; BERGLUND *et al.*, 2020; FOROUGH *ET AL.*, 2021).

Some environmental impact categories in that each nanocellulose production route can be investigated are Global Warming Potential (GWP, in kg of CO₂ equivalents), fossil fuel depletion (in kg of oil equivalents); ozone depletion (in kg of CFC-11

equivalents), terrestrial acidification (in kg of SO₂ equivalents), eutrophication (in kg of phosphorus equivalents for freshwater, or kg nitrogen equivalents for marine), and human toxicity (in kg of 1,4-dichlorobenzene equivalents) (Figure 26). The purpose of using LCA in this work was to identify environmental hotspots that can direct to process design changes, thus leading to reductions in the environmental footprint of nanocellulose production in sugarcane biorefineries.

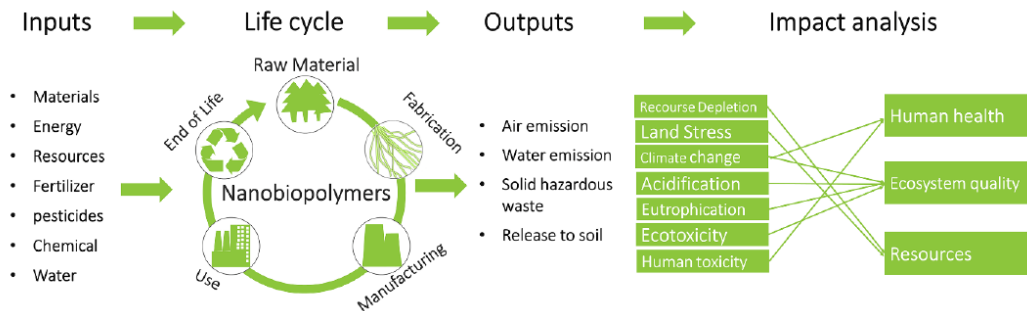


Figure 26 – A typical LCA roadmap for nanobiopolymers (Source: YANG *et al.*, 2018).

4.1 Technical Feasibility of CNMs from sugarcane bagasse

Previous works in literature evidenced the technical feasibility of obtaining cellulose nanomaterials (including CNCs, CNFs and LCNCs) from sugarcane bagasse and sugarcane straw, and by using different methodologies.

OLIVEIRA *et al.* (2016) successfully produced cellulose nanocrystals from different cell types (fibers and pith) of bleached / unbleached sugarcane bagasse pulps by conventional H₂SO₄ hydrolysis. The nanocrystals obtained from sugarcane bagasse fibers exhibited higher lengths and crystallinity indices, while the bleaching process increased sample whiteness and decreased nanocrystal lengths.

The technical feasibility of producing CNCs as a co-product in the process of E2G production using sugarcane bagasse was demonstrated in the work of CAMARGO *et al.* (2016). The authors determined that, after the E2G enzymatic hydrolysis, significant amounts of recalcitrant crystalline cellulose remained in solid phase (~54%). After alkaline purification and acid hydrolysis, the residual bagasse resulted in nanocrystals that were stable at temperatures close to 200 °C, with adequate morphology, dimensions (lengths of 193–246 nm and diameters of 14–18 nm), crystallinity levels (~ 80%) and physicochemical characteristics. The type of pretreatment (steam explosion or hydrothermal) and the enzymatic load in the hydrolysis step did not result in statistically significant effects to change the characteristics of the obtained nanocrystals. The use of the residual fraction of bagasse showed promising results for adding value to the sugarcane industry.

FERREIRA *et al.* (2018) explored the isolation of CNCs extracted from bleached sugarcane bagasse pulp by acid hydrolysis followed by functionalization with adipic acid. The authors employed organosolv pretreatment followed by H₂O₂ purification. The extracted CNCs exhibited a hydrophilic feature and a good aspect ratio (L/W of 41). Surface modification with adipic acid changed the affinity of the CNCs to a more hydrophobic behavior, which would enable the use of modified nanocrystals in lower hydrophilicity matrices applications.

One investigation of the production of CNMs by enzymatic hydrolysis from both sugarcane bagasse and straw was carried out in the work of DE AGUIAR *et al.* (2020).

The fibers were submitted to a purification process (alkali + sodium chlorite) followed by enzymatic hydrolysis with *Cellic CTec3*[®] enzyme cocktail. The cellulose nanomaterials obtained from both fibers presented a high crystallinity index (approximately 70%) and thermal stability, with degradation onset temperatures higher than 300 °C. The increase of enzymatic hydrolysis time resulted in an increase of the CNCs content and also decreased the average diameter and average length of the CNCs.

PEREIRA & ARANTES (2020) evaluated the viability of integrating CNCs production via high solid loading enzymatic hydrolysis into the biochemical platform process for the production of sugars from sugarcane bagasse. The resulting hydrolysate had high sugar concentration (> 120 g/L glucose) and the CNCs, with average diameter of 20 nm, showed higher thermal stability, higher crystallinity index, and higher particle diameter uniformity than CNCs alternatively prepared from bleached eucalyptus Kraft pulp. The costly ultrasonic dispersion treatment step was not necessary in the nanoparticles obtaining.

The production of nanomaterials with lignin contents from sugarcane bagasse has also been highlighted in the literature recently. BILATTO *et al.* (2020) investigated the production of lignocellulose nanocrystals (LCNCs) using sugarcane straw as feedstock. Organosolv pretreatment process was first applied to the straw for partial removal of lignin and hemicellulose contents (reductions of 72.2 and 62.1 %, respectively) and to increase the surface area. The following acid hydrolysis resulted in high yields of LCNCs (40 to 64 %). The LCNCs crystallinity increased from 65 to 80 %, with an estimated average elementary crystallite size of 3.3 nm, and aspect ratios ranging from 18.0–30.1. The thermal stability of the LCNCs was also high, with onset of thermal degradation occurring between 145 and 191 °C.

One of the works that underline the production of CNMs from sugarcane bagasse with hydrolysis by organic acid was the one of JI *et al.* (2019). In this work, citric acid hydrolysis was used to prepare cellulose nanocrystals (CNCs) and cellulose nanofibrils (CNFs) from bleached bagasse pulp. CNCs were successfully produced with diameters between 20–30 nm and lengths between 250–450 nm, while CNFs presented diameters between 30–60 nm and lengths between 500–1000 nm. At least one carboxylic group of the citric acid was simultaneously introduced to the cellulose via esterification during acid hydrolysis to form carboxylic CNCs and CNFs, which is an important feature for further functionalization. CNCs and CNFs also presented highly stable dispersibility.

The work developed by FENG *et al.* (2018) compared pretreatments in the obtaining of cellulose nanofibrils from sugarcane bagasse by mechanical nanofibrillation. Pretreatment types included continuous steam explosion, dilute alkali-catalyzed hydrothermal treatment, and bleaching with hydrogen peroxide. The results shown that continuous steam explosion pretreatment could strip the primary wall, loosen the structure of fiber cell wall, and promote sequent nanofibrillation of the cellulose fibers. Dilute NaOH solution removed hemicellulose, and destroyed the structure of lignin in the fibers, by removing of a large fraction of the fiber binding materials. A high-purity cellulose fraction was also obtained after bleaching with H₂O₂, as this method helped to remove remaining lignin and expose the uniform microfibrils in the secondary wall. The final CNFs had a diameter of about 20–40 nm and a presented a high L/W ratio.

Another work that explored the *biorefinery* concept in the CNMs production was the one of MARCONDES *et al.* (2020). The authors investigated a two-stage hydrothermal treatment of sugarcane bagasse for the co-production of xylooligosaccharides and CNFs by defibrillation with disc ultra-refining. The cellulosic fraction was delignified and bleached to obtain a cellulose-rich pulp. Except for viscosity, the sugarcane CNFs showed properties (i.e., thermal stability, crystallinity and diameter sizes) comparable or superior to the CNFs prepared from commercial bleached eucalyptus Kraft pulp. In addition, lignin was also recovered as a co-product.

Table 6 summarizes some other literature works in which the production of cellulose nanomaterials from sugarcane bagasse residues was explored. The methodologies of production and the main results obtained are also described.

Table 6 – Some other works that explored the production of CNMs from sugarcane bagasse.

Work	CNMs	Methodologies	Main Results
TEIXEIRA <i>et al.</i> (2011)	CNCs	Alkaline peroxide pretreatment followed by sulfuric acid hydrolysis at 45 °C.	<ul style="list-style-type: none"> - Needle-like structures with average length 255±55 nm and L/W around 64 - More drastic hydrolysis conditions (75 min) resulted in less thermally stable whiskers
MANDAL & CHAKRABARTY (2011)	CNCs	Purification by sodium chlorite (0.7% m/v) followed by sulfuric acid hydrolysis	<ul style="list-style-type: none"> - CNCs were obtained in the form of a stable dispersions - 311 °C was the temperature degradation of the CNCs - More than 90% of the volumetric fraction of particles obtained lied in the nanometric range
KUMAR <i>et al.</i> (2014)	CNCs	Purification by sodium chlorite (0.7% m/v) followed by sulfuric acid hydrolysis	<ul style="list-style-type: none"> - Rod-shaped CNCs with sizes in the range of 250-480 nm (length) and 20-60 nm (diameter) - Elemental analysis showed 0.72 wt% sulfur impurity in CNCs - CNCs with crystallinity index of (72.5%)
LAM <i>et al.</i> (2017)	CNCs	Steam explosion + sodium chlorite bleaching followed by sulfuric acid hydrolysis	<ul style="list-style-type: none"> - Cellulose used in hydrolysis had 92.59 ± 0.12 whiteness index and 87% α-cellulose content - CNCs with average diameters of 280.1 ± 73.3 nm and L/W of 20–25 - Low concentration of sulfate (0.2%) on surface and no evidence of cytotoxicity was obtained for CNCs
ZHANG <i>et al.</i> (2020)	CNFs	Chemical pretreatment (sodium chlorite + HCl) followed by mechanical treatments	<ul style="list-style-type: none"> - CNFs with average diameter of 23.18 and tensile strength of 153.6 MPa - High-pressure homogenization and ultrasonic treatments increased the aspect ratio and size uniformity of CNFs when compared to grinding
PINTO <i>et al.</i> (2019)	CNCs, CNFs	Organosolv + bleaching followed by TEMPO-mediated oxidation	<ul style="list-style-type: none"> - CNFs with diameters in the 3–5 nm range were obtained - After 30 min of sonication step, some content of CNFs was broken down into CNCs by mechanical action with perpendicular cleavage of the elementary fibers
GOND & GUPTA, 2020	CNFs	Treatment, by sodium bicarbonate (10% m/v, 96h) followed by mechanical grinding	<ul style="list-style-type: none"> - Removal of hemicelluloses and lignin from treated fibers was confirmed by Fourier transform infrared analysis - Antibacterial properties against <i>Escherichia coli</i> (E. coli) and <i>Bacillus</i> bacteria were obtained for the isolated nanofibers

4.2 Economic Analysis of Cellulose Nanomaterials Production

Some authors have already explored the economic analysis of cellulose nanomaterials production from some feedstocks, mainly cellulose pulp. Nevertheless, to the best of our knowledge, the economic analysis of the production of CNMs from sugarcane residues is a topic not yet investigated in the literature.

One of the first works to assess the economic feasibility of producing nanocellulose in a biorefinery concept was proposed by LEISTRITZ *et al.* (2006). The author analyzed the CNCs production from wheat straw as a co-product of an ethanol biorefinery in the US state of North Dakota by *Aspen Plus*[®] modeling. In that study, the economic analysis indicated that the production of nanocellulose would bring a considerable improvement for the economic use of wheat straw, widely available in that location. The production cost of CNCs was determined to be US\$ 1260 per ton (US\$ 1503 per ton in updated values), while the model generated 1050 tons of CNCs per year with a projected selling price of US\$ 1880 per ton (US\$ 2243 per ton in updated values). Capital costs were estimated at US\$ 1.31 million, and total operating costs, excluding by-product credits, were estimated at US\$ 1.19 million per year, while revenue from sales of CNCs were estimated to be US\$ 1.78 million per year (US\$ 1.56, US\$ 1.42 and US\$ 2.12 million in updated values, respectively).

In the work of ASSIS *et al.* (2017) a TEA of the production of cellulose nanocrystals from cellulose pulp was carried out using information from the Pilot Plant of the *USDA Forest Products Laboratory*[®] (USA), literature data and discussions with experts in the field. Greenfield scenarios (starting from empty land) or with co-location to a pulp mill were evaluated with or without H₂SO₄ recovery in the acid hydrolysis stage. The authors found that raw materials represented the largest sources of costs in all scenarios evaluated. The best scenario found involved no recovery of H₂SO₄ in the hydrolysis step and co-location to a pre-installed industry. In this case, the Minimum Product Selling Price (MPSP) was estimated at US\$ 7200 / ton of CNCs with a projected return time of 7.6 years for the investment. Moreover, this scenario presented 95% of probability of the production costs be less than US\$ 5900 / ton of cellulose nanocrystals in a Monte-Carlo uncertainty analysis where capital investment (-20% to 35%) and the costs of sulfuric acid, lime and dissolving pulp were taken as simulation inputs. Yang (2017) also carried out TEA for a process of obtaining CNCs from delignified cellulose

pulp using acid hydrolysis and specified a selling price of € 20,000 / dry ton of CNCs in the Cash Flow Analysis.

A TEA of the production of cellulose nanocrystals (CNCs) and nanofibers (CNFs) using eucalyptus cellulose kraft pulp as feedstock, and citric acid as hydrolyzer, was evaluated in the work of BONDANCIA *et al.* (2020). Six hydrolysis time scenarios (1.5, 3.0, 4.5 and 6.0 hours) were analyzed. The Minimum Attractiveness Rate (MAR) used by the authors on the work was 11% per year. The authors found MPSPs of US\$ 16460 and US\$ 11520 per dry ton of produced CNCs and CNFs, respectively. Parametric sensitivity analysis determined that the cost of citric acid was the main influence on the MPSP values. Authors also determined MPSP of US\$ 12540 per dry ton of CNCs for a process using the same feedstock but with hydrolysis by sulfuric acid. In this latter case, the price of cellulose kraft pulp and the costs of acid recovery stage in multi-effect evaporators were the factors with the highest impact on total operating costs.

BLAIR & MABEE (2021) carried out an initial techno-economic assessment for an integrated process to produce sugar, lignosulfonate, and nanocellulose from softwood chips by *American Value-Added Pulping* (AVAP) method, which starts with SO₂-ethanol-water pulping and uses mechanical treatment followed by enzymatic hydrolysis to produce nanocelluloses (CNCs and CNFs) along with sugars. Calculated net manufacturing costs (total manufacturing cost minus co-product credits) was US\$ 999 per ton of produced CNCs, while the estimated MPSP of nanocellulose (US\$ 1656 per ton) was found to be considerably lower than for more conventional nanocellulose-producing methods that use Kraft or dissolving pulp as a starting point. Utility costs were equivalent to ~25% of the total operating costs, while capital cost was US\$ 318.7 million for 150,000 tons of dry woodchips processed by year. The CNCs / CNFs recovery processes heavily influenced the capital costs of production. In a $\pm 30\%$ sensitivity analysis, capital investment costs, sugar sales price, steam production costs and raw material costs were the most influential on the MPSP of CNCs.

Recently, ROSALES-CALDERON *et al.* (2021) evaluated the techno-economic viability of using sulfuric acid and enzymatic hydrolysis technologies to produce CNCs from bleached eucalyptus Kraft pulp in stand-alone facilities, using scale up process models of the production of CNCs modeled by *Aspen Plus*[®]. The estimated MPSP for the CNCs production using sulfuric acid was US\$ 10031 / dry ton, with manufacturing expenses of US\$ 7779 / dry ton of CNCs. The production of CNCs via enzymatic

hydrolysis required a lower capital investment than the sulfuric acid hydrolysis one, but due to low reaction yield (6%), the MPSP obtained for this methodology was US\$ 65740 / dry ton of CNCs. According to the authors, this last MPSP price was too high to be commercially attractive.

4.3 Life Cycle Analysis of Cellulose Nanomaterials Production

Due to growing concerns about the global warming and other environmental indicators, LCA studies have been published in the literature for the various production processes and in different areas of research. For example, some literature works analyzed the environmental impacts by LCA of the CNMs production from different feedstocks and by using different processing methodologies.

HOHENTHAL *et al.* (2012) evaluated the environmental impacts of CNF for the first time, as described by FOROUGH *et al.* (2021). The authors performed cradle-to-gate LCA for the production of CNFs from sulfite pulp in a pilot plant. Compared methodologies involved enzymatic pre-treatments, *TEMPO* oxidation and high-pressure homogenization. LCA was performed using the *ReCiPe*[®] method and included GWP, eutrophication, terrestrial acidification, water depletion, and fossil fuel depletion. Values for GWP between 0.75 and 3.1 kg of CO₂ equiv. / kg of CNC produced were found for the different methodologies analyzed. The authors determined that the enzymatic pretreatment had the highest yield in CNFs obtaining. The production process by *TEMPO* oxidation, in turn, presented lower energy consumption, although it also presented low production yield. Another conclusion found was the significant difference in wastewater production between the analyzed processes.

A cradle-to-gate environmental impacts study of three production routes for cellulose nanofibrils (CNFs) was carried out by ARVIDSSON *et al.* (2015). The authors used wood pulp as feedstock, and three production routes investigated were: enzymatic pretreatment, carboxymethylation pretreatment and no previous pretreatment. The results obtained showed that processes without pre-treatment and using enzymatic treatment had relatively low environmental impact in terms of GWP (0.79 and 1.2 kg of CO₂ equiv. / kg of CNFs produced, respectively), while CNFs produced via the carboxymethylation route clearly had the highest environmental impacts due to the large use of fossil-based solvents.

NASCIMENTO *et al.* (2016) evaluated the LCA of the CNCs production from coconut fibers by extraction with high powered ultrasound, while using the residual lignin as power source for energy cogeneration to the process. The authors quantified the GWP of the process as 0.207 g of CO₂ equiv. / g of CNC produced, and pointed that power consumption and acetic acid production were the critical process production points for the LCA, indicating the substitution of the acetic acid for ethanol/water solutions on pulping process.

One study that has assessed the environmental analysis of the production of CNMs from sugarcane bagasse is that of LEÃO *et al.* (2017). The authors evaluated the technical and environmental feasibility for the production of cellulose nanocrystals from sugarcane bagasse. Life Cycle Assessment was performed considering a gate-to-gate process (the system boundaries of the LCA end at the manufacture gate) involving from the sugarcane cultivation and harvesting until the stages of pre-treatment, bleaching and hydrolysis of nanocrystals in twelve different assessment scenarios. The authors concluded that the pretreatment stage had the most significant contribution to the generation of environmental impacts, also verifying that improvements are needed in areas as water consumption, process time and use of solvents in this stage. Among all the evaluated scenarios, (pre-treatment and bleaching 1x with NaClO₂ / NaOH, hydrolysis with H₂SO₄ for 30 min) and (pre-treatment and bleaching 1x with NaClO₂ / NaOH / HNO₃, hydrolysis with H₂SO₄ for 30 min) were detected in the LCA as the most environmentally suitable methodologies for the preparation of CNCs from sugarcane bagasse.

PICCINNO *et al.* (2018) evaluated the production of microfibrillated cellulose from carrot waste, with special emphasis on the consequences of increasing the process scale, from the laboratory for the industrial one. The authors developed a five-step procedure scale-up framework for chemical processes, which was later applied for a MFC production pathway by enzymatic depolymerization followed by homogenization. A scaled-up LCA study was also performed. The authors showed that, while in the lab scale, the enzymatic treatment step was the dominant LCA impact contributor, this step proved to be negligible in terms of environmental impact at the industrial-scale production, given that a more efficient and well-insulated reactor was used. A 6.5-fold reduction in the impact of the industrial scale process (compared to the impact of the lab one) indicated great inefficiencies during laboratory-scale production. The solvents used, energy sources

and electricity consumption were, according to the authors, the variables with the greatest impact on the LCA results.

Some other studies that evaluated the environmental impacts of several nanocellulose production technologies are LI *et al.* (2013) (a cradle-to-gate LCA analysis for lab-scale MFC fabrication from wood pulp, with four fabrication routes composed of two interchangeable chemical and mechanical processes), PICCINNO *et al.* (2015) (a LCA comparison of CNFs production from vegetable food waste by various routes involving enzymatic hydrolysis), and TURK *et al.* (2020) (a LCA of CNFs production from wood pulp using the combined thermogroundwood method - the results showed that the purification process contributed with more than 95% of the environmental impacts).

It is highlighted once again that, to the best of our knowledge, the technical, economic, and environmental analysis of the production of CNMs from sugarcane biorefinery residues, as an integrated approach, is a topic not yet investigated in literature. Previous works, such as those by CAMARGO *et al.* (2016) and LEÃO *et al.* (2017) performed specific analyzes types (technical and environmental, respectively). Therefore, this study aimed to fill this gap, in order to direct R&D efforts in the area and guide investment alternatives for the nanocellulose production sector from biorefinery wastes.

CHAPTER 5 – METHODOLOGY

This work considered the modeling of different scenarios for cellulose nanomaterials (CNMs) industrial production (hereinafter named Case Studies), using data obtained in literature and laboratory data obtained by partner researcher (Dr. Thalita Jessika Bondancia). Eight production methodologies for CNMs from sugarcane bagasse were analyzed in technical, economic and environmental aspects. In all Case Studies analyzed, the evaluated production unit was always attached to a sugarcane biorefinery with fully functional production of E1G and E2G already implemented, and located in the central-south region of Brazil. Therefore, one considered that there is availability of feedstock for the CNMs hydrolysis, which consists of raw sugarcane bagasse (hereinafter referred as *raw bagasse*) or its solid derivative of the enzymatic hydrolysis from E2G process (hereinafter referred as *E2G bagasse* – CAMARGO *et al.*, 2016).

The different Case Studies compared different methodologies for obtaining cellulose nanocrystals (CNCs), lignin-containing cellulose nanocrystals (LCNCs), or cellulose nanofibers (CNFs) in a sugarcane biorefinery. The backbone of the CNMs Case Studies involved chemical routes for upstream (pretreatment by hydrothermal and organosolv methods); presence or absence of biomass H_2O_2 purification process (removing or not the residual lignin); production through mineral (sulfuric) acid and/or organic (citric) acids in hydrolysis, evaluation by enzymatic hydrolysis route was also carried out; downstream with or without acid recovery step; purification of the obtained nanocellulose; and presence or absence of drying of CNCs and CNFs (generating products as dry materials or liquid suspensions, respectively). 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. Usage cycle times were increased by 15% to account for eventual loading, unloading and washing times.

5.1 The Virtual Sugarcane Biorefinery

The research group of the *Laboratory of Development and Automation of Bioprocesses (LaDABio)* developed in the *EMSO*[®] simulator several mathematical models that integrate a Virtual Biorefinery of production of E1G, E2G and cogeneration

energy from sugarcane. Many of these models are based on typical relationships of process found in real sugarcane biorefineries of Brazil (FURLAN *et al.*, 2016). The Virtual Biorefinery simulates an autonomous ethanol refinery with medium-large production scale, when compared to the sugarcane plants currently installed in the country (NOVACANA, 2021). The association between the mathematical models generates a complex problem involving non-linear equations that are simultaneously solved by EMSO[®]. In the typical production scenario, the Virtual Biorefinery simulates interconnected E1G and E2G processes, with the production of 85 m³ / h of anhydrous ethanol (or 89 m³ / h of hydrated ethanol) from 833.33 ton / h of sugarcane, also generating 804 m³ / h of residual vinasse. The process steps simulated in the production unit (sugarcane milling, treatment, evaporation, fermentation, distillation, E2G pretreatment, E2G hydrolysis, and xylose liquor fermentation) consume 697 ton / h of self-sufficient steam. The heat and power generation (in boiler and turbines) produces 92 MWh of electricity for export to the grid. At the output filter after the enzymatic hydrolysis of E2G, 37.6 ton/h of solid from non-hydrolyzed sugarcane bagasse (*E2G bagasse*) is generated. The block diagram in Figure 23 illustrates the operating scheme of the E1G and E2G processes in the base case of Virtual Sugarcane Biorefinery.

In this work, two residues were considered as potential feedstocks in the modeling of CNMs production. In Case Studies C1 and C8 it was used the sugarcane bagasse generated after the milling stage of E1G production (*raw bagasse*). This residue is originally destined for burning in boilers for the generation of energy and steam (FURLAN, 2012). On the other hand, in Case Studies C2 to C7 the *raw bagasse* underwent hydrothermal pretreatment and enzymatic hydrolysis to generate pentose and hexose sugars that are exported to the biorefinery. In these methodologies, the production of CNMs was carried out through a second hydrolysis process, using the solid portion of the sugarcane bagasse that exits from enzymatic hydrolysis of the E2G process (*E2G bagasse*). The approximate compositions of *raw bagasse* and *E2G bagasse* were obtained from the Virtual Biorefinery and are detailed in Table 7. These specifications are in accordance with data also found in previous experimental studies (CAMARGO *et al.*, 2016; OLIVEIRA *et al.*, 2016). The Virtual Biorefinery *E2G bagasse* mass composition is also in accordance with the lab results for hydrothermal pretreatment and enzymatic hydrolysis yields that were used in this work.

Table 7 - Mass compositions % (on a dry basis) of raw bagasse and E2G bagasse that were used as feedstocks in the Case Studies of this work.

	<i>Raw Bagasse</i>	<i>E2G Bagasse</i>
Main Components	Mass %	Mass %
Cellulose	45.68	36.24
Hemicellulose	26.91	15.50
Lignin	24.40	46.04
Impurities	3.01	2.21
Solids fraction at input stream	50.0	49.15

Source: Raw bagasse: data from the Virtual Sugarcane Biorefinery; E2G bagasse: laboratory tests of Thalita J. Bondancia.

5.2 The Case Studies

Industrial processes are almost always more efficient than laboratory-scale processes, once they generally operate with optimized process inputs and conditions. The scale-up tends to proportionally decrease implantation and production costs per feedstock unit, while higher-scale processes also make economically feasible the recovery of by-products that can represent additional market potential (TURTON *et al.*, 2009). As an example, *CelluForce*[®] nanocellulose production process recycles the sulfuric acid and separates hydrolyzed carbohydrates for fermentation and biofuel production. It can be said that embracing the biorefinery concept is an obvious next step for nanocellulose producers (VANDERFLEET AND CRANSTON, 2021).

Several sources of literature data, external sources and laboratory data were used as input parameters of the Case Studies analyzed in this work. These references will be cited throughout the text. Mass and energy balances were performed on Microsoft Excel[®] electronic spreadsheets, for which *LaDaBio* has a valid license use. In the energy balances, the thermodynamic calculations for the equipment were performed using the *Aspen Plus*[®] software (*LaDaBio* also has a valid license use for this 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. The vapor phases were considered ideal due to the low pressure in the processes. Thermodynamic data related to sugarcane biomasses that was absent in the *Aspen Plus*[®] were inserted into this simulator using values obtained in DOMALSKI *et al.* (1986).

The annual sugarcane bagasse utilization as feedstock was set at 72000 tons / year for the all the analyzed Case Studies. Thus, the sugarcane bagasse mass flow that directs to the production of nanocellulose (and so is not burned in boiler for the production of

steam and energy for the biorefinery plant) represents approximately 5% of the total bagasse flow produced in the *Virtual Sugarcane Biorefinery*.

Table 8 presents a comparison between the Case Studies proposed in this work. The following processes of biomass pretreatment and hydrolysis were selected for the Case Studies modeling:

- The organosolv pretreatment process with ethanol was selected over other treatment options (Table 4) because it provides high rates of removal of lignins and residual hemicelluloses, whilst being environmentally less aggressive than the chemical processes (NASCIMENTO *et al.*, 2016; LEÃO *et al.*, 2017). It also uses ethanol, an easily recyclable solvent that is already available on large scale as a product in sugarcane biorefineries. This last implies in a “domestic” cost of this solvent for the pretreatment step;
- Complementary alkaline delignification was selected for its high effectiveness in removing residual lignin content, generating biomasses with high-purity cellulose contents (HIGA *et al.*, 2012);
- The acid hydrolysis by concentrated H₂SO₄ was chosen because it is the state-of-art hydrolysis process in the CNMs production (VANDERFLEET & CRANSTON, 2021). It provides high process yields in mild conditions and allows the recovery of the acid by multistage evaporation;
- Concentrated citric acid hydrolysis (with or without H₂SO₄ complementary addition) was selected as the production method using organic acid. Compared to the CNCs produced by sulfuric acid hydrolysis, CNMs obtained through citric acid present suitable physicochemical characteristics that differentiate their later applicability (BONDANCIA *et al.*, 2020);
- Since E2G biorefineries use enzymatic cocktails for biomass hydrolysis and generation of fermentable sugars (FURLAN *et al.*, 2016; LONGATI *et al.*, 2018; ELIAS *et al.*, 2019), the production process of CNMs by enzymatic hydrolysis was also evaluated in this work;
- Spray-drying has been selected as a scalable, continuous process to dry CNMs suspensions, once it is the standard industrial dehydration method (NG *et al.*, 2015; MALUCELLI *et al.*, 2017).

Each of the methodologies and the main input parameters for each Case Study analyzed in this work will be described in the following pages.

Table 8 - Comparison between the main process characteristics of each Case Study analyzed in this work.
 LCNCs refers to cellulose nanocrystals with lignin content in the composition.

Process Features	Case Study							
	C1	C2	C3	C4	C5	C6	C7	C8
CNMs Production Feedstock	Raw Bagasse	E2G Bagasse						Raw Bagasse
Hydrothermal Pret. and Enzymatic Hydrolysis for E2G		✓	✓	✓	✓	✓	✓	
Ethanol Organosolv Delignification & Recovery	✓	✓	✓	✓	✓	✓	✓	✓
Lignin Precipitation & Recovery for Selling	✓	✓	✓	✓	✓	✓	✓	✓
H ₂ O ₂ Complementary Delignification	✓	✓		✓	✓	✓	✓	✓
Concentrated H ₂ SO ₄ Hydrolysis	✓	✓	✓	✓	✓			
CNMs Concentrated Citric Acid Hydrolysis						✓		
CNMs Conc. Citric + Sulfuric Acid (9:1 v/v) Hydrolysis							✓	
Enzymatic Hydrolysis								✓
Acid Recovery	✓	✓	✓		✓	✓	✓	
Neutralization and Dialysis	✓	✓	✓	✓	✓	✓	✓	✓
Spray-Drying	✓	✓	✓	✓		✓	✓	✓
CNMs Product Types	CNCs ~95% purity (dry)	CNCs ~95% purity (dry)	LCNCs ~82% purity (dry)	CNCs ~95% purity (dry)	CNCs ~8% purity (in water)	CNCs ~95% purity (dry) + CNFs ~95% purity (dry)	CNCs ~95% purity (dry) + CNFs ~95% purity (dry)	CNCs ~95% purity (dry) + CNFs ~95% purity (dry)

5.2.1 Case Study C1

The first methodology for the production of CNMs, in this case cellulose nanocrystals (CNCs) from the *raw bagasse*, is detailed in Table 9 and in the Figure A1 of the annexes. This methodology consists in an adaptation of the process route used in the work of Assis *et al.* (2017) for CNCs production from dissolving pulp that was based on the *USDA Forest Products Laboratory Pilot Plant* (Madison, WI, USA). Sugarcane bagasse initially undergoes organosolv pretreatment with ethanol solution to remove hemicellulose and lignin contents. Part of the input cellulose (mostly in amorphous phase) hydrolyses and also incorporates into the liquid phase of the process. The ethanol solution comes from the recycle streams generated by the recovery processes (flash and distillation), however it is necessary to make up contents of solvent and water in the process.

After the organosolv pretreatment there is a filtration step of the solid phase generated on delignification (enriched in cellulose) and stream forwarding to the complementary delignification with H_2O_2 . The liquid phase resulting from this filtration proceeds to adiabatic flashing at ambient pressure (BOTELLO *et al.*, 2006) in order to recover partially the ethanol content for recycle and reuse in a subsequent cycle process. The bottom stream of the flashing is then acidified by H_2SO_4 in order to precipitate the lignin removed in the organosolv pretreatment. The fraction of precipitated and filtered lignin has some impurities resulted from pretreatment and needs to be washed extensively with water to be purified. After filtering, the purified lignin is dried at room temperature and can be sold as a by-product of the process. On the other hand, the fluid stream that passes through the precipitated lignin filter is neutralized with lime to prevent H_2SO_4 contents from saturating the ethanol recovery process. Thereby, there is a small precipitation of $CaSO_4$ (gypsum) which is filtered. The fluid stream goes to a distillation column to recover ethanol that is recycled back to the organosolv treatment at a high recovery rate. The bottom stream of the distillation tower consists of residual water, lignins and hemicelluloses, hydrolyzed sugars, impurities, dissolved salts and a small fraction of unrecovered ethanol, and it is sent to wastewater treatment.

The solid phase filtered after the organosolv treatment proceeds to a complementary alkaline delignification with hydrogen peroxide (H_2O_2) and sodium hydroxide (NaOH). This is a more aggressive treatment of the cellulosic fraction that aims to remove the lignin, hemicellulose and impurities contents still present in the solid.

Although H₂O₂ purification is very effective (KARP *et al.*, 2013), its uses chemicals of higher costs than the organosolv solvent that can also generate potential impacts to the environment. Thus, one opted to use this bleaching treatment only as a complementary step for the organosolv delignification of the lignocellulosic matrix. The liquid phase originated in the alkaline delignification is sent to wastewater treatment, once chemicals are in low mass concentrations in the stream and recovery processes would not be as effective for H₂O₂. The solid phase resulting from the delignification process is filtered and consists a white matrix with high purity in cellulose that, however, does not yet have nanometric characteristics. For the generation of cellulose nanocrystals (CNCs), acid hydrolysis is carried out with a concentrated solution of sulfuric acid (H₂SO₄) recycled from the evaporator recovery process. An H₂SO₄ make-up input is also necessary to compensate losses in the acid recycling. The acid hydrolysis of cellulose generates CNCs, but there is also significant generation of sugars such as glucose in the process. The partial concentration of the obtained nanocrystals is done with the use of multistage decanters, i.e., a series of three tanks interspersed with three 6500 rpm centrifuges used to wash and separate CNCs from H₂SO₄ and sugars (as proposed in the work of Assis *et al.*, 2017). This concentration step generates an aqueous phase rich in CNCs and another phase rich in sugars and recoverable H₂SO₄. While the nanocrystal-rich phase proceeds to neutralization of the residual sulfuric acid (preventing H₂SO₄ contents from reaching the dialysis equipment), the acidic phase is forwarded to recovery and recycling.

After being neutralized with NaOH (generating Na₂SO₄, a salt easily removable in the dialysis), the CNCs-rich stream undergoes an exhaustive dialysis process to remove dissolved salts, hydrolyzed sugars and impurities that can still be present. This process makes it possible to obtain CNCs as a water suspension of high purity solids, practically free of contaminants, at the cost of an extensive use of water. In order to achieve dry mass nanocrystals a spray-drying process is carried out after dialysis. This results in dry CNCs with a high degree of purity (minimum 95% by mass) which are the main product of the process. The spray-dryer equipment uses hot air to remove water by vaporization. This hot air is generated by a heating system that accompanies the equipment unit and where a second stream of sugarcane bagasse is used as fuel for energy generation.

The acid stream that is obtained in the multi-stage decanters stage also contains sugars originated from hydrolysis, non-hydrolyzed cellulose fractions and other impurities. An organics retention membrane is used to prevent these components from

returning to the hydrolysis reactor in the recycle stream. This membrane is capable of removing considerable amounts of the carbohydrate contents in the retentate (DE ASSIS *et al.*, 2017). The membrane permeate stream is forwarded to a system of evaporators operating in three stages, two of which operate at vacuum pressure (1 atm, 300 mbar and 100 mbar). This recovery system is capable to reconcentrate the H₂SO₄ solution to the initial concentration used in the hydrolysis step (SCIENTIA, 2019, VÁRNAI *et al.*, 2020). The top flow stream (rich in water) is condensed and proceeds to effluents treatment for later reuse in process utilities.

The effluents treatment receives streams from different processes (lignin washing, distillation, alkaline delignification, dialysis and H₂SO₄ recovery). Large amounts of water are used in the processes to generate the nanocelulose and by-products, so partial reuse was performed between the dialysis step and the heat exchangers for flashing, distillation, and others. An effluent filtering system recovers part of the water for reuse in the process utilities. The remaining stream consists in chemicals, lignocellulosic materials, sugars and impurities, and it is sent to the biorefinery effluents management station.

Table 9 - Main specification inputs used in the process modeling of Case Study C1.

Process	Description	Inputs	Sources
Organosolv Delignification (ethanol)	Temperature	200 °C	AGNIHOTRI <i>et al.</i>
	Time	1 hour	(2015); LI <i>et al.</i> (2016a);
	Water / ethanol ratio	50% v /v	OLIVEIRA <i>et al.</i> (2016);
	Water + ethanol input	5 x dry mass	FERREIRA <i>et al.</i> (2018)
	Lignin removal	72.8 % by mass	FERREIRA <i>et al.</i> (2018)
	Hemicelulose removal	80.7 % by mass	FERREIRA <i>et al.</i> (2018)
	Cellulose removal	39.5 % by mass	FERREIRA <i>et al.</i> (2018)
Flashing	Heating source	Steam 17 bar	-
	Output pressure	Atmospheric	-
	Thermal load	Adiabatic	-
Lignin Precipitation	H ₂ SO ₄ input	0,1 x prec. lignin mass	ARNI (2018)
	Precipitated lignin fraction	45.5 % by mass	Lab result*
	Washing water	3.5 x prec. lignin mass	Lab result*
Distillation	Minimal ethanol recovery	98 % by mass of ethanol at distillation input	Calculated; WEINWURM (2014)
	Reboiler heat source	Steam 2,5 bar	-
Complementary delignification (alkaline)	Time	1.5 hour	ROCHA <i>et al.</i> (2012)
	Water input	2 x solid input mass	ROCHA <i>et al.</i> (2012)
	H ₂ O ₂ concentration	2.5 % by mass	ROCHA <i>et al.</i> (2012)
	NaOH concentration	2 % by mass	ROCHA <i>et al.</i> (2012)
	Temperature	55 °C	ROCHA <i>et al.</i> (2012)
	Residual lignin removal	86.2 %	FERREIRA <i>et al.</i> (2018)

Table 9 - Main specification inputs used in the process modeling of Case Study C1 (continuation).

Complementary delignification (alkaline)	Res. hemicel. removal	53.7 %	FERREIRA <i>et al.</i> (2018)
	Cellulose removal	24.8 %	FERREIRA <i>et al.</i> (2018)
Acid Hydrolysis (H₂SO₄)	Time	45 minutes	OLIVEIRA <i>et al.</i> , 2016
	H ₂ SO ₄ concentration	64 % by mass	OLIVEIRA <i>et al.</i> , 2016
	Acid solution input (mass)	4.2 x cellulose mass	ASSIS <i>et al.</i> (2017)
	Temperature	45 °C	OLIVEIRA <i>et al.</i> , 2016
	Yield in CNCs	24 %	OLIVEIRA <i>et al.</i> , 2016
Multistage Decanters	Water input	45 x mass of CNCs	ASSIS <i>et al.</i> (2017)
	CNCs losses	0.5 % of initial mass	ASSIS <i>et al.</i> (2017)
	% water in acid output	85 % by mass	ASSIS <i>et al.</i> (2017)
Dialysis	Water input	100 x mass of CNCs	ASSIS <i>et al.</i> (2017)
	Processing time	72 hours	ASSIS <i>et al.</i> (2017)
	CNCs output conc.	3% by mass	ASSIS <i>et al.</i> (2017)
Spray-Drying	Raw bagasse	9304.9 MJ / ton	Calculated
	Heat of Combustion		
	Drying air temperature	200 °C	ASSIS <i>et al.</i> (2017)
	CNCs output conc.	95 % by mass	Calculated
H₂SO₄ recovery	Sulfuric acid loss	0.4 % by mass	ASSIS <i>et al.</i> (2017)
	Recovered H ₂ SO ₄ conc.	64 % by mass	Arbitrated
Effluents Treatment	Water recovery for use in utilities	42 % by mass	ASSIS <i>et al.</i> (2017)

* Laboratory results were obtained by Thalita J. Bondancia.

5.2.2 Case Study C2

The proposed methodology for Case Study C2 considers the production of CNCs in a similar way to that already detailed for Case Study C1. However, instead of using the *raw bagasse* as the main feedstock, this methodology utilizes the solid portion that is filtered after the enzymatic hydrolysis in the E2G process (i.e., the *E2G bagasse*) whose composition specifications are detailed in Table 7. In this way, Case Study C2 analyses a CNCs production unit attached to a sugarcane biorefinery that already has a pre-established E2G technology by hydrothermal pretreatment and enzymatic hydrolysis. Fermentable sugars process streams (mainly xylose and glucose) were considered as by-products to be sent to fermentation and distillation sectors of the E2G biorefinery for later obtaining cellulosic ethanol and its derivatives.

E2G bagasse has different characteristics from the *raw bagasse*. While the second retains the physical and chemical properties obtained after sugarcane milling in the E1G process, the first also presents characteristics obtained in the processes of hydrothermal pretreatment and enzymatic hydrolysis of the E2G process. *E2G bagasse* has a low

content of hemicelluloses and a higher content of lignins since the hydrothermal pretreatment is highly effective in removing hemicelluloses but slightly effective for delignification. It has also a diminished percentual cellulosic mass content when compared to *raw bagasse*. Nevertheless, this cellulosic fraction presents higher crystallinity levels (more suitable for the production of CNCs) due to the previous enzymatic attack in the E2G process that produces fermentable sugars mainly from degrading the amorphous phase of the original cellulose. Another possible advantage in the use of E2G bagasse is that the recalcitrant lignocellulosic structures of this biomass have already been partially degraded in previous E2G processes. These characteristics make this residue a potential feedstock for the generation of CNCs. Table 10 presents some input data used in the modeling of Case Study C2, while Figure 27 shows a box diagram to represent this methodology. Input data that are not shown in Table 4 follow the same values exposed for Case Study C1 in Table 9.

Table 10 - Main specification inputs used in the modeling of Case Study C2.

Process	Description	Input	Sources
Hydrothermal Pretreatment	Temperature	195 °C	BATISTA <i>et al.</i> (2018)
	Time	10 min	BATISTA <i>et al.</i> (2018)
	Water / bagasse input	3.33 x dry mass	BATISTA <i>et al.</i> (2018)
	Hemicellulose removal	82.1 %	Lab result*
	Lignin removal	22.1 %	Lab result*
	Cellulose removal	19.8 %	Lab result*
	Heating Source	Steam 17 bar	-
Enzymatic Hydrolysis	Temperature	50 °C	DE AGUIAR <i>et al.</i> (2020)
	Time	48 h	DE AGUIAR <i>et al.</i> (2020)
	Enzyme addition	11.4 FPU / g cellulose	LONGATI <i>et al.</i> (2018)
	Enzyme activity	205 FPU / mL	Lab result*
	Cellulose sugars yield	61.7 %	Lab result*
Organosolv Delignification (ethanol)	Lignin removal	70.1% by mass	Lab result*
	Hemicelulose removal	60.0% by mass	Lab result*
	Cellulose hydrolysis	10.9% by mass	Lab result*
Complementary delignification (alkaline)	Time	1.5 hour	ROCHA <i>et al.</i> (2012)
	Residual lignin removal	91.8 %	Lab result*
	Res. hemicel. removal	50.0 %	Lab result*
	Cellulose hydrolysis	17.4 %	Lab result*
Acid Hydrolysis (H₂SO₄)	Yield in CNCs	35.5 %	Lab result*

* Laboratory results were obtained by Thalita J. Bondancia.

5.2.3 Case Study C3

The Case Study C3 is an adaptation for Case Study C2. In this methodology, the process step of complementary delignification in alkaline medium is suppressed (Figure A2 of the annexes). So, the solid fraction obtained in the filtering after organosolv treatment is sent directly to sulfuric acid hydrolysis. This adaptation provides costs savings in chemical inputs that can be potentially aggressive to the environment (H_2O_2 and NaOH) and in equipment costs. However, the presence of considerable lignin fractions in the hydrolyzed biomass decreases the acid hydrolysis yield (TROVAGUNTA *et al.*, 2021). Furthermore, lignin contents not removed by E2G processing and by organosolv delignification may be present in the final product along with the CNMs structures. As an example, ZHANG *et al.* (2019) found Klason lignin contents between 6.24% and 22.81% for the lignin-containing CNFs obtained from sugarcane bagasse. Cellulose nanocrystals that incorporate lignin fractions in the structures are called LCNCs. Some works investigated the specific properties of LCNCs (ROJO *et al.*, 2015; EWULONU *et al.*, 2018; AGARWAL *et al.*, 2018, BILATTO *et al.*, 2020). EWULONU *et al.* (2018) determined that cellulose nanocrystals and nanofibrils enriched with lignin showed higher yields and lower environmental impacts when compared to CNCs and CNFs. The greater hydrophobicity due to the presence of lignin in the nanocrystals is an attractive component for the use of these structures in polymer biocomposite (EWULONU *et al.*, 2018; AGARWAL *et al.*, 2018).

5.2.4 Case Study C4

The Case Study C4 consists in another process adaptation of Case Study C2. As will be detailed in the “Results and Discussion” Section, the acid recovery step (mass concentration) of H_2SO_4 in the multiple effect evaporators presents fairly high capital (equipment) and operational costs (use of steam). In this way, Case Study C4 considered that the steps for recovering sulfuric acid (membrane filtration and evaporation in three stages) were removed from the process (Figure A3 of the annexes). The acidic stream from the multistage decanters is forwarded to neutralization by lime generating extra CaSO_4 precipitation (gypsum) for sale as a by-product of the unit. The acid hydrolysis is fed by 64% H_2SO_4 each cycle, leading to an increase in the necessary flowrate of this input. However, as the Case Study C4 also involves a significant increase in the production of CaSO_4 (sold as by-product) and zero acid recovery costs, the economic

analysis and the environmental assessment were necessary to determine its competitiveness in relation to the methodology proposed in Case Study C2.

5.2.5 Case Study C5

The Case Studies C5 is another modification of the Case Study C2. It considers the absence of the spray-drying step in the production of CNCs (Figure A4 of the annexes). Thus, the main product should be sold in the form of aqueous suspension (as shown in Figure 22a) in concentrations close to 8% that are obtained at the end of the dialysis process. This adaptation takes the capital and operational costs of CNMs drying to zero, but it certainly increases the costs of transportation and handling of the material, once the physical volume occupied by the product increases considerably.

5.2.6 Case Study C6

Case Study C6 used citric acid in the hydrolysis step. As in the Case Study C2, the feedstock processing was directly linked to an E2G biorefinery with sharing of pre-treatment and enzymatic hydrolysis facilities, being a small part of the residual solid from enzymatic hydrolysis sidetracked to the production of nanocellulose. Differently from what occurs in the laboratory scale, industrial processes require the recovery of high flow and relatively high-cost inputs like the hydrolysis citric acid, as the absence in the reuse of this input would make the process non-optimized and thus hindering economic aspects.

Since citric acid is a high molecular weight, high boiling point organic acid (JIANG *et al.*, 2021), the separation of hydrolysis residues by distillation is hampered. The water solubility of this acid is also high in a wide range of temperatures, precluding crystallization recovery processes. So, the recovery of citric acid was carried out in the modeling calculations through the classic process of recovery for this input (MATTEY & KRISTIANSEN, 2002) – it basically includes the addition of CaO for precipitation of citrate salt, separation of unhydrolyzed biomass and residual sugars by filtering, and subsequent regeneration and recycling of the citric acid by the addition of diluted H₂SO₄.

As citric acid is a weak organic acid, in this Case Study there is the simultaneous production of two types of CNMs in hydrolysis: CNCs and CNFs. Such varieties can be separated after dialysis through a mixed cellulose esters membrane filter (BONDANCIA *et al.*, 2020). The production of residual lignin as a by-product also took place in this Case Study. Figure 28 presents a block diagram referring to Case Study C6, while Table 11

presents some input data obtained in laboratory and used in the modeling of this methodology (missing data in Table 11 follows the same as proposed for Case Study C2).

Table 11 - Main specification inputs used in the modeling of Case Study C6.

Process	Description	Inputs	Sources	
Acid Hydrolysis (citric acid)	Acid / water concentration	60% (m/m)	BONDANCIA <i>et al.</i> (2020)	
	Temperature	120 °C		
	Hydrolysis time	4.5 h		
	Acid solution input (m / m)	11 x cellulose mass		
	Yield in CNCs	11.7%		Lab result*
	Yield in CNFs	45.9%		Lab result*
Acid Recovery	CaO tank – temperature	85 °C	MATTEY & KRISTIANSEN, 2002	
	CaO tank – yield	99%		
	H2SO4 tank – time	1 h		
	H2SO4 tank – yield	97%		

* Laboratory results were obtained by Thalita J. Bondancia.

5.2.7 Case Study C7

Even at high acid concentrations and higher extraction temperatures, hydrolysis under organic acids is not completely effective, leading to the formation of larger nanocrystals or incomplete hydrolysis when compared to sulfuric acid hydrolysis at high concentrations (VANDERFLEET & CRANSTON, 2021). With that, Case Study C7 is an adaptation of Case Study C6 with hybrid hydrolysis between organic acid (citric acid) and mineral acid (sulfuric acid) in a 9:1 v/v ratio (Figure A5 of the annexes). A blend of these compounds allows increasing in the concentration of protons in the hydrolysis reaction medium, and one should expect an enhancing in the production of CNCs.

The input parameters of Case Study C7 are similar to those of C6, except for the hydrolysis temperature (100 °C). The citric acid recovery process is also similar to the previous Case Study. In this methodology, the priority for recycling is the majorly used, more expensive citric acid - sulfuric acid is not recovered, requiring make-up at each hydrolysis cycle. In Case Study C7, the hydrolysis yield was 14.0% for CNCs and 40.8% (by mass) for CNFs production (laboratory results).

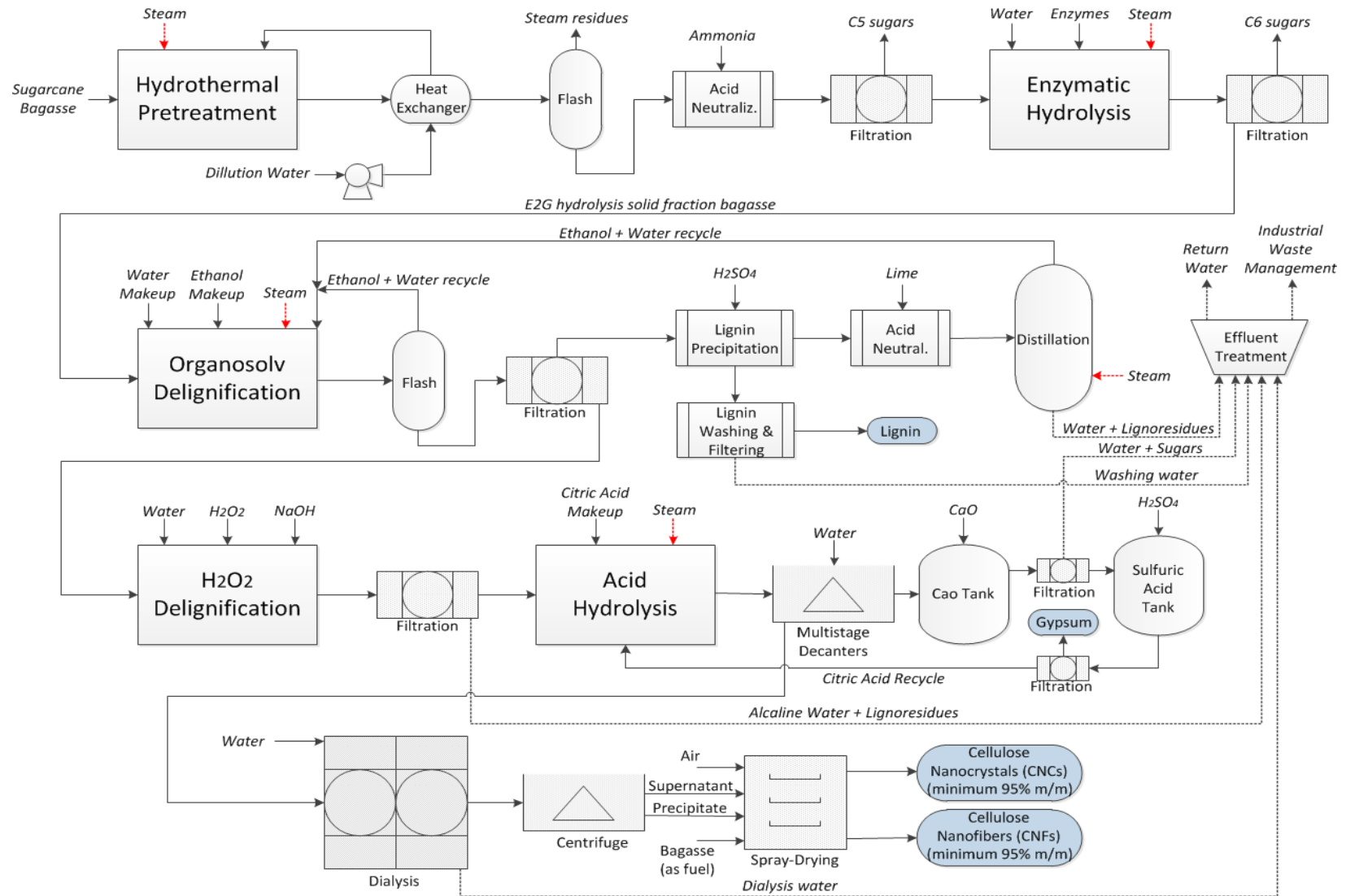


Figure 28 - Block diagram for the CNCs / CNFs production methodology proposed in Case Study C6.

5.2.8 Case Study C8

Case Study C8 considers the enzymatic hydrolysis of *raw bagasse* after hydrothermal pretreatment, organosolv delignification and alkaline delignification with hydrogen peroxide. Enzymatic hydrolysis produces as a by-product C6 sugars that are filtered and then exported to the sugarcane biorefinery for fermentation and ethanol generation. In this sense, this methodology is an adaptation of the production of CNMs and fermentable sugars (C5 and C6) that was first described in Case Study C2, but with one hydrolysis step only, and without the use of mineral or organic acids. The *Cellic Ctec-3* enzyme cocktail fabricated by *Novozymes*[®] was used in the experimental assays. The parameters related to the Case Study C8 methodology are described in Table 12 (data not present follow the same parameters of the Case Study C2), while Figure 29 illustrates the block diagram of the process. As enzymatic hydrolysis does not degrade all amorphous cellulose fractions present in the hydrolyzed matrix, both CNCs as CNFs were formed as products.

Table 12 - Main specification inputs used in the modeling of Case Study C8.

Process	Description	Input	Sources
Hydrothermal Pretreatment	Hemicellulose removal	83.1 %	Lab result*
	Lignin removal	20.6 %	Lab result*
	Cellulose removal	19.2 %	Lab result*
Organosolv Delignification (ethanol)	Hemicellulose removal	49.3 %	Lab result*
	Lignin removal	84.9 %	Lab result*
	Cellulose removal	25.9 %	Lab result*
Complementary delignification (alkaline)	Hemicellulose removal	34.0 %	Lab result*
	Lignin removal	74.5 %	Lab result*
	Cellulose removal	35.5 %	Lab result*
Enzymatic Hydrolysis	Temperature	50 °C	DE AGUIAR <i>et al.</i> (2020)
	Time	48 h	DE AGUIAR <i>et al.</i> (2020)
	Water input	6.66 x dry mass	BONDANCIA <i>et al.</i> , 2018
	Enzyme cocktail input	10 FPU / g biomass	DE AGUIAR <i>et al.</i> (2020)
	Enzyme activity (measured)	205 FPU / ml enzyme	Lab result*
	CNCs yield	6.0 %	Lab result*
	CNFs yield	10.7 %	Lab result*
Sugars yield	50.7 %	Lab result*	
Multistage Decanters	Water input	20 x (CNC + CNF) mass	DE AGUIAR <i>et al.</i> (2020)

* Laboratory results were obtained by Thalita J. Bondancia.

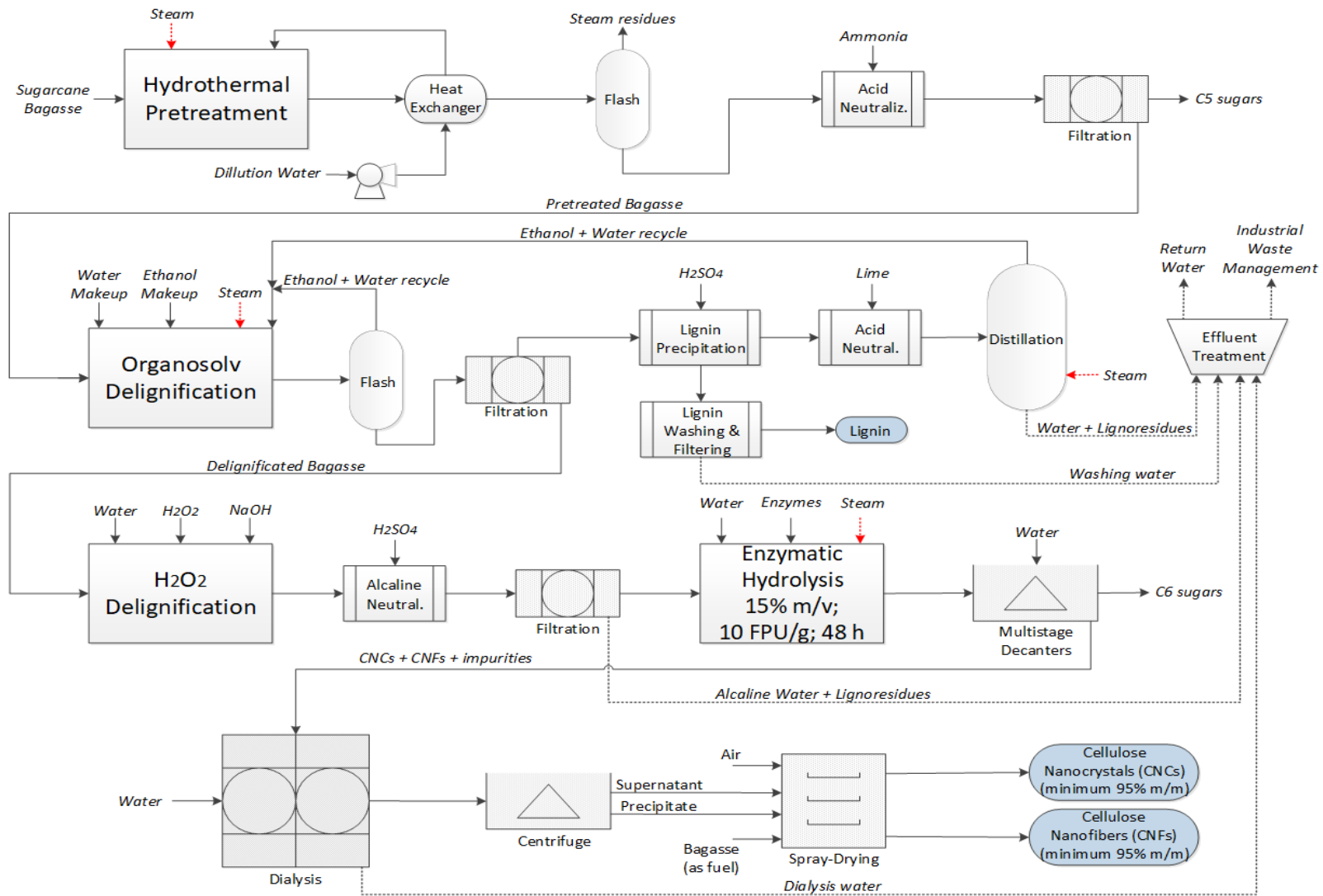


Figure 29 - Block diagram for the CNCs / CNFs production methodology proposed in Case Study C8.

5.3 Techno-Economic Analysis (TEA)

Techno-economic analyses of the Case Studies proposed in this work for obtaining CNMs were carried out to compare the feasibility between the processes. The results of the sugarcane biorefinery-derived CNMs were also compared to with other cellulose nanomaterials production technologies already described in literature.

5.3.1 TEA Premises

All Case Studies analyzed in this work consider the premise of incremental economic analysis. Therefore, the units for obtaining CNMs from sugarcane residues in all Case Studies should be considered as attached units to an E2G sugarcane biorefinery, and only the implementation of these units will be economically evaluated. This premise enables to integrate land areas (i.e., the land for the construction of the incremental unit has zero cost) and also to share feedstocks (*raw bagasse* and *E2G bagasse*), inputs, outputs and utilities with the existing biorefinery to reduce costs. Another premise was that the E2G biorefinery has availability of boilers, so the steam costs were accounted only for its generation. Lastly, the effluents generated in the CNMs methodologies were sent to the E2G biorefinery effluent treatment station, and only the effluent treatment costs were considered in the analysis. This process integration premises aimed to generate options of direct investment for the sugarcane sector inside the *biorefinery* concept.

Cash Flow Analysis (CFA) was used to obtain the MPSP of CNCs for each of the analyzed Case Studies. MPSP was assumed as the decision metric for comparing economically the different production methodologies. It is also assumed that the nanocellulose market will expand rapidly in the coming years (Figure 14) in a way that all CNMs production will be assimilated in the national and international market scenarios.

5.3.2 Costs of Inputs and Utilities and By-Products Selling Prices

The costs for process inputs and utilities and the selling prices for process by-products were estimated using updated information from literature and market data for central-south region of Brazil. Correction of values due to inflation rates was made through the *Chemical Engineering Plant Cost Index* (CEPCI) for 2021 year when necessary (Equation 1). The US Dollar / Brazilian Real conversion rate used was

US\$ 1 = R\$ 4.98 (last two-year average). Table 13 summarizes the estimated inputs and utilities costs and the by-products selling prices that were used in the economic analysis of the Case Studies from this work. The electricity consumption of each equipment (when applicable) was also estimated and accounted in the operating costs.

$$Cost_{2021_year} = Cost_{base_year} * \left(\frac{CEPCI_Index_{2020_year}}{CEPCI_Index_{base_year}} \right) \quad (1)$$

Table 13 - Estimated costs for inputs and utilities and selling prices for by-products of the Case Studies.

Inputs	Estimated Costs (US\$ / metric ton)	Sources
Sugarcane Bagasse (raw)	14.58	Potrich <i>et al.</i> (2019)
Ethanol (in biorefinery)	564	NOVACANA site (2-year avg.)
H ₂ SO ₄	85	FisherSolve [®] (2020)*
NaOH	362.5	FisherSolve [®] (2020)*
H ₂ O ₂	550	FisherSolve [®] (2020)*
CaO	125	FisherSolve [®] (2020)*
Ammonia	250	FisherSolve [®] (2020)*
Citric Acid	1400	FisherSolve [®] (2020)*
Cellulase Mix Enzyme	5000 (in biorefinery)	Humbird <i>et al.</i> (NREL), 2011; Liu <i>et al.</i> , 2015; Ferreira <i>et al.</i> , 2020
Utilities	Estimated Costs	Sources
Water (25° C)	US\$ 0.625 / ton	SAAE (2020)
Steam (low&medium pressure)	US\$ 12.5 / ton	FisherSolve [®] (2020)*
Electricity	US\$ 50 / MWh	ANEEL (2020)
Effluent Treatment	US\$ 0.62 / treated m ³	Expert info**
By-products	Estimated Selling Prices (US\$ / metric ton)	Sources
Lignin (<i>low purity</i>)	250	Based on lower heating value**
C5 Sugars	192	Estimated from ethanol conversion efficiency and ethanol sales price
C6 Sugars	260	Estimated from ethanol conversion efficiency and ethanol sales price
CaSO ₄	11.25	FisherSolve [®] (2019)*

* FisherSolve[®] is a software from Fisher International[®] licensed for the *Department of Forest Biomaterials of North Carolina State University*.

** Information kindly provided by Dr. Ronalds Gonzalez and Dr. Hasan Jameel - *Department of Forest Biomaterials of North Carolina State University*.

5.3.3 Unit Deployment Costs

On all Case Studies analyzed in this work, the costs of industrial equipment related to the steps of E2G hydrothermal pretreatment, E2G enzymatic hydrolysis, organosolv delignification, lignin precipitation and washing, ethanol recovery and alkaline delignification were estimated using *Aspen Process Economic Analyzer[®]* (*LaDaBio* has a valid license use for this software). The costs of equipment for the steps of acid

hydrolysis and neutralization, purification and drying of the CNCs were adapted from values used previously in the work of ASSIS *et al.* (2017). These values were based on information provided by *American Process Inc.*[®] (API) regarding the *USDA Forest Products Laboratory Pilot Plant*. The price of the dialysis system was quoted through the website of the SAMCO company (2020). Corrections of estimated costs were carried out using an exponential factor of 0.6 to consider the equipment scales (i.e., the “six tenth rule” – Equation 2). Equipments were quoted in AISI 316 steel (when applicable) due to the use of severe conditions, alkaline and acid solutions, in the organosolv delignification, alkaline delignification and hydrolysis stages (respectively). The downstream equipment units were also quoted in AISI 316 steel due to the level of purity required for the final product. The values were updated (when necessary) using the CEPCI Index for 2020 year.

$$Cost_{required_equip.} = Cost_{base_equip.} * \left(\frac{Capacity_{required_equip.}}{Capacity_{base_equip.}} \right)^{0.6} \quad (2)$$

Additional direct and indirect costs for deployment of each equipment were taken into account along with the simple costs (SC) (PETERS *et al.*, 2003; TOWLER & SINNOTT, 2009). Installation, instrumentation and control and piping costs are considered examples of direct costs of deployment of equipment (DC). Otherwise, costs as engineering and supervision are examples of indirect deployment costs (IC). The estimated costs for each equipment must also be increased by a *tropicalization* factor, since all values are obtained originally for the US Gulf Coast as *Free on Board* (FOB) costs. It is necessary to consider logistics costs until the delivery to the industrial unit in the center-south region of Brazil, including costs with sea freight, import taxes of industrial products and land freight (Table 14). A tropicalization factor (TF) equal to 75% of the equipment simple cost (expert info) was arbitrated for imported equipment. Equipment for which manufacturing is available in Brazil (such as process tanks and decanters) had their tropicalization factor reduced to 25% (expert info) referring to transportation costs and fees.

Total equipment deployment costs (EC), including DC, IC and TF additions, resulted in bare cost multiplication factors ranging from 3.98 (for domestic-manufactured equipment) to 4.48 (for imported equipment). Table 15 summarizes the methodology used to calculate DC, IC and TC (total equipment deployment cost) for the Case Studies of this work.

Table 14 – Types of costs for the tropicalization of industrial equipment.

Description	Estimated Tropicalization Costs
Sea freight (US Gulf Coast → Brazil)	US\$ 100 / ton
Import taxes	14% of FOB cost
Landing fees	1.5% of FOB cost
Ship cargo insurance	0.5% of FOB cost
Tax on Industrialized Products (IPI)	Generally, 9% of FOB cost
Freight additional	25% of sea freight value
Land freight from seaport to the installation site	US\$ 20 / ton
Tax on Goods and Services (ICMS)	12% of inner cost

Source: adapted from EPE – EMPRESA DE PESQUISA ENERGÉTICA (2018).

Table 15 - Methodology for obtaining direct and indirect costs of equipment deployment (adapted from PETERS *et al.*, 2003; TOWLER & SINNOTT, 2009) and arbitrated equipment tropicalization factor.

DIRECT COSTS OF DEPLOYMENT (DC)	
Equipment Installation	0.32 x SC
Piping	0.34 x SC
Instrumentation and Control	0.15 x SC
Electrical Equipment and Materials	0.10 x SC
Buildings	0.23 x SC
Service Facilities	0.55 x SC
Yard Improvement	0.10 x SC
Land	0.06 x SC
Total Direct Costs (DC)	1.85 x SC
INDIRECT COSTS OF DEPLOYMENT (IC)	
Engineering and Supervision	0.08 x (SC + DC)
Construction Expenses	0.10 x (SC + DC)
Contractors Fee	0.05 x (SC + DC)
Contingency	0.08 x (SC + DC)
Total Indirect Costs (IC)	0.31 x (SC + DC)
TROPICALIZATION USA – BRAZIL	0.75 x SC (imported)*
(TF)	0.25 x SC (domestic)*
TOTAL SINGLE EQUIPMENT DEPLOYMENT COST (EC)	DC + IC + TF or 4.48 x SC (or 3.98 x SC)
TOTAL EQUIPMENT DEPLOYMENT COST (TC)	∑ EC

* Information kindly provided by Dr. Ronalds Gonzalez - *Department of Forest Biomaterials* of North Carolina State University.

5.3.4 Project Execution Costs

Unlike single equipment deployment costs, project execution costs (PEC) are estimated for the linear full operation of the process unit, such as engineering costs for equipment design and startup. Contingency costs are also included in this category. Land acquisition costs were not accounted for CNC production units as one assumes the

availability of land area in the E2G sugarcane biorefinery. The sum of total equipment deployment costs (TC) and project execution costs (PEC) resulted in the *Capital Expenditure* (CAPEX) for each Case Study. Table 16 shows the methodology that was used to calculate PEC for the Case Studies analyzed in this work.

Table 16 - Methodology for calculating project execution costs (PEC) from total equipment deployment cost (adapted from PETERS *et al.*, 2003; TOWLER and SINNOTT, 2009).

PROJECT EXECUTION COSTS (PEC)	
Project Execution	0,04 * TC
Basic Engineering of Project	0,06 * TC
Detailed Engineering of Project	0,12 * TC
Contingency	0,25 * TC
Buildings	0,02 * TC
Total Project Execution Costs (PEC)	0,49 * TC
CAPITAL EXPENDITURE OF PROJECT (CAPEX)	TC + PEC

5.3.5 Cash Flow Analysis

Using data obtained in the mass and energy balances and costs of inputs and utilities, and sale prices of by-products, one obtained the *Operational Expenditure* (OPEX) for each Case Study of this work. Thus, Cash Flow Analysis (CFA) was carried out using data related to CAPEX and OPEX to determine the Minimum Product Selling Price (MPSP) for cellulose nanocrystals (CNCs) in each Case Study. The main input parameters arbitrated for CFA are detailed in Table 17.

It was considered that the construction of the attached unit production (for all Case Studies) would take 3 years from projecting and deployment until full operation. In this case, 2018 was selected as the zero year, with 2021 being the first year of unit operation. The expected lifespan of the incremental unit was 25 years. The production time was taken as 200 days / year due to the regular period of operation for sugarcane biorefineries (excepting the cane off-season period). Given the industrial unit startup and the initial period of adjustments, the production on first year was fixed at 80% of the calculated nominal production, increasing to 100% from the second year onwards. Capital reinvestment costs refer to the costs of scheduled repairs (for improving and updating the industrial plant) over time, and were set at 1% of CAPEX per year. Such upgrading makes it possible to increasing annual production, which was set at 0.5% per year from the second year of operation. The business operating costs include advertising and marketing,

R&D investments, legal fees, license fees, office supplies, third-part workers' salaries, and travel expenses, and were set at 2% of gross sales revenue each year. Depreciation consists of accounting for assets value loss due to obsolescence, in accordance with the expected equipment lifetime. Finally, working capital is the operating liquidity available to the business, i.e., the short-term liquid assets available after short-term liabilities have been paid off. The sum of CAPEX and working capital totals the total invested capital of the project (TURTON *et al.*, 2009).

Table 17 - Input parameters for the Cash Flow Analysis of Case Studies analyzed in this work.

Unit Deployment	
Total time for unit construction	3 years, starting in 2018
CAPEX direct costs in construction years	2 first years, 50% + 50%
CAPEX indirect costs in construction years	3 years, 35% + 35% + 30%
Capital reinvestment costs	1% of CAPEX per year*
Minimum project lifespan (expected)	25 years
Unit Production	
Annual production time	200 days / year
Production on first year of operation	80% of designed capacity
Annual production increase	0.5% per year after 2 nd year of operation (2022)*
Indirect Costs of Operation	
Regular maintenance costs	1.5% of CAPEX per year
Business operating costs	2% of projected gross sales per year*
Labor trainings	US\$ 430,000 on before-zero (2020) year*
Labor costs	US\$ 860,000 / year*
Unit insurance costs	0.2% of CAPEX per year
Property taxes	1% of CAPEX per year
Financial Assumptions	
Analysis time horizon	Project lifespan (25 years)
US Dollar / Brazilian Real conversion	US\$ 1 = R\$ 4.98 (two-year average)
Expected average inflation for Brazil	4.3% per year (five-year average)
Taxes on EBIT	34%
Depreciation	Linear, 10 years
Working Capital	10% of next year expected gross sales
Minimum Attractiveness Rate (MARR)	11% per year

* Information kindly provided by Dr. Ronalds Gonzalez - *Department of Forest Biomaterials* of North Carolina State University.

The Minimum Product Selling Price (MPSP) for CNCs is obtained iteratively, as the Annual Cash Flow (ACF) depends of all cash flow analysis inputs. The MPSP is one that satisfies Equation 3 when IRR is numerically equal to the MARR and NPV is equal to zero. In Equation 3, the ACF sub-index refers to the relative year of the project; for

example, ACF_0 refers to the first year of operation (2021). If the real sales price of CNCs is different from MPSP, the IRR of the investment can also be obtained by Equation 3. In its turn, the Time of Return for the Investment (TR) can be obtained when the sum of the annual values of ACF (starting from the project onset) reaches zero. In the case studies which CNCs and CNFs are produced simultaneously (such as organic acid hydrolysis and enzymatic hydrolysis), it was considered that the minimum product selling price for CNFs would be equivalent to 70% of the MPSP for CNCs. Such consideration was based on data presented in Table 13.

$$NPV = \frac{ACF_{-3}}{(1+IRR)^{-3}} + \frac{ACF_{-2}}{(1+IRR)^{-2}} + \frac{ACF_{-1}}{(1+IRR)^{-1}} + \frac{ACF_0}{(1+IRR)^0} + \frac{ACF_1}{(1+IRR)^1} + \frac{ACF_2}{(1+IRR)^2} + \dots + \frac{ACF_{24}}{(1+IRR)^{24}} \quad (3)$$

5.4 Sensitivity Analysis of Parameters

Although the costs of process inputs utilities and the sale prices of by-products have been used in TEA as fixed values, they are subject to market variations for different causes. Likewise, experimental parameters may vary depending on operating conditions and the scale-up factor of the process. In addition, financial assumptions are subject to government policies and macroeconomic frameworks of each country and / or region. Although the economic viability of a process can be TEA-evaluated, variations in the input parameters can result in uncertainties that do not propagate to the final metrics obtained (such as the MPSP). A sensitivity analysis of the main inputs of TEA can determine the inputs (be they cost, price, process parameters or financial assumptions) whose variation have the greatest impact on the generated data.

Sensitivity analysis for the Case Studies of this work considered a variation of -25% / +25% for the costs of inputs and utilities and also for the sale prices of by-products. One key process parameter was also evaluated: acid hydrolysis (or enzymatic hydrolysis) yield ($\pm 25\%$ variation). Three financial assumptions also had their impact on MPSP measured by sensitivity analysis: minimum attractiveness rate (MARR) (7.5% / 14.5%), CAPEX ($\pm 25\%$ in relation to the original CAPEX of each Case Study) and the unit operating time per year (185 / 215 days). All inputs of sensitivity analysis were considered independent from each other.

5.5 Probabilistic Risk Assessment of Parameters

Although some inputs of sensitivity analysis have higher impacts on the TEA results, one should consider that actually they do not vary one at a time. In a hypothetical example scenario, at the same time that the price of H₂SO₄ changes due to market fluctuations, better yields can be obtained in the mineral acid hydrolysis by process optimization - these two factors end up simultaneously impacting the cost of acid hydrolysis step and thereby the MPSP of CNCs production by H₂SO₄ hydrolysis. The Probabilistic Risk Assessment of parameters is a useful tool to determine an output interval (given a certain statistical confidence) within the possible impacts of the main inputs of sensitivity analysis can directly influence the MPSP.

Probabilistic Risk Assessment was performed using *Crystal Ball*[®] software that is an add-on for Microsoft Excel[®] (*Crystal Ball*[®] is a software from *Oracle*[®] licensed for the *Department of Forest Biomaterials* of North Carolina State University). TEA inputs for the different Case Studies that had major influence in determining the MPSPs in the sensitivity analysis (selective criterion: inputs that generated more than US\$ 100 of MPSP variation) were taken as inputs for the simulations using the *Monte-Carlo* statistical method. The inputs were redefined from deterministic values for triangular probability density functions whose minimum and maximum values followed the same input data as used in each sensitivity analysis. The Monte-Carlo method assumes that these inputs are independent of each other. A total of 10,000 random simulation cases were performed for the Monte-Carlo simulation on each Case Study. The main output of the tool consists in a graph of frequencies for different values of output MPSPs, generating a probability distribution whose 95% confidence interval determines the best-case scenario and the worst-case scenario MPSP values that can be expected in a real-world scenario for each Case Study.

5.6 Life-Cycle Assessment (LCA)

Life Cycle Assessment was performed for each of the Case Studies analyzed in this work. 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. The *Global Warming Potential* (GWP) for 100 years of

operation was used as the standard metric for comparing environmental impacts between the evaluated scenarios, and was found for each one of the inputs and outputs of the proposed CNMs production methodologies (Table 18). The GWP coefficient quantified the Greenhouse Gas Emissions (GHG) as grams of equivalent CO₂ emitted per each produced kg of CNMs.

The carbon intensity of residues from any process stage was equaled to zero in the *cradle-to-gate* approach. Thereby, the sugarcane bagasse that used as feedstock for the nanocellulose production in the different Case Studies was assumed to inherit zero GWP from the harvest fields. A small amount of extra sugarcane bagasse was used to generate heat for the spray-dryer air, so the environmental impacts for this biomass burning was accounted for.

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 (*SimaPro*[®] is a software from *PRé Sustainability*[®] for which *LaDaBio* has a valid license use). For the allocation of environmental impacts to the products and by-products from the processes, energetic allocation was carried out as the impact's distribution factor. Lignin, streams of C5 and C6 sugars (that are exported to the E2G biorefinery to ethanol obtaining) and gypsum were taken as by-products for each Case Study (when applicable). The environmental impacts of process steam were calculated for sugarcane bagasse burning in biorefinery, considering the lower heating value of sugarcane bagasse (9774 MJ / ton, moisture of 50%) and overall boiler efficiency of 86% (LONGATI *et al.*, 2019).

Table 18 - GWP data obtained on SimaPro[®] software for inputs and outputs of the Case Studies analyzed in this work.

Inputs and Outputs	GWP (g of CO₂ equiv. per unit)	Simplified description on <i>SimaPro</i>[®]
Sugarcane bagasse	Zero	(Taken as residue input)
Water	0.568 / kg	Tap water {GLO}
Ethanol	579 / kg	Ethanol, in 95% solution, from fermentation {RoW}
Ammonia	2140 / kg	Ammonia, liquid {RER}
Enzymatic cocktail	2040 / kg	Cellulase, Novozymes Celluclast {RER}
Steam	11.2 / kg of boiler burnt bagasse	Bagasse, from sugarcane, heat and power cogeneration unit {GLO}
Sulfuric acid	163 / kg	Sulfuric acid {GLO}
Lime	40.4 / kg	Lime {GLO}
Hydrogen peroxide	1170 / kg	Hydrogen peroxide, in 50% solution state {GLO}
Sodium hydroxide	500 / kg	Sodium hydroxide (50% NaOH) {RER}
Citric acid	2800 / kg	Citric acid {RER}
Electricity	296 / kWh on Brazil	Electricity, high voltage, cane sugar production {BR}
Sugarcane bagasse burnt (spray-dryer)	11.2 / kg	Bagasse, from sugarcane, heat and power cogeneration unit {GLO}
CNC, CNF	Calculated	(Main Products – Energetic allocation)
Lignin	Calculated	(By-Product – Energetic allocation)
C5 Sugars	Calculated	(By-Product – Energetic allocation)
C6 Sugars	Calculated	(By-Product – Energetic allocation)
Gypsum	Calculated	(By-Product – Energetic allocation)

In this Section, the results obtained for technical, economic and environmental assessments of the CNMs production in incremental units to a sugarcane biorefinery will be presented and discussed for each Case Study proposed this work.

6.1 Modeling CNM production routes - Technical Analysis

The technical analysis of the production methodologies discussed in this work was carried out through comparisons between the results obtained by modeling, mass and energy balances. In order to allow a better understanding of the results, the analyzes were discussed comparing specific Case Studies, starting from primary selection factors (such as the feedstock selection) to specific changes in the upstream and downstream of the acid hydrolysis process. The sequence of results, therefore, was presented following this hierarchy:

- Comparison of feedstocks, considering the state-of-the-art hydrolysis methodology (sulfuric acid 64% by mass), and comparing Case Studies C1 (*raw bagasse*) and C2 (*E2G bagasse*) for the production of CNCs;
- Comparison of hydrolysis methodologies. Case Studies C1 and C2 were compared with Case Study C8, which considers the production by enzymatic hydrolysis from *raw bagasse*;
- Comparison of acid hydrolysis methodologies. Case Study C2 - in which sulfuric acid is used in hydrolysis – was compared with Case Study C6 (in which an organic acid (citric acid) is used for hydrolysis) and the Case Study C7 (in which a 9:1 v/v mixture of citric and sulfuric acids is used – characterizing a hybrid hydrolysis between organic and mineral acids);
- Comparison of Case Study C2 with methodologies proposed for modifying the upstream and/or downstream of acid hydrolysis. In this category, the following are listed: Case Study C3, with no alkaline delignification by hydrogen peroxide, generating nanocrystals with lignin contents – LCNCs; Case Study C4, in which the sulfuric acid recovery step of hydrolysis is replaced by neutralization with

CaO; and Case Study C5, in which spray-drying is not performed, generating 8% m/m suspensions of CNCs;

6.1.1 Acid hydrolysis using different feedstocks - Case Studies C1 and C2

A comparison between the results obtained from modeling and mass and energy balances for Case Study C1 (whose main input specifications and block diagram are described, respectively, in Table 9 and Figure A1) and Case Study C2 (described by Table 10 and Figure 27) is shown in Table 19.

Table 19 – Main results obtained in modeling and mass / energy balances for the Case Studies C1 and C2.

Process Stage	Description	Unit	Case Study C1	Case Study C2
Primary Input	Feedstock for E2G sugars generation	kg / h	-	7500 (<i>raw bagasse</i> on a dry basis)
	System pressure	bar	-	14
Hydrothermal Pretreatment	Water make-up	kg / h	-	17475
	Steam 17 bar use	kg / h	-	8144
Hydrothermal Flash Tank	Water removed by flashing	kg / h	-	1523
Hydrothermal Acetic Acid Neutralization	Acetic acid formation	kg / h	-	91
	Ammonia input	kg / h	-	45
C5 Sugars Filtering	Water on cake (%)	% of cake mass	-	55
	Hemicellulose on cake	% of dry mass	-	10.3
	C5 Sugars on filtered	kg / h	-	1972
	C6 Sugars on filtered	kg / h	-	623
	Biomass yield	% of input mass	-	58.2
	Water on filtered	kg / h	-	18117
Enzymatic Hydrolysis	Enzymatic cocktail input	L / h	-	141
	Water input	kg / h	-	9200
C6 Sugars Filtering	C6 Sugars on filtered	kg / h	-	1560
	C5 Sugars on filtered	kg / h	-	38
	Cellulose on cake	kg / h	-	968
	Cellulose purity on cake	% of dry mass	-	36.2
	Lignin on cake	% of dry mass	-	46.0
	Water % on cake	% of total cake	-	54.0
	Biomass yield	% of input mass	-	61.2
	Water on filtered	kg / h	-	11401
Hydrolysis Input	Feedstock for CNCs production	kg / h	7500 (<i>raw bagasse</i> on a dry basis)	Cake of C6 sugars filtering (<i>E2G bagasse</i>)
Organosolv Delignification (ethanol)	System pressure	bar	27.0	27.1
	Water make-up	kg / h	6108	1806
	Ethanol make-up	kg / h	571	296
	Steam 17 bar use	kg / h	15542	5439

Table 19 – Main results obtained in modeling and mass / energy balances for the Case Studies C1 and C2 (continuation).

Process Stage	Description	Unit	Case Study C1	Case Study C2
Organosolv Flashing	Ethanol recovery	kg / h	9506	3384
	Water recovery	kg / h	4292	1528
	Output temperature	°C	85.5	85.7
Organosolv Filtering	Cellulose on cake	kg / h	1906	863
	Lignin % on cake	% of dry mass	15.5	25.4
	Biomass yield	% of input mass	39.7	54.2
Lignin Precipitation & Recovery	H ₂ SO ₄ input for pH down	kg / h	56	39
	Lignin % at precipitated	% of mass	77.0	77.1
	Washing water	kg / h	1666	1142
	Washed lignin (by-product)	kg / h	561	392
Acid Neutralization	Lime input	kg / h	30	19
Distillation for Organosolv Ethanol Recovery	Ethanol recovery	kg / h	4548	1526
	Water recovery	kg / h	1787	541
	Condenser temperature	°C	99.5	98.0
	Water use on condenser	kg / h	45450	13759
	Reboiler temperature	°C	118.2	119
	Steam use on reboiler	kg / h	7762	2532
Alkaline Delignification (H₂O₂)	Cellulose % at input	% of dry input	64.08	59.6
	H ₂ O ₂ input	kg / h	222	108
	NaOH input	kg / h	178	87
	Water input	kg / h	5948	2893
Alkaline Delignification Filtering	Cellulose on cake	kg / h	1433	713
	Cellulose % on cake	% of dry mass	79.2	82.7
	Biomass yield	% of input mass	60.8	59.6
Acid Hydrolysis	H ₂ SO ₄ total	kg / h	4459	2125
	H ₂ SO ₄ make-up	kg / h	638	265
	Nanocrystals production	kg / h	434	306
Multistage Decanters	Water input	kg / h	29945	14146
	Biomass residuals removed	kg / h	1359	549
Acid neutralization	NaOH 25% input	kg / h	57	108
Dialysis	Water input	kg / h	42342	30191
	Removed salts & sugars	kg / h	108	48
Spray-Drying	Air input	kg / h	19004	12816
	Raw bagasse burnt	kg / h	5279	3560
	Vaporized water	kg / h	14229	10079
CNC Product Output	CNC 95% min. (m/m)	kg / h	455	322
H₂SO₄ Recovery	H ₂ SO ₄ recovery on evaporators	kg / h	3822	1860
	Vaporized water	kg / h	25664	12418
	Steam 2.5 bar input	kg / h	11666	5648
Effluent Treatment	Biorefinery waste manag. station output (non-water)	kg / h	7923	5616
Electricity	Electricity use	kWh / day	4781	4750

It can be seen in Table 19 that Case Studies C1 and C2 use the same amount of primary feedstock (*raw bagasse*), but that the yields in CNCs turn out to be different: while in Case Study C1, 455 kg/h of CNCs 95% by mass are generated, with an overall yield in nanocrystals of 14.4% in relation to the initial *raw bagasse* biomass, in Case Study C2 are generated 322 kg/h of CNCs 95% by mass, rendering 10.2% overall yield in relation to *raw bagasse* use. However, Case Study C2 presents two hydrolysis processes: an enzymatic process for the generation of fermentable sugars, and an acid one for the generation of CNCs. Therefore, Case Study C2 uses *E2G bagasse*, an output from the enzymatic hydrolysis, as feedstock for the generation of CNCs.

According to Table 19, in Case Study C1, 561 kg/h of lignin are also generated (33.0% yield in relation to the initial lignin mass on *raw bagasse*), while in Case Study C2, 392 kg/h of lignin are generated (23.1% of yield relative to the initial lignin). Lignin is sold as a by-product of the nanocrystals production unit. However, one can affirm that the most remarkable difference between the highlighted methodologies is in the fact that, in Case Study C2, there is production of sugars (totaling 2010 kg/h of pentoses and 2183 kg/h of hexoses) that are redirected to the biorefinery, while in Case Study C1 the production of these by-products does not occur. This is due to Case Study C2 methodology to consider the use of pre-treatment and enzymatic hydrolysis steps as part of the installations for E2G generation. In these extra stages, there is use of considerable steam streams in the pre-treatment reactor and the use of enzyme cocktails for hydrolysis of biomass to sugars, generating extra costs for the process. Though, the degradation of *raw bagasse* at these previous stages removes much of the hemicellulose contents from the lignocellulosic matrix, and the hydrolysis of the hydrothermally pretreated biomass ends up degrading, for the most part, the amorphous fractions of cellulose (CAMARGO et al., 2016). Thus, in Case Study C2, a biomass containing cellulose with a higher crystallinity index (i.e., *E2G bagasse*) is generated. After the treatments for delignification, this biomass presents a higher yield in hydrolysis with sulfuric acid (35.5% of yield on CNCs in relation to the initial biomass of hydrolysis) when compared to the delignified *raw bagasse* of Case Study 1 (24% yield on CNCs in relation to the initial biomass of hydrolysis - here a higher output of sugars and / or non-hydrolyzed biomass is (are) also generated. The CNCs 95% by mass production in Case Study 2 equates to approximately 16% conversion when compared to the *E2G bagasse* input. This

value is slightly lower than the conversion observed experimentally by CAMARGO *et al.* (2016) for a similar methodology (~18%).

Comparing Figures A1 (Annexes Section) and 27 (Methodology Section), it can be seen that Case Studies C1 and C2 present a similar processing methodology for the generation of CNCs after the organosolv delignification stage. While C1 uses *raw bagasse*, C2 inputs *E2G bagasse* to the organosolv process. Given that *E2G bagasse* is a previously processed biomass that contains a dry mass fraction of approximately 35.6% of *raw bagasse* that inputs the hydrothermal pretreatment, it can be said that the process scale in the upstream and hydrolysis stages becomes higher in Case Study C1. On C1, 41.3% more CNCs final product is generated when comparing to C2, but C1 uses greater amounts of inputs and utilities, also triggering the need for larger process equipment.

Some remarkable characteristics of the CNCs generation process by sulfuric acid hydrolysis can be highlighted: the intense use of inputs such as process water (mainly in the CNCs purification steps, i.e., the multistage decanters and the dialysis stages, this last being used to remove minor impurities in order to produce market-driven high purity cellulose nanomaterials), steam (in the H₂SO₄ recovery), and hydrogen peroxide and sodium hydroxide (in the complementary alkaline delignification). The water output in the dialysis process contains minimal levels of impurities and was subject to partial reuse in the process, being utilized in the condenser of the ethanol distillation as cold fluid. Hydrothermal pretreatment (for C1) and organosolv delignification (for C1 and C2) also require high inputs of energy (supplied by steam) to achieve the required degree of severity (high temperatures and pressures) for the process.

In Case Studies C1 and C2, respectively, flashing and distillation steps recover and recycle approximately 96% and 94% of the ethanol that is used in the organosolv process. This significantly reduces the need for this solvent make-up inputs. Distillation stage presents considerable use of hot (steam 2.5 bar) and cold (cooling water from dialysis output) utilities in the reboiler and condenser substages, respectively. The recovery of sulfuric acid in the system composed by a membrane for sugars retention and the multi-effect evaporators is approximately 86% of the total acid used in hydrolysis stage. The multistage evaporators use steam 2.5 bar for water evaporation. This reduced hot utility consumption is due to vacuum pressure of operation in two of the evaporators, allowing 2.2 kg of water to be vaporized for each kg of steam used. In turn, the spray-dryer is capable of generating CNCs with the desired degree of purity (95% by mass), but

it uses amounts of sugarcane bagasse to generate heat to the system, which operates with hot drying air at 200 °C.

6.1.2 Enzymatic Hydrolysis - Case Study C8

Table 20 shows the most important results obtained for the modeling and mass and energy balances for Case Study C8 (that is represented in Figure 29). C8 considers the enzymatic hydrolysis of *raw bagasse* after the steps of hydrothermal pretreatment, organosolv delignification and alkaline delignification. In this methodology, two varieties of CNMs are generated: CNCs and CNFs.

Table 20 – Main results obtained in modeling and mass / energy balances for the Case Study C8.

Process Stage	Description	Unit	Case Study C8
Primary Input	Feedstock for E2G sugars generation	kg / h	7500 (<i>raw bagasse</i> on a dry basis)
C5 Sugars Filtering	Hemicellulose on cake	% of dry mass	9.7
	C5 Sugars on filtered	kg / h	1997
	C6 Sugars on filtered	kg / h	605
	Biomass yield	% of input mass	58.3
Organosolv Delignification (ethanol)	Water make-up	kg / h	2725
	Ethanol make-up	kg / h	462
	Steam 17 bar use	kg / h	8914
Organosolv Flashing	Ethanol recovery	kg / h	5546
	Water recovery	kg / h	2504
Organosolv Filtering	Cellulose on cake	kg / h	1885
	Lignin % on cake	% of dry mass	8.8
	Biomass yield	% of input mass	53.3
Lignin Recovery	Washed lignin (by-product)	kg / h	550
Alkaline Delignification (H₂O₂)	H ₂ O ₂ input	kg / h	174
	NaOH input	kg / h	139
	Water input	kg / h	4661
Alkaline Delignification Filtering	Cellulose on cake	kg / h	1217
	Cellulose % on cake	% of dry mass	84.6
	Biomass yield	% of input mass	61.7
Enzymatic Hydrolysis	Cellulase cocktail input	L / h	70
	Water input	kg / h	9255
Multistage Decanters	Water input	kg / h	9945
	C6 sugars (by-product)	kg / h	607
Dialysis	Water input	kg / h	20311
Spray-Drying	<i>Raw bagasse</i> burnt	kg / h	2482
CNMs Product Output	CNC 95% min. (m/m)	kg / h	77
	CNF 95% min. (m/m)	kg / h	137
Effluent Treatment	Biorefinery waste manag. station output (non-water)	kg / h	3049
Electricity	Electricity use	kWh / day	4839

It can be seen in Table 20 that enzymatic hydrolysis has a low yield for the generation of CNMs (6.79% in relation to the cellulose content of the *raw bagasse*, considering the sum of CNCs and CNFs production). However, C8 methodology also generates three by-products: pentose sugars after hydrothermal pretreatment, hexose sugars (by-product of enzymatic hydrolysis, equivalent to 55.5% of the hexose sugars output obtained in Case Study C2, and lignin (40% more than in C2, practically the same as in C1).

One of the characteristics that differentiate enzymatic processes in relation to acid hydrolysis processes is that, in the first, there is no need for recovery and recycling of the acid, decreasing the use of inputs and utilities (also leading to lower generation of effluents for treatment), and also decreasing the equipment costs. Hydrolysis without the use of acids also allows that smaller amounts of water are needed in the purification of CNMs in multistage decanters (68.5% less water than in C1 and 33.2% less than in C2).

The combination of hydrothermal pretreatment, organosolv delignification and alkaline delignification generates an input biomass with 84.6% purity in cellulose for the enzymatic hydrolysis. A high level of purity for cellulose is considerably important for enzymatic hydrolysis to be effective in the generation of CNMs (ZHANG & LYND, 2004; RIBEIRO *et al.*, 2019).

6.1.3 Citric Acid Hydrolysis - C6 and C7 Case Studies

Table 21 shows the main results obtained in the modeling and mass and energy balances for the Case Studies C6 and C7 (Figures 28 and A5 represent the diagram blocks for these methodologies, respectively). Data not shown in Table 21 for the upstream acid hydrolysis follows the same results shown for Case Study C2 (Table 19). As the enzymatic hydrolysis process from C8, citric acid does not completely hydrolyze the amorphous phases of the input cellulose, and so, two types of CNMs are produced: CNCs and CNFs.

Table 21 - Main results obtained in the modeling and mass and energy balances for Case Studies C6 and C7.

Process Stage	Description	Unit	Case Study C6	Case Study C7
Acid Hydrolysis	Citric acid total	kg / h	6719	6047
	Citric acid makeup	kg / h	585	527
	Sulfuric acid makeup	kg / h	-	1688
Multistage	Water input	kg / h	22677	25543
Decanters	Biomass residuals removed	kg / h	357	386
Acid Recovery –	CaO input	kg / h	3729	4329
CaO Addition	Calcium citrate filtering	kg / h	8198	7378
Acid Recovery –	Sulfuric acid input	kg / h	4840	4356
H ₂ SO ₄ Addition	Gypsum filtering	kg / h	6648	8300
Dialysis	Water input	kg / h	47735	45150
Spray-Drying	<i>Raw bagasse</i> burnt	kg / h	5776	5495
CNMs Products	CNC 95% min. (m/m)	kg / h	106	127
Output	CNF 95% min. (m/m)	kg / h	416	370
Effluent	Biorefinery waste manag.	kg / h	9478	9507
Treatment	station output (non-water)			
Electricity	Electricity use	kWh / day	7652	7669

From Table 21, one can infer some important aspects of Case Studies C6 and C7. As citric acid is a low pKa acid, a higher amount of this hydrolysis agent is needed for a given biomass (3.16 times more acid mass input in C6 when compared to the sulfuric acid in C2). However, considering the sum of the total cellulose nanomaterials generated, Case Studies C6 and C7 present the highest mass yield in CNMs among the evaluated methodologies (16.6% and 15.8% of the cellulose mass present in the *raw bagasse* is converted to CNMs, respectively). The addition of sulfuric acid 1:10 v/v in the hydrolysis of Case Study C7 increases the product fraction of CNCs (19.8% higher) and decreases the fraction of CNFs (12.4% lower) when compared to Case Study C6. Hydrolysis H₂SO₄, by the way, is not recovered in C7, generating the need for total make-up of the acid, and also higher gypsum generation (24.8% more) when compared to C6.

The citric acid recovery process uses high amounts of chemical inputs (CaO and H₂SO₄) to precipitate calcium citrate and then to regenerate the citric acid from this salt, respectively. Yet, CaO and H₂SO₄ are not recycled in the process, increasing its environmental impacts (as will be detailed in the Life-Cycle Assessment section). Also, the aforementioned inputs have a relatively considerable cost, while gypsum, a by-product generated in the process, has low commercial value. Citric acid recovery recycles approximately 91% of the total contents of this acid in Case Studies C6 and C7, a higher recovery percentage than for sulfuric acid in Case Study C2, for example. However, citric acid has a market price almost 17 times higher than that of sulfuric acid. Thus, despite the

high yields in CNMs from the *raw bagasse*, the citric acid hydrolysis processes of Case Studies C6 and C7 also present economic bottlenecks in the acid recycling process, which will be detailed in the Economic Analysis section.

6.1.4 No alkaline delignification – Case Study C3

In Case Study C3 (block diagram shown in Figure A2; modeling and mass and energy results illustrated in Table 22) the alkaline delignification of the biomass (with H₂O₂ and NaOH inputs) is not carried out. The absence of alkaline treatment leads to production of cellulose nanocrystals containing non-removed lignin (LCNCs). In this methodology, the biomass that inputs the hydrolysis stage contains a high fraction of lignin (25.4% on dry mass), and this decreases the yield of acid hydrolysis. The use of a biomass that had one less pretreatment step (no alkaline pretreatment) also increases the total input flow in the hydrolysis, as less biomass contents are removed in the upstream (67.6% more biomass input than in the C2 case, for example). This increases the use of sulfuric acid and inputs in the downstream processes. At the end of the process, nanocrystals with high lignin contents (approximately 21.8% by mass) are obtained. Literature describes specific characteristics and possible applications for these LCNCs, as seen in the Introduction section.

Table 22 - Main results obtained in the modeling and mass and energy balances for Case Study C3.

Process Stage	Description	Unit	Case Study C3
Acid Hydrolysis	Cellulose % at input	% of dry mass	59.6
	Lignin % at input	% of dry mass	25.4
	H ₂ SO ₄ total	kg / h	3567
	H ₂ SO ₄ make-up	kg / h	522
Multistage Decanters	Water input	kg / h	19032
Dialysis	Water input	kg / h	44752
Spray-Drying	<i>Raw bagasse</i> burnt	kg / h	5222
LCNC Product Output	LCNC 73% min. (m/m)	kg / h	475

6.1.5 No sulfuric acid recovery – Case Study C4

In Case Study C4, the sulfuric acid recovery step from hydrolysis is not performed, that is, there is no membrane for solids and sugars removing and also no multistage evaporators. In C4, the output stream produced in the acid hydrolysis and later separated in the multistage decanters is neutralized with CaO, generating large amounts of gypsum which is sold as by-product (as shown in the block diagram of Figure A3).

After this process, the remaining residue flow (containing sugars, impurities, biomass residues and residual sulfuric acid) is sent to effluent treatment. The main results obtained in the modeling and mass and energy balances for Case Study C4 are shown in Table 23.

Case Study C4 uses around 7 times more H₂SO₄ than Case Study C2. However, the steam use is substantially reduced. Since there is no multistage evaporation, approximately 35% less steam is necessary in Case Study C4. A decrease in the capital costs is also expected, as acid recycling equipment is not needed. Furthermore, the acid hydrolysis yield is not affected at all, being the same to that of Case Study C2.

Table 23 – Main results obtained in modeling and mass and energy balances for Case Study C4.

Process Stage	Description	Unit	Case Study C4
Acid Hydrolysis	H ₂ SO ₄ total	kg / h	2125
	H ₂ SO ₄ make-up	kg / h	2125
CNC Product Output	CNC 95% min. (m/m)	kg / h	322
H₂SO₄ Neutralization	Hydrolysis H ₂ SO ₄ input	kg / h	2092
	Lime input	kg / h	1195
	Gypsum Precipitation	kg / h	2899
Effluent Treatment	Biorefinery waste manag. station output (non-water)	kg / h	6123

6.1.6 No spray-drying section – Case Study C5

Case Study C5 considers a process adapted from Case Study C2 in which there is no CNC drying, that is, the spray-dryer is absent from the process, as illustrated in the block diagram in Figure A4. Thus, highly-purified nanocrystals are obtained from dialysis output, and sold as aqueous suspensions with a minimal concentration of 8% by mass. In total, 3830 kg/h of CNCs suspensions are generated as C8 main product. Without the drying step, the use of sugarcane bagasse is decreased (23.7% less when compared to C2), once there is no biomass burning for generation of drying conditions. A reduction in the capital costs of the process is also expected, since the spray-dryer is one of the most expensive equipment in the CNM production processes analyzed in this work.

6.2 Techno-Economic Analysis (TEA)

The Techno-Economic Analysis of the processes (TEA) was carried out for Case Studies C1 to C8, in order to determine the Minimum Selling Prices of cellulose nanomaterials (MPSPs). Furthermore, the process parameters for which MPSP was more sensitive and statistical confidence scenarios for MPSP values were also determined by Parametric Sensitivity Analysis and Probabilistic Risk Assessment of Parameters, respectively.

6.2.1 Capital Expenditure (CAPEX)

Table 24 shows the total single equipment deploying costs (EC) that were estimated for the C2 Case Study methodology considering the simple price (SC) of the equipment (updated to 2020 through *CEPCI Index*) and the total sum of equipment installation factors, i.e., direct costs (DC), indirect costs (IC) and tropicalization factor (TF). Data calculated for the other Case Studies follow the “six tenths rule” applied to the simple prices, also considering the scale factor defined for each equipment.

Table 24 – Equipment deployment costs for Case Study C2.

Sector	Equipment	Scale Unit	Scale	SC in 2020 (US\$)	EC (US\$)
Hydrothermal Pretreatment & C5 recovery	Hydrothermal Reactor	Volume (m ³)	6.5	492.665	1.962.533
	Heat Exchanger	Exchange area (m ²)	18	30.731	122.419
	Flash Tank	Input*h (ton)	2	26.509	105.600
	Ammonia Add Tank	Volume (m ³)	8	44.633	177.796
	C5 Filter	Input (ton / h)	31	77.075	345.569
Enzymatic Hydrolysis & C6 recovery	Hydrolysis Reactor	Volume (m ³)	1404	942.179	3.753.172
	C6 Sugars Filtering	Input (ton / h)	19	57.536	257.963
Organosolv Pretreatment	Organosolv Reactor	Volume (m ³)	7.3	530.287	2.112.398
	Flash Tank	Input*h (ton)	2.5	34.186	136.181
	Output filter	Input (ton / h)	10	39.032	175.001
Lignin Recovery	Lignin Precipitator	Volume (m ³)	1.8	18.556	83.200
	Lignin Washing	Volume (m ³)	4.6	32.670	130.142

Table 24 – Equipment deployment costs for Case Study C2 (continuation).

Sector	Equipment	Scale Unit	Scale	SC in 2020 (US\$)	EC (US\$)
Ethanol Recovery	Acid Neutralization	Volume (m ³)	1.5	16.723	66.616
	Distillation	Input (ton / h)	6.0	95.268	379.504
	Flash Heat Exchanger	Exchange area (m ²)	26	38.435	153.108
	Distillation Heat Exchanger	Exchange area (m ²)	8	18.973	75.582
Alkaline Delignification (H₂O₂)	Delignification Reactor	Volume (m ³)	8.9	87.188	347.315
	Output Filter	Input (ton / h)	5.9	28.546	127.989
Acid Hydrolysis	Hydrolysis Reactor	Volume (m ³)	3.9	83.205	331.447
Neutralization and Purification	Multistage Decanters	Water adding (m ³ / h)	14.1	469.423	2.104.659
	Acid Neutralization	Volume (m ³)	0.2	4.825	19.221
Dialysis Treatment	Dialysis	Input water per day	725	487.559	2.185.971
Spray-Drying	Spray-dryer	Input (ton / day)	492	781.272	3.502.834
H₂SO₄ Recovery	Membrane for Sugars	Removed sugars (ton / day)	11.6	115.671	518.611
	Multistage Evaporators	Water removed (ton / day)	298	440.456	1.974.786
TOTAL (TC)				21.149.630	

Using the total equipment deployment costs (TC) of Case Study C2 from Table 24, the project execution costs were calculated, reaching US\$ 10.36 million. Thereby, CAPEX for C2 methodology for producing CNMs was US\$31.52 million for 2021 values. Figure 30 illustrates a graph of stacked bars for each process stage with the CAPEX costs obtained for each of the Case Studies evaluated in this work for the production of CNMs. CAPEX values were estimated between US\$ 26.30 and US\$ 38.14 million dollars for the adopted production scale of 72000 ton / year of *raw bagasse* feedstock. When adjusting the production scale by the “six tenth rule” (PETERS, 2003), the processes analyzed in this work have CAPEX values that are compatible with the values proposed by ASSIS et al. (2017), ROSALES-CALDERÓN *et al.* (2021) and BLAIR & MABEE (2021).

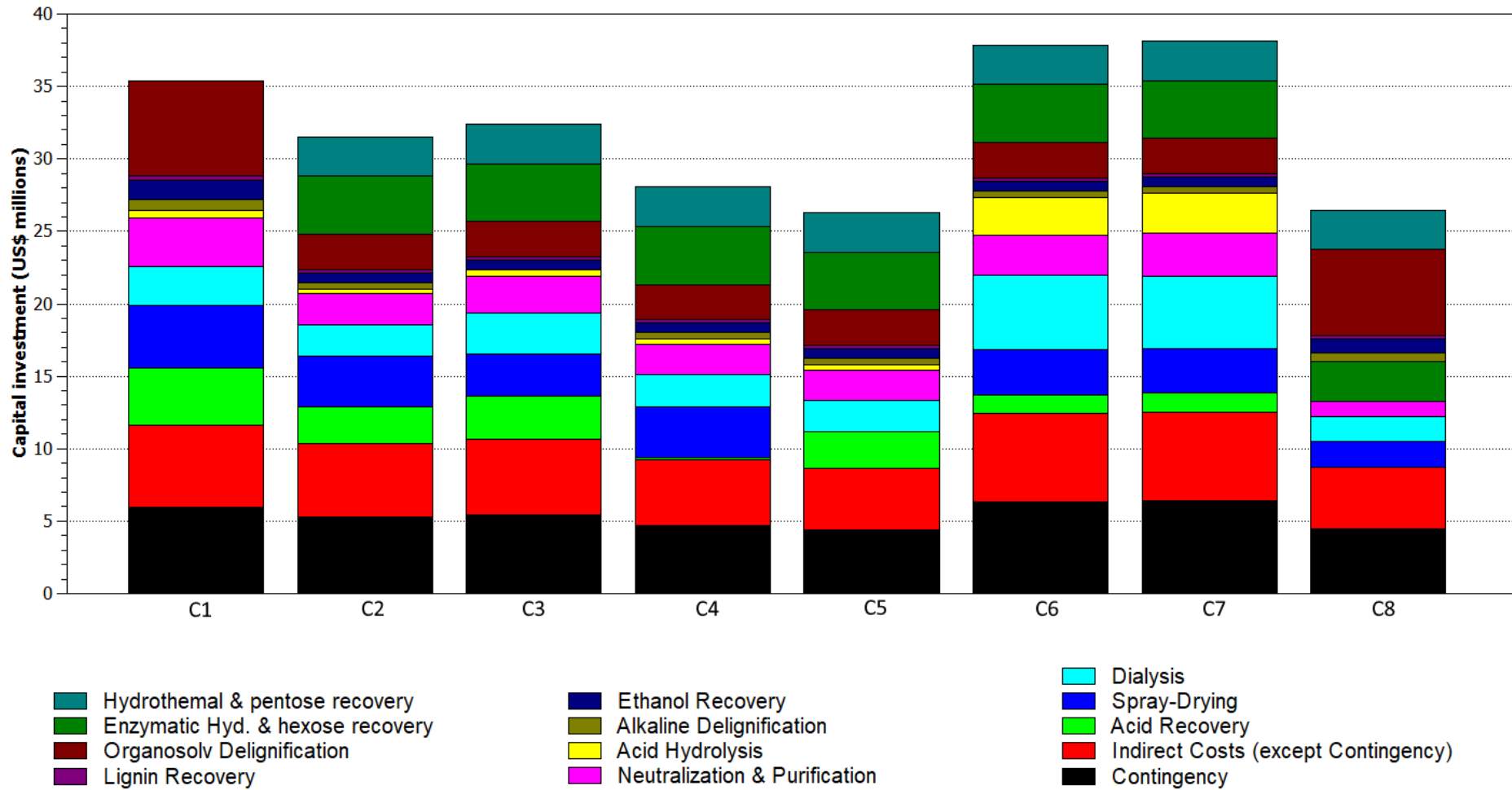


Figure 30 – Capital expenditure (CAPEX) estimated for Case Studies C1 to C8.

Figure 30 shows the prevalence of CAPEX costs for certain stages of CNMs processing in all Case Studies. Capital costs of multistage decanters, dialysis and spray-drying equipment stages represent high capital investment in all processes (adding up to 37% of the total equipment deployment costs (TC) in Case Study C2, for example). Hydrothermal pretreatment and organosolv delignification (in reactors that operate under high severity degree conditions), and sulfuric acid recovery (in three-stage evaporators, two at vacuum) are other steps of the processes C1 to C5 with high capital investment, representing 10.3%, 11.4% and 11.8% of TC costs in C2, respectively. Organosolv delignification has great influence on CAPEX in case studies in which *raw bagasse* is used in CNMs hydrolysis (C1 and C8), since higher biomass flows are treated, requiring equipment with greater physical volumes.

Figure 30 also shows an increasing CAPEX when replacing sulfuric acid with citric acid in the hydrolysis stage (capital expenditure increases 20.10% in C6 Case Study when comparing to C2). One explanation for it is that the hydrolysis with the organic acid uses a longer time, a lower concentration of the biomass in hydrolysis, and a higher temperature for the reaction – such factors require larger hydrolysis reactors. Since there is also the production of CNFs in C6 and C7 Case Studies (in addition to CNC), an increase in the costs of downstream equipment, (mainly in dialysis) also occurs, as more material has to be purified.

Case Study C4 presents a capital investment that is US\$ 3.5 million lower than Case Study C2, mainly due to the absence of the sulfuric acid recovery step, being replaced by acid neutralization and gypsum precipitation steps that present low capital costs. Apart from no alkaline delignification, Case Study C3 presents capital investment higher than C2, since the presence of lignin-rich cellulose nanocrystals (LCNCs) increases the outflow of acid hydrolysis implying in higher downstream equipment costs. The absence of sulfuric acid recovery and drying stages of CNCs in C4 and C5 methodologies, respectively, reduces CAPEX by 12.3% and 19.8% when comparing to C2. The enzymatic process (Case Study C8), in turn, had the lowest CAPEX costs among the analyzed Case Studies, mainly due to the hydrolysis reactor operate under mild conditions (low capital investment, even for a long time, high volume of reaction), and also because recycling of hydrolysis acid is not necessary.

6.2.2 Operational Expenditure (OPEX)

Figure 31 presents the operational expenditure (OPEX) in terms of inputs and utilities, as well as the returns from the sale of by-products, for each methodology proposed in Case Studies C1 to C8. Operational costs showed values between \$3258 (C1) and \$7865 (C8) per dry ton of produced CNMs, while the revenues varied between \$323 (C1) and \$3912 (C8) per dry ton of CNMs.

It can be seen in Figure 31 for Case Studies C2 to C8 that the cost of the enzyme cocktail is quite significant in the composition of OPEX costs (~40% of the costs in C2, for example). Other inputs that presented remarkable costs in these methodologies are sugarcane bagasse and ethanol. Despite the intensive use of water in the processes, steam presents itself as the process utility with the highest costs per amount of produced nanomaterials (~31% of the costs in the C1 methodology, mainly due to organosolv delignification).

The generation of by-products (specially the fermentable sugars) generally presented good returns in relation to the operational costs of inputs and utilities. It is verified, for example, that in Case Study C2 the costs of inputs and utilities for the production of a ton of CNCs is approximately 51% higher than the same cost for Case Study C1, mainly due to the cost of enzymatic hydrolysis. However, the production of lignin and fermentable sugars in C2 (absent in C1) generates returns equivalent to 63% of production costs, considerably improving the viability of this methodology. In C1, returns on lignin by-production recover only 10% of production costs with inputs and utilities from this methodology. These results emphasize the use of the E2G processing (hydrothermal pretreatment followed by enzymatic hydrolysis) in the upstream for the generation of CNCs in sugarcane biorefineries.

The adaptations proposed for Case Study C2 methodology presented different responses regarding the variation in OPEX costs. In C3, in addition to the absent costs with H₂O₂, there was an increase in the mass of nanocrystals produced (as LCNCs) – it proportionally reduced both the costs and the returns from by-products per ton of LCNCs produced. In C4, the absence of sulfuric acid recovery process increased input costs by approximately 16% when compared to Case Study C2, mainly due to the higher consumption of H₂SO₄ and lime for neutralization. In turn, Case Study C5 presented little

reduction (~4%) in inputs costs due to the lower use of sugarcane bagasse, since it is not necessary to use it as fuel for the spray-dryer.

The costs of inputs and utilities per ton of produced CNMs for Case Studies C6 and C7 (that use citric acid in hydrolysis) are 30.4% and 40.6% higher than the costs in C2. Among the factors that led to this, the following ones can be highlighted: (1) the biomass concentration inside the hydrolysis reactors is lower than in the C2 Study Case, requiring higher volumes of citric acid for hydrolysis (BONDANCIA et al., 2020); (2) citric acid is a high-cost compound, and it is still necessary for makeup in the hydrolysis reactors; and (3) extensive uses of CaO and H₂SO₄ are necessary for the recovery of the organic acid, while gypsum is obtained as a by-product. Although the traditional method for citric acid purifying is the simplest and the most used industrially, as it results in low acid losses (4 to 5% of the total), the use of large amounts of chemical inputs and the generation of a solid, low value by-product still presents disadvantages that have not yet been overcome (MATTEY and KRISTIANSEN, 2002).

Figure 32 shows the OPEX for Case Studies C1 to C8 as annual operating costs and revenues from by-products. It can be seen that the annual costs in inputs and utilities for the C8 process with enzymatic hydrolysis are equivalent to these same costs generated in Case Studies C1 to C5. Yet, C8 presents a lower production of CNMs when compared to the other methodologies, resulting in higher OPEX costs per ton of CNMs produced (as seen in Figure 30). Studies C6 and C7, by the way, presented the highest annual operating costs (111% and 117% higher than in C2, respectively), mainly due to inputs necessary in the citric acid recovery process.

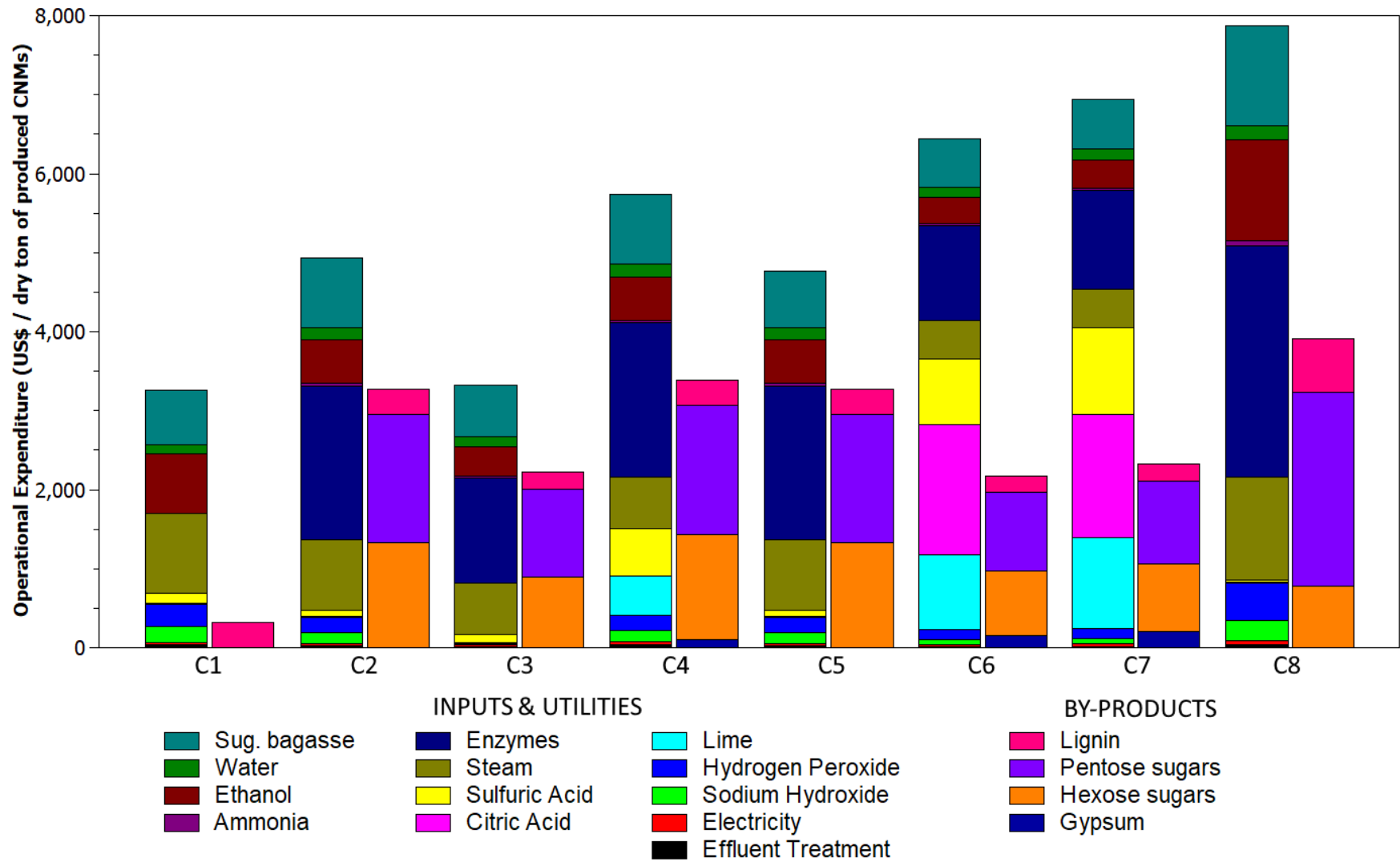


Figure 31 – Operational expenditure (US\$ per dry ton of produced CNMs) estimated for Case Studies C1 to C8.

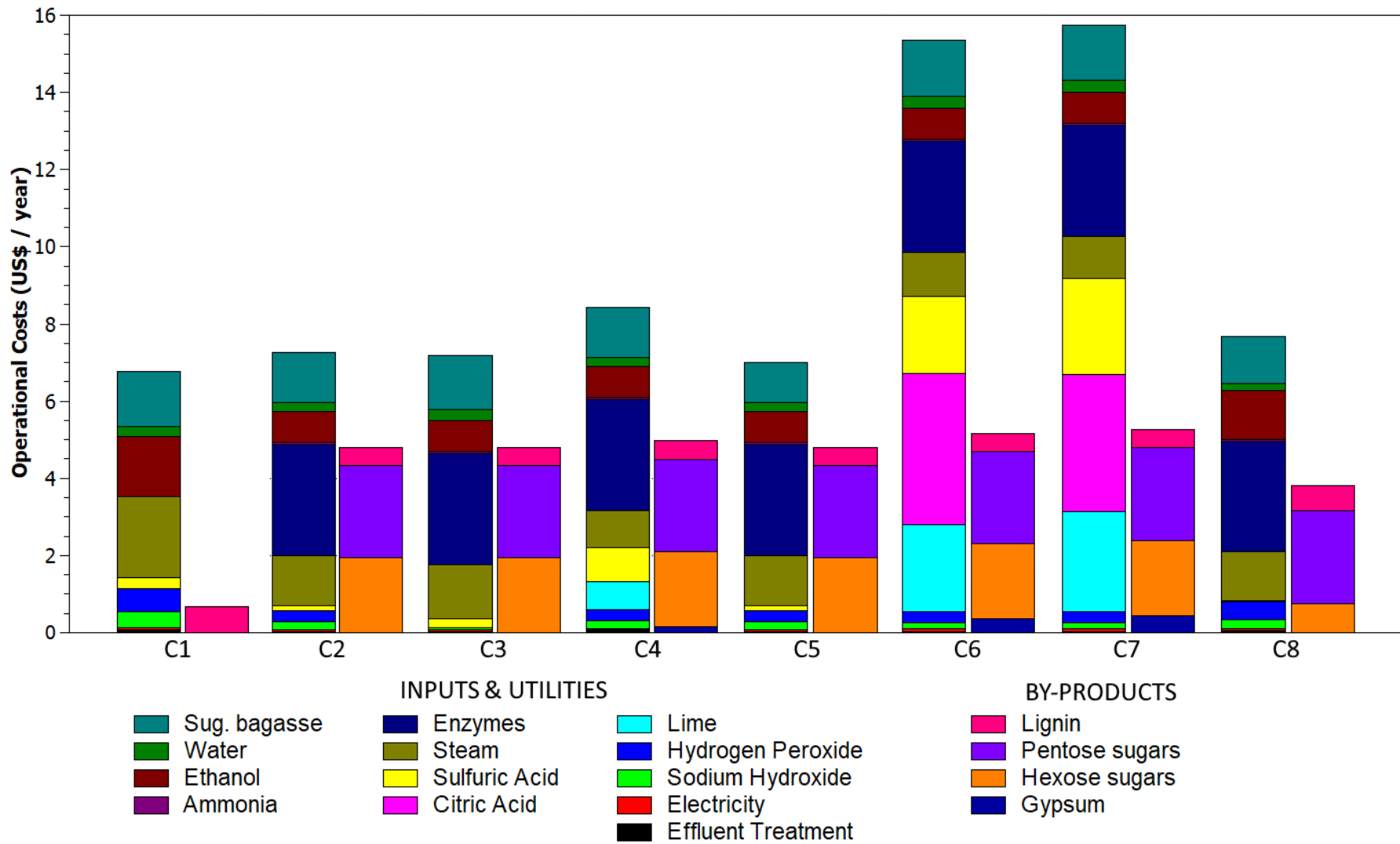


Figure 32 – Operational expenditure (US\$ million per year) estimated for Case Studies C1 to C8.

6.2.3 Cash Flow Analysis (CFA)

Table 25 details the most important data obtained through the Cash Flow Analysis (CFA) for all Case Studies analyzed in this work. The values obtained for the Minimum Selling Price of cellulose nanocrystals (MPSPs) are highlighted at the end of this table. MPSPs are obtained for the first year of operation of the incremental units (stated as the present year - 2021). Results for later years (years 2-25 of plant operation) are influenced by inflation and plant expansion factors (TURTON et al., 2009). This data is not shown, but their influence on MPSPs calculations was considered.

The lowest MPSP value was found for Case Study C3 at US\$ 4127 / dry equiv. ton of LCNCs. Otherwise, the highest MPSP was determined for route C8 at US\$ 11988 / dry ton of equivalent cellulose nanocrystals. The lower MPSP values obtained in sulfuric acid hydrolysis methodologies (Case Studies C1 to C5) highlight H₂SO₄ as an economically more suitable acid for the production of CNCs than citric acid. Acid hydrolysis with H₂SO₄ was developed in the 1940s and remains until today the state-of-art process to produce stable colloid suspensions of cellulose nanocrystals with negative charges (VANDERFLEET and CRANSTON, 2021). The Time of Return of Investment (TR) estimated for all the Case Studies was 11.2 years from the start date of the incremental CNMs unit project, i.e., 2028.

In Case Study C3, the removal of the alkaline delignification stage resulted in a MPSP value that is 31.5% lower than in Case Study C2. In fact, the C3 methodology produces lignin-rich cellulose nanocrystals (LCNCs), and not 95% dry-purity CNCs as in the other Case Studies. A brief comparison between the different functional characteristics and applications of CNCs and LCNCs is presented in the Introduction section of this work. LCNCs are indicated for specific applications, especially in matrices that require additives with greater hydrophobicity (TROVAGUNTA et al., 2021).

Albeit slightly, the MPSP obtained for Case Study C2 (US\$ 6029 / dry equiv. ton of CNCs) was lower than the MPSP obtained for Case Study C1 (US\$ 6323 / dry equiv. ton of CNCs), highlighting the *E2G bagasse* as an economically viable feedstock for the production of CNCs. Nevertheless, the difference between C1 and C2 MPSPs values was relatively low (US\$ 294 / dry equiv. ton of CNCs). Thus, the use of *raw bagasse* as main feedstock for CNCs production at biorefineries should not be a discarded option, especially if the biorefinery unit does not implemented an E2G processing process yet.

The absence of the sulfuric acid recovery steps in Case Study C4 resulted in a slight increase in MPSP values when comparing to Case Study C2 (5.5% higher). The lower CAPEX shown in Figure 30 for C4 ended up being offset by the excess costs in H₂SO₄ and in neutralization lime. Yet, the minimal difference between these MPSP values indicates that the feasibility of a unit operation without sulfuric acid recovery and recycling is close to the operation with the use of multi-stage evaporators, at least economically. This allows a sulfuric acid hydrolysis-based unit to alternate between these two arrangements according to the variation in the prices of steam, H₂SO₄ and lime in the market. Similar conclusions were found by Assis et al. (2017) when comparing scenarios with and without sulfuric acid recovery for the CNC production from cellulose kraft pulp.

One can verify in Figure 30 a substantial reduction in CAPEX costs for Case Study C5 (in relation to C2), as C5 operates without a spray-drying step. Consequently, C5 presents a decrease in MPSP (US\$ 5266 / dry equiv. ton of CNCs – 12.7% lower than C2 MPSP). However, it is important to highlight that nanocrystals suspensions present higher handling and transportation costs for the buyer. An analysis comparing the spray-drying costs with the higher logistical costs of CNCs aqueous suspensions can be found in the work by Assis et al. (2017). It is important to highlight that the use of CNMs in suspensions is more suitable for some product applications.

Case Studies C6 and C7 had 64% and 72.8% higher MPSPs than the that of Case Study C2 (respectively) despite the simultaneous production of CNFs (the minimum selling price of CNFs was set at 70% of the MPSP for CNCs). As shown in Figures 30, 31 and 32, the process methodologies that use citric acid in the biomass hydrolysis have higher CAPEX and also higher OPEX costs for production units. Given the higher CAPEX, the annual depreciation of equipment is also higher. And these factors imply in consequent increases in maintenance costs, labor, etc., while also demanding a higher working capital for the administrator. In order to balance the cash flow and meet the Minimum Attractiveness Rate of Return (MARR) of 11% for the investment, the total sales revenues need to be increased, and so, higher MPSPs values are needed for Case Studies C6 and C7.

Taking into account that the biomass *upstream* and *downstream* processes of Case Studies C2, C6 and C7 are similar, one can state that the use of the citric acid, and most importantly the recovery and recycling processes of this acid, imply in a remarkable increase in production costs, leading to the consequent increase in the MPSPs for the

products. As shown in Figures 31 and 32, the citric acid recovery through the conventional citrate precipitation route still represents a technological bottleneck in the production process, despite being used industrially for some time. Production routes using citric acid in hydrolysis, but with no acid recovery were also analyzed - however, given the high price of this input, the MPSPs obtained were higher than US\$ 30000 / dry metric ton of CNCs. In the last years, alternative citric acid recovery processes have been investigated in the Literature. Extraction processes using alcohols (such as propanol, pentanol and 2-octanol), synthetic solvents and tertiary amines have been presented as alternatives to the classical method (USLU, 2008; JU *et al.*, 2013; ARAÚJO *et al.*, 2017). The main advantage of the solvent extraction process is that it does not require the use of sulfuric acid and CaO in the recovery steps. However, the solvent extraction tends to extract impurities contained in the liquors beyond citric acid, so the liquors must contain a low number of impurities, and it is still necessary to optimize the process conditions in order to allow it to be successfully applied. Alternatively, the use of bipolar membrane electro dialysis (SUN *et al.*, 2017), adsorption with Poly(4-vinylpyridine) (VAN DEN BERGH *et al.*, 2017), reactive extraction (THAKRE *et al.*, 2017), and other processes (LI *et al.*, 2016b) have also been suggested in literature.

Despite having the lowest CAPEX costs among all the methodologies analyzed in this work (in agreement with the CAPEX results proposed by ROSALES-CALDERÓN *et al.*, 2021), Case Study C8 presented the highest MPSP among all Case Studies, practically doubling the MPSP cost of production by the acid hydrolysis route of Case Study C2. Although the cost of the enzymes is still a bottleneck in the process – Figure 31 shows that it has an estimated cost of US\$ 2926 / dry equiv. ton of CNCs produced - the low yield of this process in nanocrystals and nanofibers also contributed to a higher MPSP. Despite that, the low CAPEX to produce CNMs by enzymatic hydrolysis indicates that this process still needs R&D improvements to reach economic competitiveness with the sulfuric acid hydrolysis-based processes, mainly on the topics of enzyme costs and enzyme production yields.

Results in Table 25 show that the use of the sugarcane bagasse matrix for CNMs production is a promising alternative for adding value to the sugarcane industry. ASSIS *et al.* (2017) found an MPSP of US\$ 5125 / dry equivalent ton of CNCs for a production unit using Kraft pulp as feedstock, recycling of sulfuric acid from hydrolysis, and co-location to a pulp and paper plant. The values of MPSPs obtained in this work for 95%

purity (by mass) CNCs production are higher than this one (17.6% higher in Case Study C2, for example). However, one should consider that the production of CNCs from cellulose pulp has been investigated in Literature for some time, so the process is already optimized in a higher degree and uses a pre-delignified feedstock. Another aspect to consider is that the production of CNMs in sugarcane biorefineries use a residue as feedstock, and it certainly reduces impacts to the environment when compared to pulp-derived CNMs. The work of CAMARGO *et al.* (2016) was the first to demonstrate the technical feasibility of producing CNCs as a co-product of the second-generation ethanol process using *E2G bagasse* as feedstock.

It is important to point out that the physicochemical characteristics of nanocellulose varieties may vary according to the production process, and mainly due to the hydrolysis methodology that was employed (VANDERFLEET & CRANSTON, 2021; JIANG *et al.*, 2021). MPSP, despite being a very useful metric for comparing economic feasibilities of production technologies, cannot measure the demand market influences – the development of applications that require specific physicochemical characteristics of nanocellulose can severely change the final market price of the product. REID *et al.* (2016) studied the influence of different hydrolysis methods and conditions in the properties of the CNC products, and also the influence of scaling-up production in the nanocellulose characteristics. Cellulose feedstocks, hydrolysis conditions and downstream processing pathways impacted the properties and ultimately determined suitable applications for CNCs based on different rheological, colloidal, interfacial and reinforcing properties. The authors also found that the scale-up of the process for the case of sulfuric acid hydrolyzed CNCs had minimal impact on the nanocellulose chemical and physical properties, giving a good indication that the transition from lab scale to industrial CNCs production could be effectively achieved.

Currently, the production of nanocellulose is still a developing, incipient industry, and CNCs are produced industrially by ten organizations, which have pilot, demonstration or semi-industrial plant facilities with production capacities in the kilogram-per-day to ton-per-day range (Figure 12) (VANDERFLEET & CRANSTON, 2021).

Table 25 – Main results of the Cash Flow Analysis for the Case Studies C1 to C8. Values are in US\$ millions when not explicitly mentioned.

Case Study	C1	C2	C3	C4	C5	C6	C7	C8
Total Equipment Cost (TC)	23.74	21.15	21.75	18.83	17.65	25.41	25.59	17.76
Project Execution Costs (PEC)	11.63	10.36	10.66	9.23	8.65	12.45	12.54	8.70
Capital Expenditure (CAPEX)	35.37	31.52	32.40	28.06	26.30	37.86	38.14	26.47
Sales Revenues Totals on First Full Operational Year (2022)	14.45	14.32	14.40	15.00	13.14	24.23	24.72	13.90
Inputs & Utilities Costs on First Full Operational Year (2022)	7.08	7.60	7.53	8.83	7.34	16.08	16.50	8.04
Capital Reinvestment Costs on First Full Operational Year (2022)	0.38	0.34	0.35	0.31	0.29	0.41	0.41	0.29
Annual Plant Depreciation on First Full Operational Year (2022)	3.57	3.18	3.27	2.84	2.66	3.83	3.85	2.67
Total Indirect Costs on First Full Operational Year (Excluding Depreciation) (2022)	2.08	2.11	2.14	2.02	1.93	2.49	2.51	1.95
Earnings Before Interest and Taxes (EBIT) on First Full Operational Year (2021)	1.57	1.42	1.46	1.31	1.21	1.84	1.86	1.23
Working Capital on First Full Operational Year (2022)	1.51	1.50	1.51	1.57	1.38	2.54	2.59	1.46
Annual Cash Flow on First Full Operational Year (2022)	4.15	3.71	3.81	3.32	3.11	4.51	4.55	3.13
CNMs Production (dry equivalent tons) on First Full Operational Year (2022)	CNCs: 2074	CNCs: 1468	LCNCs: 2164	CNCs: 1468	CNCs: 1468	CNCs: 484 CNFs: 1998	CNCs: 579 CNFs: 1688	CNCs: 352 CNFs: 656
Minimum Product Selling Price (MPSP) in 2020 (US\$ per dry equivalent ton of CNCs or LCNCs)	6323	6029	4127	6363	5266	9912	10416	11988

6.2.4 Sensitivity Analysis of Parameters

Figure 33 presents tornado-shaped diagrams that represent the results obtained in the Sensitivity Analysis of Parameters on MPSP for the C1 and C2 Case Studies (both using sulfuric acid hydrolysis), while Figure 34 shows results for C6 (citric acid hydrolysis) and C8 (enzymatic hydrolysis) Case Studies. Costs of inputs and process utilities, returns with the sale of by-products, process parameters and economic premises were selected as analysis inputs. All inputs were considered independent from each other.

It can be seen in Figure 33 that steam consumption is the process parameter with the greatest influence on the MPSP value for Case Study C1 (US\$ \pm 268 / dry ton of equiv. CNCs for a \pm 25% variation in price input), followed by the cost of the ethanol solvent (US\$ \pm 199) and the cost of the sugarcane bagasse (US\$ \pm 181). These results emphasize the great dependence of the C1 methodology in relation to the organosolv pretreatment, since no previous step for biomass fractionation and delignification is carried out. In the C2 Case Study, by the way, the enzymes cost for the hydrolysis of the hydrothermally pretreated lignocellulosic matrix was the input parameter with the greatest sensitivity in the MPSP of CNCs (US\$ \pm 507). Enzymatic hydrolysis in the sugarcane biorefinery generates the solid, highly crystalline matrix that can be used for the nanocellulose production (*E2G bagasse*), but also produces fermentable sugars. The prices of these sugars (pentoses and hexoses fractions) also presented high sensitivity in the MPSP, once the mass outflow of these by-products is relatively high (US\$ \pm 407 and US\$ \pm 331, respectively). The price of sugarcane *raw bagasse*, the primary feedstock, also presented a considerable sensitivity in the MPSP. For the C2 case, for example, a reduction in the bagasse cost by 25% from the initial estimated cost value would imply in a reduction of MPSP to US\$ 5799 / dry equivalent ton of CNCs, while a 25% increase in the same cost would lead to an MPSP of \$ 6259 / dry equivalent ton of CNCs. The effective recycling of sulfuric acid in Case Studies C1 and C2 makes the input of H₂SO₄ necessary in low amounts of make-up, so that its influence on MPSP was negligible (US\$ \pm 36 and US\$ \pm 22, respectively).

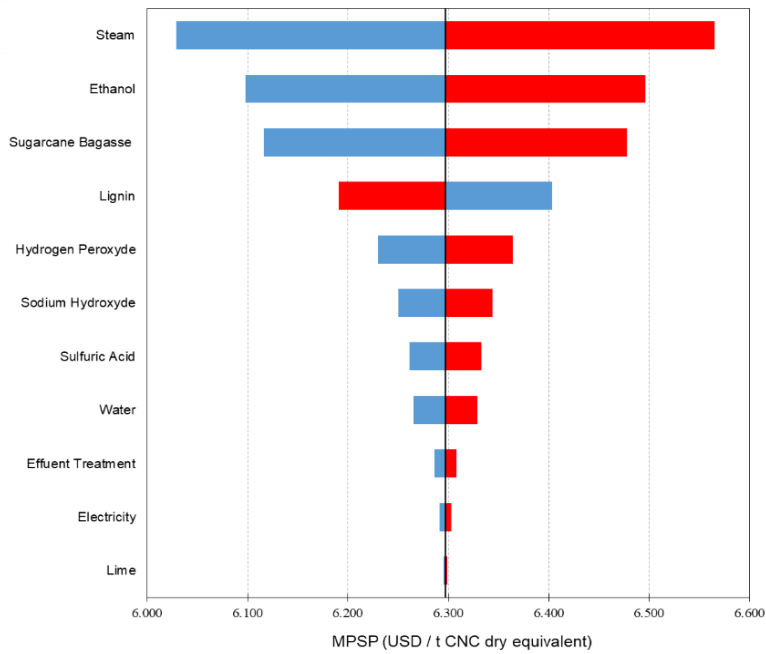
In Case Study C6, the variation of \pm 25% in the citric acid cost had the highest impact in the MPSP of CNCs (US\$ \pm 565), followed by the enzymes cost (US\$ \pm 411). This highlights the importance of the citric acid recovery methodology, although the latter also generates significant extra costs to the process - there is a noteworthy influence of lime (US\$ \pm 323) and sulfuric acid (US\$ \pm 286) prices on the MPSP of Case Study C6

due to the extensive use of these inputs. In Case Study C8, where enzymatic hydrolysis is used for the generation of CNMs, the cost of the enzyme cocktail (US\$ ± 942) had the greatest influence on the MPSP value.

The extensive use of steam in some stages of nanocellulose processing generates a sensitive impact of this utility cost in the MPSPs. Also, the high sensitivities of MPSP to the ethanol cost emphasizes the importance of flashing and distillation stages for this solvent recovery. Some other process inputs, such as the alkaline delignification agents, had lesser sensitive influence on the MPSPs. Process water, despite being extensively used, also did not represent high sensitivity impacts in the minimum selling prices of CNCs. In the Case Study C4, the absence of hydrolysis acid recovery caused the ± 25% in prices of H₂SO₄ (US\$ ± 156) and lime (US\$ ± 129) to influence more on MPSP in comparison with C2 results, also with minored influence of the cost of steam (US\$ ± 171).

Figures 33 and 34 also illustrate the sensitivity impacts on MPSPs of process parameters and economic assumptions for the C1, C2, C6 and C8 Case Studies. Among the process parameters, there is a significant impact of the acid hydrolysis yields for CNCs and CNFs, indicating that R&D should focus on the optimization at this stage. The price ratio between CNC and CNF also had high impact on MPSPs for C6 and C8 Case Studies. However, this parameter is very market-dependent, as the prices of these two varieties of CNMs tend to be determined by the real-world applications of each one. The Minimum Attractiveness Rate (MARR) was a parameter for which the MPSP was very sensitive in all Case Studies. Given the interest rate reduction policies applied to the economies of many countries in recent times, the reduction in the arbitrated MARR to 7.5% would decrease MPSPs of C1, C2, C6 and C8 Case Studies to US\$ 5483, US\$ 5016, US\$ 8916, and US\$ 10392 / dry equiv. ton of CNCs, representing 12.9%, 16.8%, 10.0% and 13.3% of reductions, respectively. Variations in the estimated value for CAPEX (± 25%) and the number of annual days of operation of the units (185 and 215 days, due to the sugarcane harvesting time fluctuations) also had considerable impacts on MPSPs.

C1



C2

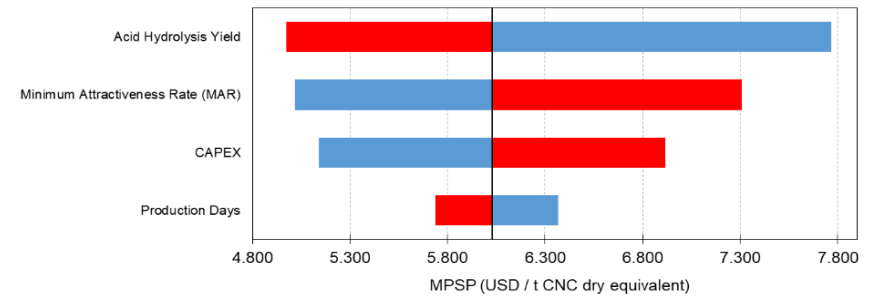
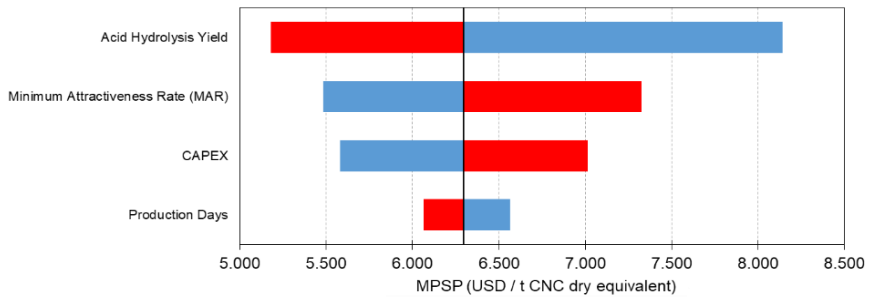
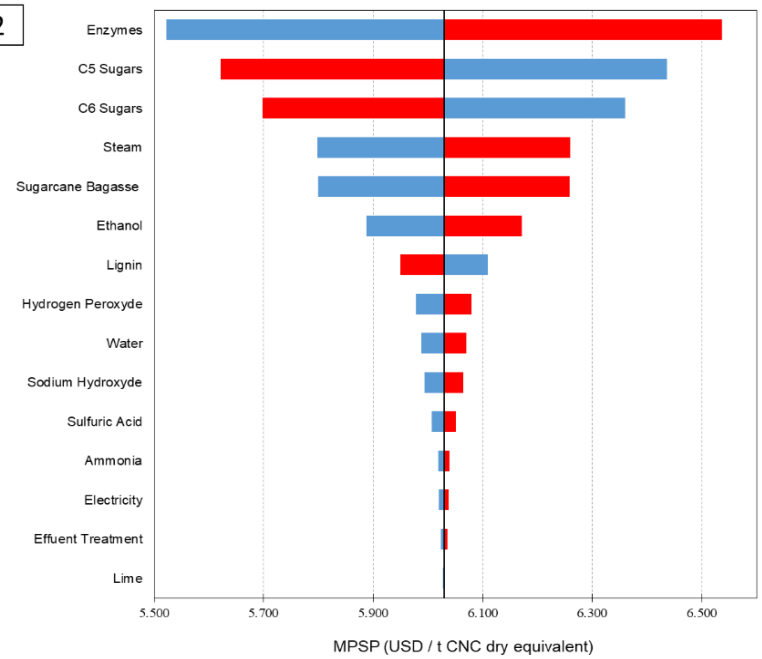


Figure 33 - Tornado-shaped graph results for the Sensitivity Analysis of Parameters on MPSP. Process inputs, utilities and by-products ($\pm 25\%$ variations) (top) and main process parameters and financial assumptions (bottom) were analyzed for Case Studies C1 (left) and C2 (right). Blue bars refer to decreasing values, while red bars refer to increasing values of parameters.

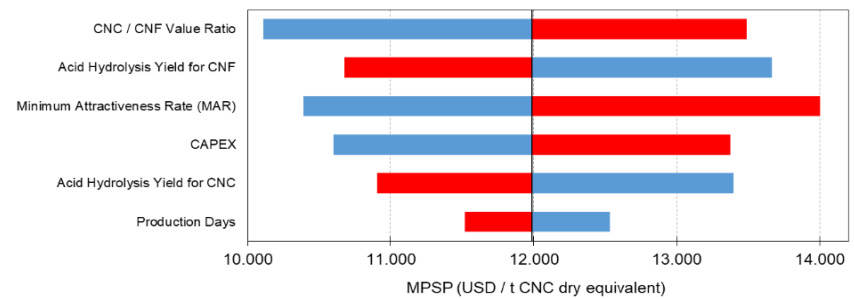
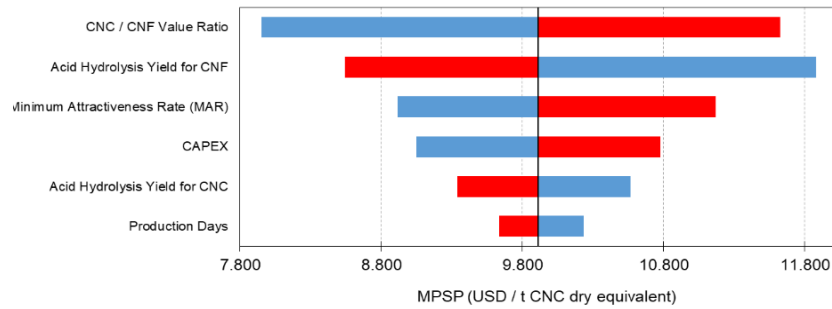
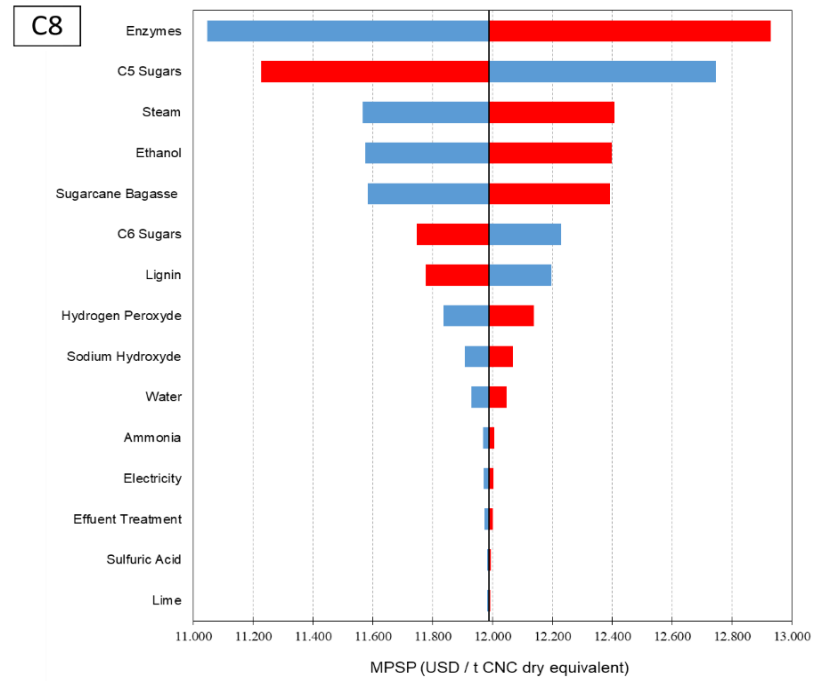
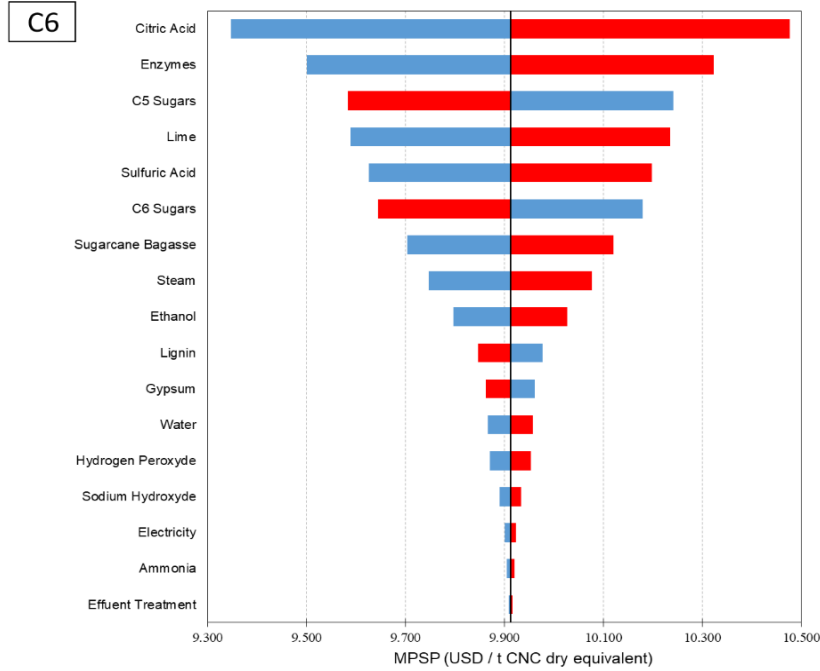


Figure 34 - Tornado-shaped graph results for the Sensitivity Analysis of Parameters on MPSP. Process inputs, utilities and by-products ($\pm 25\%$ variations) (top) and main process parameters and financial assumptions (bottom) were analyzed for Case Studies C6 (left) and C8 (right). Blue bars refer to decreasing values, while red bars refer to increasing values of parameters.

6.2.5 Probabilistic Risk Assessment of Parameters

The major impacting parameters obtained in the Parametric Sensitivity Analysis of each Case Study were selected for the Probabilistic Risk Assessment of parameters by Monte-Carlo Simulations. The deterministic, defined inputs were assumed as triangular statistical distributions, with the same minimum and maximum limits of the respective Parameter Sensitivity Analysis. For each Case Study, a total of 10000 Monte-Carlo simulation cases were performed using *Crystal Ball*[®] software. The probability distribution found for the MPSP of cellulose nanocrystals on Case Study C2 is shown in Figure 35, while Figures A6 to A12 of the annexes show the Monte-Carlo probability distributions of MPSPs for the C1 and C3 to C8 Case Studies. The graphs highlight in blue color the statistical response intervals for a 95% confidence level, providing worst-case scenario and best-case scenario values for the MPSP of each Case Study.

Results of Monte-Carlo simulations showed profiles of MPSPs that are close to normal distributions, with the curve top slightly offset in relation to the MPSP values determined in TEA. Table 26 summarizes the worst-case scenarios and best-case scenarios for MPSP values for a 95% confidence level in Case Studies C1 to C8. For example, the estimated worst-case scenario for MPSP in the C2 Case Study was US\$4546 / dry equiv., ton of CNCs, while the best-case scenario was US\$ 8016 / dry equiv. ton. At 95% confidence level, the value of MPSP for CNMs production from sugarcane bagasse in the upper limits was found for Case Study C8 (US\$ 15935 / dry equiv. ton CNCs), and the MPSP in lower limits was obtained for Case Study C4 (US\$ 3130 / dry equiv. ton of CNCs). Although market demand factors (the discovery of a promising application, for example) are also very important to be considered in this case, the values presented in Table 26 are important for investment analysis and decision by the stakeholders.

Table 26 – Best-case and worst-case scenarios (95% confidence) for MPSP values in a Monte-Carlo Probabilistic Risk Assessment for each Case Study of this work.

Case Study	MPSP best case scenario (95%)	MPSP worst case scenario (95%)	Case Study	MPSP best case scenario (95%)	MPSP worst case scenario (95%)
C1	5045	8120	C5	3962	7159
C2	4546	8016	C6	7702	12628
C3	3130	5505	C7	8175	13156
C4	4942	8341	C8	9291	15395

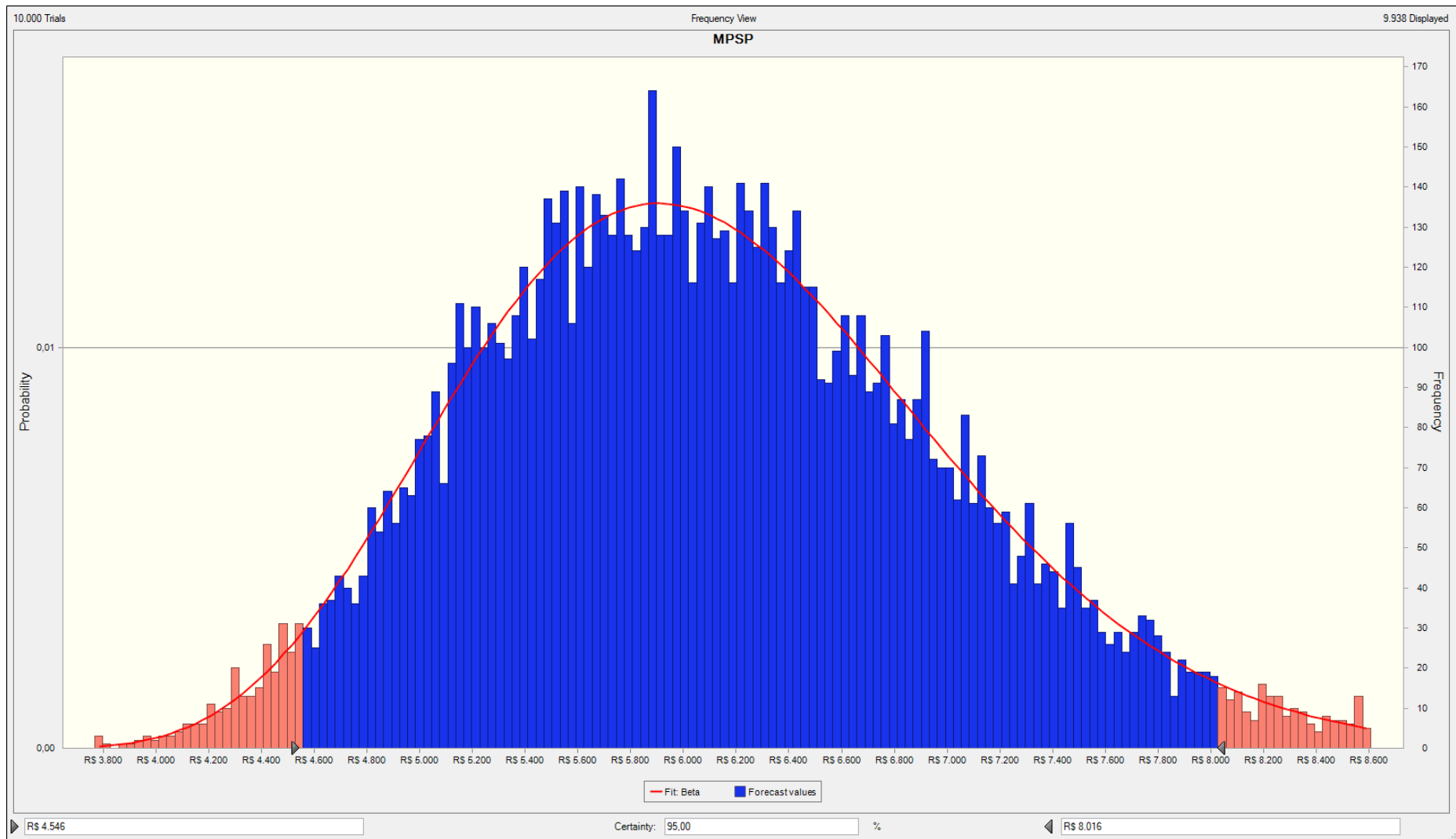


Figure 35 - Probabilistic Risk Assessment of Parameters by Monte-Carlo simulation for Case Study C2. Regions of the graph in blue denote ranges for which the MPSP can be expected with 95% statistical confidence.

6.3 Life-Cycle Assessment

Life Cycle Assessment (LCA) was carried out using data from Tables 19, 20, 21 and 23 (and other results from the modeling and mass and energy balances steps) as the Life Cycle inventory of inputs and outputs for processes. *SimaPro*[®] software was used to obtain the environmental impacts in different categories (*CML-IA Baseline v3.04 2000* method) for the selected Case Studies C2 (sulfuric acid hydrolysis of *E2G bagasse*), C4 (same as C2, but with no acid recovery), C6 (citric acid hydrolysis of *E2G bagasse*) and C8 (enzymatic hydrolysis of *raw bagasse*). The water usage and the GWP metric were selected for the comparison between CNMs production methodologies. Data from Table 18 was used to quantify the GWP of each process.

Table 27 shows the use in water for the methodologies of Case Studies C2, C4, C6 and C8, already considering the partial reuse of this utility. It can be seen that there is a high usage of water for all Case Studies, both in absolute inputs and by ton of CNMs produced. In Case Study C6, the highest water inflow is used - however, the higher yield of this process by *raw bagasse* primary feedstock makes the water intensity use the lowest among the selected cases. In the other hand, the low production in CNMs (CNCs + CNFs) in Case Study C8 makes the water intensity use of this process the highest among all cases analyzed.

Table 27 – Water usage for the methodologies proposed in Case Studies C2, C4, C6 and C8.

Case Study	C2	C4	C6	C8
Water usage (m ³ water / day)	1846	1871	2494	1443
Water intensity (m ³ water / ton CNMs)	239	242	199	281

Figure 36 shows a breakdown of the Global Warming Potential (GWP) accumulated for each of the process inputs in the simulated incremental units of nanocelulose production of C2, C4, C6 and C8 Case Studies. The daily production of 7.73 tons of CNCs (added to the by-products) in the Case Studies C2 and C4 occurs with accumulated GWP of 25.8 and 33.7 tons of CO₂ equivalent, respectively. The production of 2.5 and 10.0 tons per day of CNC and CNF (respectively) in the case study C6, along with by-products, occurs with an accumulated GWP of 87.9 tons of CO₂ equivalent. Finally, in the Case Study C8, 25.0 tons of CO₂ equivalent are accumulated in the daily production of 1.9 tons of CNC and 3.3 tons of CNF, along with by-products.

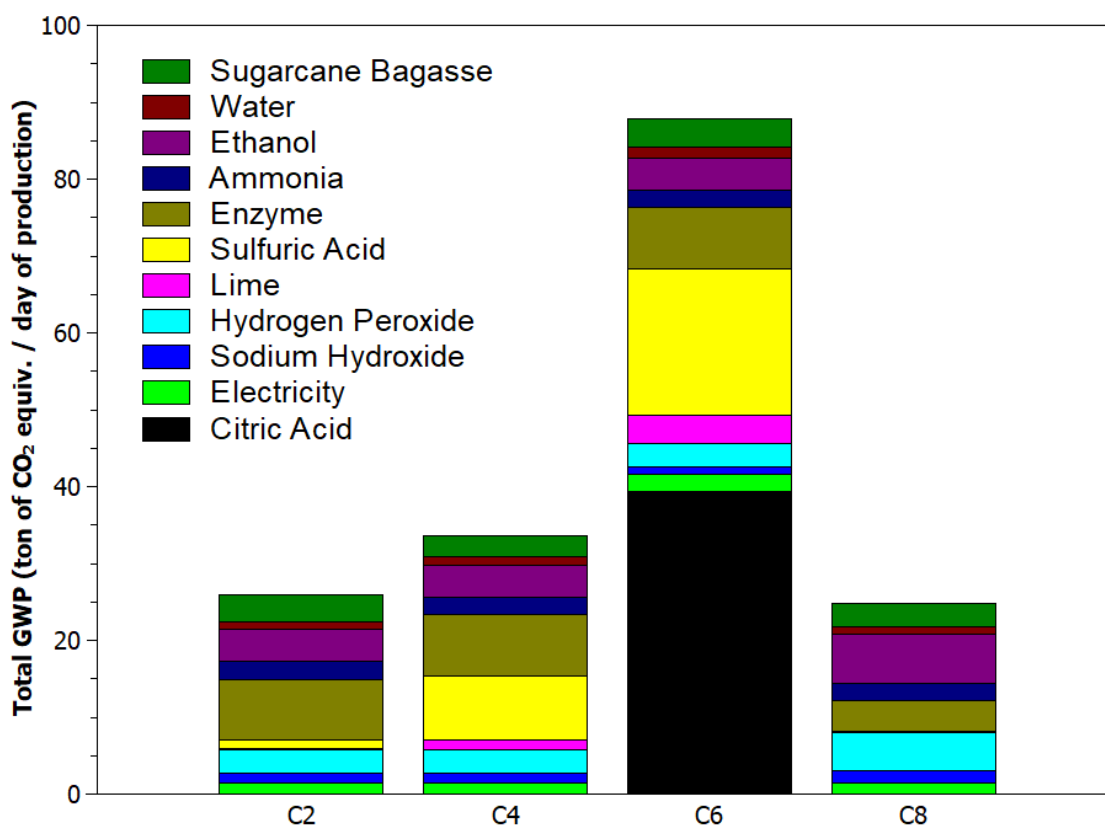


Figure 36 - Global Warming Potential (as ton of CO₂ equiv. accumulated per day) by unit sectors of C2, C4, C6 and C8 Case Studies (not allocated).

Figure 36 shows that the substitution of the sulfuric acid recovery stage by the acid neutralization in the downstream of Case Study C4 increases the accumulated GWP by 30% in relation to C2. Although less sugarcane bagasse is needed for steam generation, there is a remarkable increase in GWP by using higher amounts of sulfuric acid and lime. It is also seen that the CNMs generation process based on enzymatic hydrolysis (Case Study C8) presents the lowest total impacts on GWP among the analyzed methodologies, being slightly lower than on C2.

It can be seen that the use of the organic acid and the recovery steps of the organic hydrolysis acid generate a considerable environmental impact, adding up to approximately 70% of the calculated values for daily GWP emissions in Case Study C6. These process steps use large amounts of CaO and H₂SO₄ for the precipitation of insoluble calcium citrate and subsequent recovery, generating gypsum as a by-product. Comparing the Case Study C6 with the Case Study C2, which does not use organic acid and recycles the hydrolysis mineral acid, there is a ~3.4-fold increase in the amount of CO₂ equivalent accumulated per day of production using the organic acid. A remarkable

observation is that, even disregarding the other steps of the production cycle in the Case Study C2, the citric acid hydrolysis and recovery steps single-handedly generate a GWP impact that is greater than the one of full Case Study C2. At first, this result seems to go against common sense, since it is an organic acid. Although citric acid is a natural compound commonly associated with non-toxicity and renewability characteristics, its effective use for the application proposed in this work does not result in lower environmental impacts (at least the GWP-related), but the opposite.

Despite several reported environmental advantages of biochemicals, not all of these compounds are consistently more sustainable than functionally equivalent petrochemicals (ÖGMUNDARSON et al., 2020b). The classic process of manufacturing citric acid from fermentation by *Aspergillus niger* is intense in the use of inputs such as sugarcane molasses and in the use of industrial bioreactors. The environmental setbacks of the classic production process of citric acid by submerged fermentation (MATTEY & KRISTIENSEN, 2002) and of the recovery and recycling processes of this compound still constitute a challenge. Albeit most of the novel nanocellulose isolation processes are considered green and sustainable, the discussion on these ecological perspectives is commonly restricted to the recycling capacity and renewability of these processes. Yet, challenges with regard to environmental aspects related to the synthesis of biochemicals, water usage in upstream / downstream processes, mechanical energy consumption, and solvent loss during recycling are usually not addressed. An entire Life Cycle Assessment of nanocellulose isolation involving all solvents and chemicals should be conducted for a comprehensive and unbiased evaluation of the environmental impact of the newer, comparable technologies (JIANG et al., 2021). Complete Life Cycle Assessment studies are important to help R&D to understand which relevant hotspots (i.e., major steps with environmental problems) are occurring, and how input (resources and methodologies) and output (emissions into the environment) changes can reduce such hotspots (ÖGMUNDARSON et al., 2020a). Furthermore, despite the economic and environmental setbacks, the CNMs production by citric acid hydrolysis can contribute to a new generation of amphiphilic nanomaterials, also presenting good colloidal and thermal stability (YU et al., 2019).

From data in Figure 36, it was possible to make the energetic allocation of the GWP environmental impacts to products and by-products of each case study, that is, to allocate the impact data to the outputs of the process methodology. The results are shown

in Figure 37. For the LCA adopted functional unit (1 kg of CNMs as product), the results display that 0.216 kg, 0.281 kg, 0.705 kg and 0.249 kg of CO₂ equivalents are accounted in the production processes of the respective C2, C4, C6 and C8 Case Studies. Energetically, these results correspond to 12.47, 16.23, 40.75 and 14.36 g of CO₂ equiv. per MJ of process outputs, respectively. These values are relatively low when compared to processes that use fossil fuel derivatives and with some other bioprocesses (ÖGMUNDARSON *et al.*, 2021), indicating the relatively low GWP environmental impacts of the CNMs production technology from sugarcane bagasse in biorefineries.

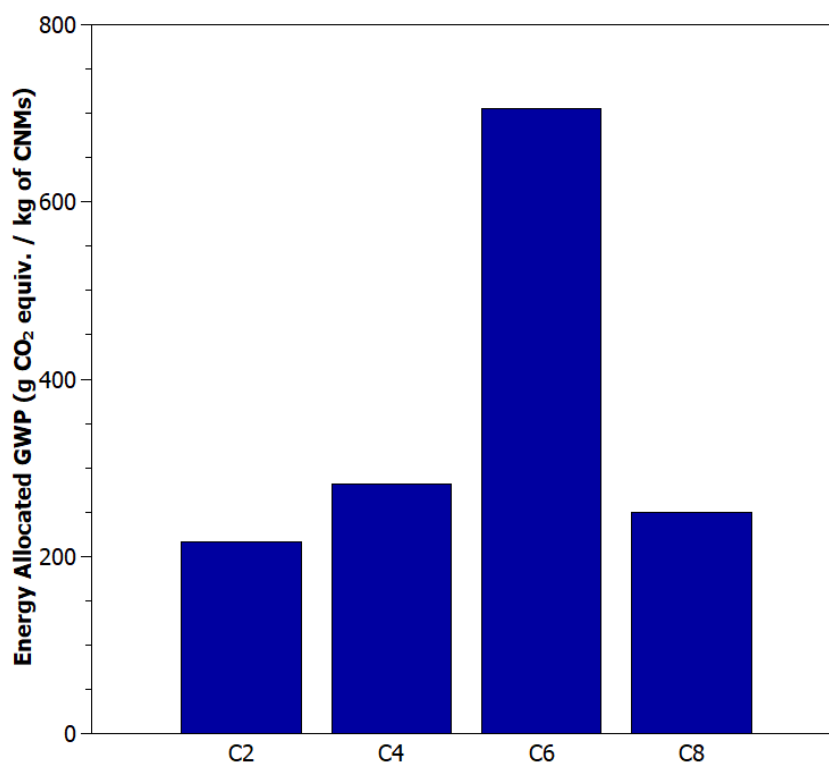


Figure 37 – Energy allocated Global Warming Potential (as ton of CO₂ equiv. accumulated per kg of process products and by-products) for the C2, C4, C6 and C8 Case Studies.

Life Cycle Assessments for the production of nanocellulose varieties using recycled hydrolysis solvents are scarce in literature. Despite the difference between GWP values for Case Studies using sulfuric acid, citric acid and enzymatic hydrolysis, the indices are comparable to those of previous works that evaluated nanocelulose production, such as those by HOHENTHAL *et al.* (2012) (750 - 3100 g of CO₂ equiv. / kg of CNCs by *TEMPO* oxidation / high-pressure homogenization of sulfite pulp), ARVIDSSON *et al.* (2015) (790 – 1200 g of CO₂ equiv. / kg of CNFs by enzymatic hydrolysis of wood pulp), and ALBARELLI *et al.* (2016) (870 g of CO₂ equiv. / kg of CNMs by sulfuric acid hydrolysis of sugarcane bagasse pretreated with SO₂-catalized

steam explosion). Some other works in the Literature (PICCINNO et al., 2018; TURK et al., 2020) presented higher GWP indices for nanocellulose obtaining, but one should consider that, in this work, the proposed methodology took place in a unit attached to a sugarcane biorefinery and used a residue as feedstock. When compared to other industrial processes, the GWP values for the production of nanocellulose varieties obtained in this work are reasonably in accordance to those of processes such as the extraction of soybean oil by hexane solvent (0.55 kg of CO₂ equiv. / kg of soybean oil - POTRICH *et al.*, 2019) and the production of biogas from anaerobic digestion of vinasse in a sugarcane biorefinery (0.498 kg of CO₂ equiv. / kg of ethanol - LONGATI et al., 2019).

Information about other impact categories (as abiotic depletion and ozone layer depletion) given by the *CML-IA Baseline v3.04 2000* method can be found in the Annexes in Figures A13 to A16 for C2, C4, C6 and C8 Case Studies, respectively. The use of acids for hydrolysis and recovery presented high impacts on the environment, according to *SimaPro*[®]. The high inputs of sulfuric acid in C4 and C6 end up generating high environmental impacts in categories such as ozone layer depletion, soil acidification and water ecotoxicity. More prominently, the impacts of H₂SO₄ inputs are equivalent to 96% and 90% of the total abiotic depletion of C4 and C6, respectively. In the Case Study C6, citric acid presented relevant environmental impacts in several categories, mainly with high accumulated GWP.

LCA is a useful tool to identify hotspots in environmental sustainability profiles of bio-based chemicals. 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 (VANDERFLEET & CRANSTON, 2021). Biochemical production faces economic and environmental challenges that need to be overcome to enable a viable and sustainable bioeconomy. There are combined analysis frameworks indicated in literature (ÖGMUNDARSON *et al.*, 2020) that consistently combine environmental and economic indicators to support optimized biochemical production at early development stages. These frameworks propose the monetization of environmental impacts that, added to the economic indicators of the process, can generate process indexes that be used in the investment analysis. Given the global appeal for government policies to reduce environmental damage, it is expected that the adoption of this type of combined framework will be important for the expansion of bioeconomy.

CHAPTER 7 – CONCLUSIONS AND OUTLOOK

The results shown in this work indicate investment opportunities for sugarcane biorefineries that plan to diversify their markets beyond sugar, ethanol and energy. Burning of sugarcane bagasse, despite the generation of steam and cogeneration electric energy to the use of plant, disables the obtaining of higher added-value biomass by-products. In a future of uncertain economic scenario for the bioproducts markets, the lack of portfolio diversification can have negative consequences for the sector.

An interesting approach in this case is the production of cellulose nanomaterials (CNMs) that are high value-added materials for which there is a prospect of high market expansion in the coming years. This work analyzed through Techno-Economic-Environmental Analysis eight spreadsheet-modeled methodologies for CNMs production using sugarcane bagasse as feedstock. The different Case Studies analyzed in this work highlighted the technical feasibility of production and estimate Minimum Selling Prices (MPSPs) for sugarcane biorefinery-derived cellulose nanomaterials between US\$ 4127 and US\$ 11988 / dry equiv. ton of CNCs, while the GWP environmental impacts were estimated between 0.216 and 0.705 kg of CO₂ equiv. per kg of CNMs, indicating that the use of the sugarcane bagasse matrix for CNMs obtaining is a promising alternative for adding value to the sugarcane industry. A process route that used the solid residue from the enzymatic hydrolysis of the E2G process as feedstock (Case Study C2) was noteworthy due to the obtaining of CNCs with 95% purity in an MPSP of US\$ 6029 per dry equiv. ton of CNCs, as it also generated C5 and C6 sugars as by-products for biorefinery utilization. Furthermore, Case Study C2 also presented the lowest environmental impact (allocated to produced CNMs) among the analyzed process routes, and MPSP of US\$ 4546 / dry equiv. ton of CNCs in the best-case scenario evaluated in a Monte-Carlo Risk Assessment with 95% statistical confidence. The best-case scenario MPSP for lignin-containing cellulose nanocrystals production (Case Study C3) was US\$ 3130 / dry equiv. ton of LCNCs, also with 95% statistical confidence.

This work highlighted some process methodologies that appear to be more promising for biorefinery-scale production, with the generation of by-products such as lignin and fermentable sugars. Yet, R&D for process improvement will be needed, mainly to increase the hydrolysis yield of CNMs. 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.

7.1 Future works suggestions

This work explored eight production methodologies for the production of different types of cellulose nanomaterials (CNCs, CNFs and LCNCs), in an incremental unit attached to a sugarcane biorefinery, and using sugarcane bagasse as raw material. However, the production routes for the biorefinery-generated cellulose nanomaterials were by no means exhausted. Some suggestions for future work related to this research area are listed below:

- Analysis of the CNMs production from the other residual biomass found in sugarcane biorefineries, i.e., the sugarcane straw;
- Evaluation of CNMs production methodologies that are different from those proposed in this work, such as the pretreatment of biomass by milling, steam explosion, or biological pretreatment, as well as alternative chemical methods for the generation of cellulose nanomaterials, such as *TEMPO* oxidation;
- Analysis of the production of microfibrillated cellulose (MFC) and microcrystalline cellulose (MCC), which also present extensive applicability and promising market expansion in the next years;
- Brazil, in addition to being a major producer of sugarcane and its derivatives, is also the largest producer of cellulose pulp in the world. Therefore, the techno-economic-environmental analysis of the production of CNMs from cellulose pulps, in different production routes, would be also important for the generation of value and market expansion of the national energy matrix. Some works have already presented relevant data in this field, such as those by BONDANCIA *et al.* (2020) and ROSALES-CALDERON *et al.* (2021).

CHAPTER 8 – REFERENCES

- AACE - AMERICAN ASSOCIATION OF COST ENGINEERS. **International Recommended Practice No. 18R-97**. 2011.
- AGARWAL, U. P. RALPH, S. A. REINER, R. S. HUNT, C. G. BAEZ, C. IBACH, R. HIRTH, K. C. **Production of high lignin-containing and lignin-free cellulose nanocrystals from wood**. *Cellulose*, v. 25, p. 5791-5805. Springer, Inc. 2018.
- AGNIHOTRI, S. JOHNSEN, I. A. BOE, M. S. OYAAS, K. MOE, S. **Ethanol organosolv pretreatment of softwood (*Picea abies*) and sugarcane bagasse for biofuel and biorefinery applications**. *Wood Science Technology*, v. 49, p. 881-896. Springer, Inc. 2015.
- AGUAYO, M. G. PÉREZ, A. F. REYES, G. OVIEDO, C. GACITÚA, W. GONZALEZ, R. UYARTE, O. **Isolation and characterization of cellulose nanocrystals from rejected fibers originated in the kraft pulping process**. *Polymers*, v. 10, p. 1145. MDPI Inc. 2018.
- ALBARELLI, J. BLÖSCH-PAIDOSH, A. SANTOS, D. T. MARÉCHAL, F. MEIRELES, M. A. A. **Environmental, energetic and economic evaluation of implementing a supercritical fluid-based nanocellulose production process in a sugarcane biorefinery**. *Chemical Engineering Transactions*, v.47, p. 49-54. The Italian Association of Chemical Engineering Inc. 2016.
- AMECO RESEARCH. **Global Nanocellulose Market Size, Regional Growth Analysis, Outlook and Forecast Data 2020-2027**. Available in: <<http://www.amecoresearch.com/market-report/nanocellulose-global-market-arr-2020-234365>>. Accessed on August 12, 2020.
- ANEEL – Agência Nacional de Energia Elétrica. **consumidores, consumo, receita e tarifa média – Classe de consumo**. Available in <<http://www2.aneel.gov.br/area.cfm?idArea=550>>. Accessed on April 22, 2021.
- ANGARITA, J. D. SOUZA, R. B. A. CRUZ, A. J. G. BISCAIA JR, E. C. SECCHI, A. R. **Kinetic modeling for enzymatic hydrolysis of pretreated sugarcane straw**. *Biochemical Engineering Journal*, v. 104, p. 10–19. Elsevier, Inc. 2015.
- ARANTES, V. DIAS, I. K. R. BERTO, G. L. PEREIRA, B. MAROTTI, B. S. NOGUEIRA, C. F. O. **The current status of the enzyme-mediated isolation and functionalization of nanocelluloses: production, properties, techno-economics, and opportunities**. *Cellulose*, v. 27, p. 10571-10630. Springer, Inc. 2020.
- ARAÚJO, E. M. R. COELHO, F. E. B. BALARINI, J. C. MIRANDA, T. L. S. SALUM, A. **Solvent extraction of citric acid with different organic phases**. *Advances in*

Chemical Engineering and Science, V. 7, P. 304-324. Scientific Research Publishing, Inc. 2017.

ARNI, S. A. **Extraction and isolation methods for lignin separation from sugarcane bagasse: a review.** Industrial Crops and Products, v. 115, p. 330-339. Elsevier, Inc. 2018.

ARVIDSSON, R. NGUYENAND, D. SVANSTRÖM, M. **Life cycle assessment of cellulose nanofibrils production by mechanical treatment and two different pretreatment processes.** Environmental Science and technology, v. 49, p. 6881-6890. American Chemical Society, Inc. 2015.

ASPEN PLUS. Software from AspenTech, Inc. Site: <<http://www.aspentech.com>>.

ASPEN PROCESS ECONOMIC ANALYZER. Software from AspenTech, Inc. Site: <<http://www.aspentech.com>>.

ASSIS, C. A. HOUTMAN, C. PHILLIPS, R. BILEK, E.M. ROJAS, O. J. PAL, L. PERESIN, M. S. JAMEL, H. GONZALEZ, R. **Conversion economics of forest biomaterials: risk and financial analysis of CNC manufacturing.** Biofuels, Bioproducts & Biorefining: Modeling and Analysis. Vol. 11, pg. 682-700. Society of Chemical Industry and John Wiley & Sons, Ltd. 2017.

AZEREDO, H. M. C. ROSA, M. F. MATTOSO, L. H. C. **Nanocellulose in bio-based food packaging applications.** Industrial Crops and Products, v. 97, p. 664-671. Elsevier, Inc. 2017.

BERGLUND, L. BREEDVELD, L. OKSMAN, K. **Toward eco-efficient production of natural nanofibers from industrial residue: eco-design and quality assessment.** Journal of Cleaner Production, V. 255, p.120274. Elsevier, Inc. 2020.

BILATTO, S. MARCONCINI, J. M. MATTOSO, L. H. C. FARINAS, C. S. **Lignocellulose nanocrystals from sugarcane straw.** Industrial Crops & Products, v. 157, p. 112938. Elsevier, Inc. 2020.

BIOETANOL. **Bioetanol de cana: energia para o desenvolvimento sustentável.** 316 p. Rio de Janeiro: BNDES and CGEE, 2008. Available in: <<http://www.bioetanoldecana.org>>. Accessed on January 20, 2018.

BLAIR, M. J. MABEE, W. E. **Techno-economic and market analysis of two emerging forest biorefining technologies.** Biofuels, Bioproducts and Biorefining. Society of Chemical Industry and John Wiley & Sons, Ltd. 2021.

BONDANCIA, T. J. CORRÊA, L. J. CRUZ, A. J. G. BADINO, A. C. MATTOSO, L. H. C. MARCONCINI, J. M. FARINAS, C. S. **Enzymatic production of cellulose nanofibers and sugars in a stirred-tank reactor: determination of impeller speed, power consumption, and rheological behavior.** Cellulose, v. 25, p. 4499-4511. Springer, Inc. 2018.

BONDANCIA, T. J. AGUIAR, J. BATISTA, G. CRUZ, A. J. G. MARCONCINI, J. M. MATTOSO, L. H. C. FARINAS, C. S. **Production of nanocellulose using citric acid in**

a biorefinery concept: effect of the hydrolysis reaction time and techno-economic analysis. *Industrial & Engineering Chemistry Research*, v. 59, p. 11505-11516. American Chemical Society, Inc. 2020.

BONDANCIA, T. J. **Biorrefinaria florestal: uma proposta para integração dos processos de obtenção de nanocelulose e etanol 2G a partir da polpa de celulose de eucalipto.** Masters Thesis. Programa de Pós-Graduação em Engenharia Química, Universidade Federal de São Carlos. 2016.

BORAND, M. N. KARAOSMANOĞLU, F. **Effects of organosolv pretreatment conditions for lignocellulosic biomass in biorefinery applications: A review.** *Journal of Renewable and Sustainable Energy*, v. 10, p. 033104. AIP Publishing, Inc. 2018.

BOTELLO, J. I. GILARRANZ, M. A. RODRÍGUEZ, F. OLIET, M. **Recovery of solvent and by-products from organosolv black liquor.** *Separation Science and Technology*, Ed. 34, v. 12, p. 2431-2445. Taylor & Francis, Inc. 1999.

CAMARGO, L. A. **Obtenção de nanocristais de celulose a partir do resíduo da produção de etanol do bagaço de cana-de-açúcar pela rota enzimática.** Masters Thesis. Programa de Pós-Graduação em Química, Universidade Federal de São Carlos. 2015.

CAMARGO, L. A. PEREIRA, S. C. CORREA, A. C. FARINAS, C. S. MARCONCINI, J. M. MATTOSO, L. H. C. **Feasibility of manufacturing cellulose nanocrystals from the solid residues of second-generation ethanol production from sugarcane bagasse.** *Bioenergy Research*, v. 9, p. 894–906. Springer, Inc. 2016.

CARPIO, L. G. T. SOUZA, F. S. **Optimal allocation of sugarcane bagasse for producing bioelectricity and second generation ethanol in brazil: scenarios of cost reductions.** *Renewable Energy*, v. 111, p. 771-780. Elsevier, Inc. 2017.

CARVALHO, M. L. SOUSA JR., R. RODRÍGUEZ-ZÚÑIGA, U. F. SUAREZ, C. A. G. RODRIGUES, D. S. GIORDANO, R. C. GIORDANO, R. L. C. **Kinetic study of the enzymatic hydrolysis of sugarcane bagasse.** *Brazilian Journal of Chemical Engineering*, v. 30, p. 437-447. Associação Brasileira de Engenharia Química, Inc. 2013.

CATALDI, A. CORCIONE, C. E. FRIGIONE, M. PEGORETTI, A. **Photocurable resin/nanocellulose composite coatings for wood protection.** *Progress in Organic Coatings*, v. 106, p. 128-136. Elsevier, Inc. 2017.

CELLULOSELAB. **2020 CelluloseLab nanocellulose products price.** Available in: <<https://www.celluloselab.com/price/CelluloseLab%20Product%20Price%20List%202020.htm>>. Accessed on August 10, 2021.

CONAB - National Supply Company of Brazil. **A geração termoeétrica com a queima do bagaço de cana-de-açúcar no brasil - análise do desempenho da safra 2017-2018.** Available in: <<https://www.gov.br/agricultura/pt-br/assuntos/sustentabilidade/agroenergia/arquivos-termoeletrica-com-a-queima-do->

bagaco-de-cana-de-acucar/termoeletrica-com-a-queima-do-bagaco-de-cana-de-acucar-no-brasil-safra-2017-2018.pdf>. Accessed on July 30, 2020.

CRYSTAL BALL. Software from Oracle, Inc. Site: <<http://www.oracle.com>>.

DE AGUIAR, J. BONDANCIA, T. J. CLARO, P. I. C. MATTOSO, L. H. C. FARINAS, C. S. MARCONCINI, J. M. **Enzymatic deconstruction of sugarcane bagasse and straw to obtain cellulose nanomaterials.** ACS Sustainable Chemistry & Engineering, v. 8, p-2287-2299. American Chemical Society, Inc. 2020.

DIAS, M. O. S. CUNHA, M. P. JESUS, C. D. F. ROCHA, G. J. M. PRADELLA, J. G. C. ROSSELL, C. E. V. MACIEL FILHO, R. BONOMI, A. **Second generation ethanol in Brazil: Can it compete with electricity production?** Bioresource Technology, v. 102, p. 8964-8971. Elsevier, Inc. 2011.

DIAS, M. O. S. JUNQUEIRA, T. S. CAVALETT, O. CUNHA, M. P. JESUS, C. D. F. ROSSELL, C. E. V. MACIEL FILHO, R. BONOMI, A. **Integrated versus stand-alone second generation ethanol production from sugarcane bagasse and trash.** Bioresource Technology, v. 103, p. 152-161. 2012.

DOMALSKI, E. S. JOBE JR., T. L. MILNE, T. A. **Thermodynamic data for biomass conversion and waste incineration.** National Bureau of Standards, US Department of Energy. 1986.

DOURADO, F. FONTÃO, A. LEAL, M. RODRIGUES, A. C. GAMA, M. **Chapter 12 - Process modeling and techno-economic evaluation of an industrial bacterial nanocellulose fermentation process.** Bacterial Nanocellulose: From Biotechnology to Bio-Economy. p. 199-214. Elsevier, Inc. 2016.

DUFRESNE, A. **Nanocellulose: From Nature to High Performance Tailored Materials.** 475 pages. Walter de Gruyter, Inc. 2012.

ELIAS, A. M. GIORDANO, R. C. SECCHI, A. R. FURLAN, F. F. **Integrating pinch analysis and process simulation within equation-oriented simulators.** Computers and Chemical Engineering, v. 130, p. 106555. Elsevier, Inc. 2019.

EMSO. Software from the ALSOC Project. Site: <<https://www.enq.ufrgs.br/trac/alsoc/wiki/EMSO>>.

EPE – EMPRESA DE PESQUISA ENERGÉTICA. **Compilação de correções de custos de equipamentos: instalações industriais de gás natural.** Ministério das Minas e Energia. Rio de Janeiro, 2018.

EXPERT MARKET RESEARCH. **Global nanocellulose market outlook.** Available in: <<https://www.expertmarketresearch.com/reports/nanocellulose-market>>. Accessed on May 30, 2021.

EWULUNU, C. M. LIU, X. WU, M. YONG, H. **Lignin-containing cellulose nanomaterials: a promising new nanomaterial for numerous applications.** Journal of Bioresources and Bioproducts, v. 4(1), p. 3-10. KeAI Publishing. 2019.

FARINAS, C. S. MARCONCINI, J. M. MATTOSO, L. H. C. **Enzymatic conversion of sugarcane lignocellulosic biomass as a platform for the production of ethanol, enzymes and nanocellulose.** Journal of Renewable Materials, v. 6, p. 203-216. Scrivener Publishing, LLC. 2018.

FENG, Y. H. CHENG, T. Y. YANG, W. MA, P. T. HE, H. YIN, X. YU, X. **Characteristics and environmentally friendly extraction of cellulose nanofibrils from sugarcane bagasse.** Industrial Crops & Products, v. 11, p. 285-291. Elsevier, Inc. 2018.

FERREIRA, F. V. MARIANO, M. RABELO, S. C. GOUVEIA, R. F. LONA, L. M. F. **Isolation and surface modification of cellulose nanocrystals from sugarcane bagasse waste: From a micro- to a nano-scale view.** Applied Surface Science, v. 436, p. 1113-1122. Elsevier, Inc. 2018.

FERREIA, R. G. AZZONI, A. R. FREITAS, S. **On the production cost of lignocellulose-degrading enzymes.** Biofuels, Bioproducts and Biorefining, v. 15(1), p. 85-99. Society of Chemical Industry and John Wiley & Sons, Ltd. 2020.

FERRER, A. PAL, L. HUBBE, M. **Nanocellulose in packaging: Advances in barrier layer technologies.** Industrial Crops and Products, v. 95, p. 574-582. Elsevier, Inc. 2017.

FISHERSOLVE. Software from Fisher International, Inc. Site: <<http://www.fisheri.com>>.

FOROUGH, F. GHOMI, E. R. DEHAGHI, F. M. BORAYEK, R. RAMAKRISHNA, S. **A review on the life cycle assessment of cellulose: from properties to the potential of making it a low carbon material.** Materials, v. 14, p. 714-736. MDPI, Inc. 2021.

FOSTER, E. J. MOON, R. J. AGARWAL, U. P. BORTNER, M. J. BRAS, J. CAMARERO-ESPINOSA, S. CHAN, K. J. CLIFT, M. J. D. CRANSTON, E. D. EICHHORN, E. J. FOX, D. M. HAMAD, W. Y. HEUX, L. JEAN, B. KOREY, M. NIEH, W. ONG, K. J. REID, M. S. RENNECKAR, S. ROBERTS, R. SHATKIN, J. A. SIMONSEN, J. STINSON-BAGBY, K. WANASEKARA, N. YOUNGBLOOD, J. **Current characterization methods for cellulose nanomaterials.** Chemical Society Reviews, v. 47, p. 2609-2679. The Royal Society of Chemistry, Inc. 2018.

FURLAN, F. F. COSTA, C. B. B. FONSECA, G. C. SOARES, R. P. SECCHI, A. R. CRUZ, A. J. G. GIORDANO, R. C. **Assessing the production of first and second generation bioethanol from sugarcane through the integration of global optimization and process detailed modeling.** Computers and Chemical Engineering, v. 43, p. 1-9. Elsevier, Inc. 2012.

FURLAN, F. F. TONON FILHO, R. PINTO, F. H. P. B. COSTA, C. B. B. CRUZ, A. J. G. GIORDANO, R. L. C. GIORDANO, R. C. **Bioelectricity versus bioethanol from sugarcane bagasse: is it worth being flexible?** *Biotechnology for Biofuels*, v. 6, p. 142. BioMed Central Ltd. 2013.

FURLAN, F. F. GIORDANO, R. C. COSTA, B. B. C. SECCHI, A. R. WOODLEY, J. M. **Process alternatives for second generation ethanol production from sugarcane bagasse.** 12th International Symposium on Process Systems Engineering and 25th European Symposium on Computer Aided Process Engineering, Copenhagen, Denmark. Elsevier, Inc. 2015.

FURLAN, F. F. COSTA, C. B. B. SECCHI, A. R. WOODLEY, J. M. GIORDANO, R. C. **Retro-techno-economic analysis: using (bio)process systems engineering tools to attain process target values.** *Industrial & Engineering Chemistry Research*, v. 55, p. 9865-9872. American Chemical Society, Inc. 2016.

GEORGE, J. RAMANA, K. V. BAWA, A. S. SIDDARAMAIAH. **Bacterial cellulose nanocrystals exhibiting high thermal stability and their polymer nanocomposites.** *International Journal of Biological Macromolecules*, v. 48 (1), p. 50-57. Elsevier, Inc. 2011.

GHAZYA, M. B. ESMAILA, F. A. EL-ZAWAWYB, W. K. AL-MAADEED, M. A. OWDA, M. E. **Extraction and characterization of Nanocellulose obtained from sugarcane bagasse as agro-waste.** *Journal of Advances in Chemistry*, v. 12, p. 4256-4264. Council for Innovative Research, Inc. 2016.

GOND, R. K. GUPTA, M. K. **A novel approach for isolation of nanofibers from sugarcane bagasse and its characterization for packaging applications.** *Polymer Composites*, v. 41(12), p. 5216-5226. Society of Plastics Engineers, Inc. 2020.

HABIBI, Y.; LUCIA, L. A.; ROJAS, O. J. **Cellulose nanocrystals: chemistry, self-assembly, and applications.** *Chemical Reviews*, v. 110(6), p. 3479-3500. American Chemical Society, Inc. 2010.

HAYWOOD, J. M. COOPER, C. D. **The economic feasibility of using hydrogen peroxide for the enhanced oxidation and removal of nitrogen oxides from coal-fired power plant flue gases.** *Journal of the Air & Waste Management Association*, v. 48(3), p. 238-246. Air & Waste Management Association, Inc. 1998.

HERVY, M. EVANGELISTI, S. LETTIERI, P. LEE, K. Y. **Life cycle assessment of nanocellulose-reinforced advanced fibre composites.** *Composites Science and Technology*, v. 118, p. 154-162. Elsevier, Inc. 2015.

HIGA, F. G. R. TAMBOURGI, E. B. GIANNETTI, A. A. M. **Aplicação do peróxido de hidrogênio como reforço da deslignificação do bagaço de cana-de-açúcar.** *Exacta*, v. 10(2), p. 281-288. 2012.

- HONGRATTANAVICHIT, I. AHT-ONG, D. **Nanofibrillation and characterization of sugarcane bagasse agro-waste using water-based steam explosion and high-pressure homogenization.** *Journal of Cleaner Production*, v. 277, p. 123471. Elsevier, Inc. 2020.
- HUBBE, M. A. ROJAS, O. J. LUCIA, L. A. SAIN, M. **Cellulosic nanocomposites: a review.** *Bioresources*, v. 3, p. 929-980. 2008.
- HUNTLEY, C. J. CREWS, K. D. ABDALLA, M. A. RUSSELL, A. E. CURRY, M. L. **Influence of strong acid hydrolysis processing on the thermal stability and crystallinity of cellulose isolated from wheat straw.** *International Journal of Chemical Engineering*, v. 2015, p. 658163. Hindawi Publishing Corporation, Inc. 2015.
- IBICT - Instituto Brasileiro de Informação em Ciência e Tecnologia. **Desenvolvimento Sustentável e Avaliação do Ciclo de Vida.** CNI. Brasília, 38 p. 2014.
- ISO 14040:2006. **Environmental management – Life Cycle Assessment – Principles and framework.** International Organization for Standardization, p. 1-20. 2006.
- ISO 14044:2006. **Environmental management – Life Cycle Assessment - Requirements and guidelines.** International Organization for Standardization, p. 1-54. 2006.
- ISO TS 20477:2017. **Nanotechnologies — Standard terms and their definition for cellulose nanomaterial.** International Organization for Standardization, p. 1-7. 2017.
- JI, H. XIANG, Z. QI, H. HAN, T. PRANOVICH, A. SONG, T. **Strategy towards one-step preparation of carboxylic cellulose nanocrystals and nanofibrils with high yield, carboxylation and highly stable dispersibility using innocuous citric acid.** *Green Chemistry*, v. 21, p. 1956-1964. The Royal Society of Chemistry, Inc. 2019.
- JIANG, J. ZHU, Y. JIANG, F. **Sustainable isolation of nanocellulose from cellulose and lignocellulosic feedstocks: recent progress and perspectives.** *Carbohydrate Polymers*, v. 267, p. 118188. Elsevier, Inc. 2021.
- JU, H. WEI, Q. REN, X. CHEN, Y. DONG, H. **Study on solvent extraction of citric acid from fermentation broth.** *Advanced Materials Research*, v. 781-784, p. 1915-1922. Trans Tech Publications, Inc. 2013.
- KAMM, B. KAMM, M. **Principles of biorefineries.** *Applied Microbiology and Biotechnology*, v. 64, p. 137-145. Springer-Verlag, Inc. 2004.
- KARP, S. G. WOICIECHOWSKI, A. L. SOCCOL, V. T. SOCCOL, C. R. **Pretreatment strategies for delignification of sugarcane bagasse: a review.** *Brazilian Archives of Biology and Technology*, v. 56(4), p. 679-689. 2013.
- KLEIN, B. C. CHAGAS, M. F. JUNQUEIRA, T. L. REZENDE, M. C. A. F. CARDOSO, T. F. CAVALETTI, O. BONOMI, A. **Techno-economic and environmental assessment of renewable jet fuel production in integrated Brazilian sugarcane biorefineries.** *Applied Energy*, v. 209, p. 290-305. Elsevier, Inc. 2018.

- KUMAR, A. NEGI, Y. S. CHOUDHARY, V. BHARDWAJ, N. K. **Characterization of cellulose nanocrystals produced by acid-hydrolysis from sugarcane bagasse as agro-waste.** Journal of Materials Physics and Chemistry, v. 2(1), p.1-8. Science and Education Publishing, Inc. 2014.
- LAM, N. T. CHOLLAKUP, R. SMITTHIPONG, W. NIMCHUA, T. SUKYAI, P. **Characterization of cellulose nanocrystals extracted from sugarcane bagasse for potential biomedical materials.** Sugar Tech, v. 19(5), p. 539-552. Springer, Inc. 2017.
- LEÃO, R. M. MILÉO, P. M. MAIA, J. M. M. L. LUZ, S. M. **Environmental and technical feasibility of cellulose nanocrystal manufacturing from sugarcane bagasse.** Carbohydrate Polymers. v. 175, p. 518-529. Elsevier, Inc. 2017.
- LEISTRITZ, F. L. SENECHAL, D. M. STOWERS, M. D. MCDONALD, W. F. SAFFRON, C. M. HODUR, N. M. **Preliminary feasibility analysis for an integrated biomaterials and ethanol biorefinery using wheat straw feedstock.** Agribusiness & Applied Economics Report No. 590. Department of Agribusiness and Applied Economics, Agricultural Experiment Station, North Dakota State University. 2006.
- LI, Q. MCGINNIS, S. SYDNOR, C. WONG, A. RENNECKAR, S. **Nanocellulose life cycle assessment.** ACS Sustainable Chemistry and Engineering, v. 1(8), p. 919-928. American Chemical Society, Inc. 2013.
- LI, Y. LIU, Y. CHEN, W. WANG, Q. LIU, Y. LI, J. YU, H. **Facile extraction of cellulose nanocrystals from wood using ethanol and peroxide solvothermal pretreatment followed by ultrasonic nanofibrillation.** Green Chemistry, v. 18(4), p. 1010-1018. The Royal Society of Chemistry, Inc. 2016a.
- LI, Q. Z. JIANG, X. L. FENG, X. J. WANG, J. M. SUN, S. ZHANG, H. B. XIAN, M. LIU, H. Z. **Recovery processes of organic acids from fermentation broths in the biomass-based industry.** Journal of Microbiology and Biotechnology, v. 26(1), p. 1-8. The Korean Society for Microbiology and Biotechnology, Inc. 2016b.
- LI, K. HUANG, J. XU, D. ZHONG, Y. ZHANG, L. CAI, J. **Mechanically strong polystyrene nanocomposites by peroxide-induced grafting of styrene monomers within nanoporous cellulose gels.** Carbohydrate Polymers, v. 199, p. 473-481. Elsevier, Inc. 2018.
- LI, T. CHEN, C. BROZENA, A. H. ZHU, J. Y. XU, L. DRIEMEIER, C. DAI, J. ROJAS, O. J. ISOGAI, A. WÅGBERG, L. HU, L. **Developing fibrillated cellulose as a sustainable technological material.** Nature, V. 590, P. 47-56. 2021.
- LIMAYEM, A. RICKE, S. C. **Lignocellulosic biomass for bioethanol production: Current perspectives, potential issues and future prospects.** Progress in Energy and Combustion Science, v. 38(4), p. 449-467. Elsevier, Inc. 2012.
- LIN, N. DUFRESNE, A. **Nanocellulose in biomedicine: Current status and future prospect.** European Polymer Journal, v. 59, p. 302-325. Elsevier, Inc. 2014.

LINDSTRÖM, T. AULIN, C. **Market and technical challenges and opportunities in the area of innovative new materials and composites based on nanocellulosics.** Scandinavian Journal of Forest Research, v. 29(4), p. 345-351. Taylor & Francis, Inc. 2014.

LIU, G. BAO, J. **Evaluation of electricity generation from lignin residue and biogas in cellulosic ethanol production.** Bioresource Technology, v. 243, p. 1232-1236. Elsevier, Inc. 2017.

LIU, G. ZHANG, J. BAO, J. **Cost evaluation of cellulase enzyme for industrial-scale cellulosic ethanol production based on rigorous Aspen Plus modeling.** Bioprocess and Biosystems Engineering, v. 39, p.133-140. Springer-Verlag, Inc. 2015.

LIU, X. JIANG, Y. QIN, C. YANG, S. SONG, X. WANG, S. LI, K. **Enzyme-assisted mechanical grinding for cellulose nanofibers from bagasse: energy consumption and nanofiber characteristics.** Cellulose, v. 25, p.7065-7078. Springer Nature B.V., Inc. 2018.

LONGATI, A. A. LINO, A. R. A. GIORDANO, R. C. FURLAN, F. F. CRUZ, A. J. G. **Defining research & development process targets through retro-techno-economic analysis: the sugarcane biorefinery case.** Bioresource Technology, v. 263, p. 1-9. Elsevier, Inc. 2018.

LONGATI, A. A. LINO, A. R. A. GIORDANO, R. C. FURLAN, F. F. CRUZ, A. J. G. **Biogas production from anaerobic digestion of vinasse in sugarcane biorefinery: a techno-economic and environmental analysis.** Waste and Biomass Valorization, v. 11, p.4573-4591. Springer Nature B.V., Inc. 2020.

MALUCELLI, L. C. LACERDA, L. G. DZIEDZIC, CARVALHO FILHO, M. A. S. **Preparation, properties and future perspectives of nanocrystals from agro-industrial residues: a review of recent research.** Reviews in Environmental Science and Biotechnology, v. 16, p. 131-145. Springer Science+Business Media Dordrecht, Inc. 2017.

MANDAL, A. CHAKRABARTY, D. **Isolation of nanocellulose from waste sugarcane bagasse (SCB) and its characterization.** Carbohydrate Polymers, v. 86, p. 1291-1299. Elsevier, Inc. 2011.

MANDEGARI, M. A. FARZAD, S. GÖRGENS, J. F. **Recent trends on techno-economic assessment (TEA) of sugarcane biorefineries.** Biofuel Research Journal, v. 4, p. 704-712. Biofuel Research Team, Inc. 2017.

MARABEZI, K. **Deslignificação de bagaço de cana-de-açúcar: reações, isolamento e utilização de ligninas.** Doctorate Thesis. Instituto de Química de São Carlos, Universidade de São Paulo. São Carlos, 2014.

MARKETS AND MARKETS. **Nanocellulose Market worth \$661.7 million by 2023.** Available in: <<https://www.marketsandmarkets.com/PressReleases/nanocellulose.asp>> Accessed on August 04, 2021.

MARCONDES, W. F. MILAGRES, A. M. F. ARANTES, V. **Co-production of xylo-oligosaccharides, xylose and cellulose nanofibrils from sugarcane bagasse.** Journal of Biotechnology, v. 321, p. 35-47. Elsevier, Inc. 2020.

MARIANO, M. EL KISSI, N. DUFRESNE, A. **Cellulose nanocrystals and related nanocomposites: review of some properties and challenges.** Journal of Polymer Science Part B: Polymer Physics, v. 52, p. 791-806. Wiley Periodicals, Inc. 2014.

MATCHES - **Matches' process equipment cost estimates.** Available in: <<http://www.matche.com/EquipCost/>>. Accessed on May 03, 2019.

MATTEY, M; KRISTIANSEN, B. **A Brief Introduction to Citric Acid Biotechnology.** Citric Acid Biotechnology, Taylor & Francis, Ltd. London, UK, 2002.

MCGRAW-HILL HIGHER EDUCATION. **Equipment Cost Estimator.** Available in <<http://www.mhhe.com/engcs/chemical/peters/data/>>. Accessed on May 03, 2019.

MEESUPHONG, R. YINGKAMHAENG, N. NIMCHUA, T. PINMANEE, P. MUSSATTO, S. I. LI, B. SUKYAI, P. **Xylanase pretreatment of energy cane enables facile cellulose nanocrystal isolation.** Cellulose, v. 28, p. 799-812. Springer Nature B.V., Inc. 2021.

MENDES, F. M. DIAS, M.O.S. FERRAZ, A. MILAGRES, A.M.F. SANTOS, J.C. BONOMI, A. **Techno-economic impacts of varied compositional profiles of sugarcane experimental hybrids on a biorefinery producing sugar, ethanol and electricity.** Chemical Engineering Research and Design, v. 125, p. 72-78. Elsevier, Inc. 2017.

MENÉNDEZ, R. P. MARTÍN, A. P. VARELA-CANDAMIO, L. GARCÍA-ÁLVAREZ, M. T. **An enhanced techno-economic analysis of LCOE: public incentives vs private investment.** Technological and Economic Development of Economy, v. 1, p. 23. VGTU Press, Inc. 2020.

MOOD, S.H. *et al.* **Lignocellulosic biomass to bioethanol, a comprehensive review with a focus on pretreatment.** Renewable & Sustainable Energy Reviews, v. 27, p. 77-93, 2013.

MUKTHAM, R. BHARGAVA, S. K. BANKUPALLI, S. BALL, A. S. **A review on 1st and 2nd generation bioethanol production – recent progress.** Journal of Sustainable Bioenergy Systems, v. 6, p. 72-92. Scientific Research Publishing, Inc. 2016.

NANOGRAFI NANOTECHNOLOGY. **Nanocellulose Products Page.** Available in: <<https://nanografi.com/popular-products/cellulose-nanocrystal-nanocrystalline-cellulose-cnc>> and <<https://nanografi.com/popular-products/cellulose-nanofiber-cellulose-nanofibril-nanofibrillated-cellulose-cnfs/>>. Accessed on August 08, 2021.

NASCIMENTO, D. M. DIAS, A. F. ARAÚJO JUNIOR, C. P. ROSA, M. F. MORAIS, J. P. S. FIGUEIRÊDO, M. C. B. **A comprehensive approach for obtaining cellulose nanocrystal from coconut fiber. Part II: Environmental assessment of technological pathways.** Industrial Crops and Products, v. 93, p. 58-65. Elsevier, Inc. 2016.

NELSON, K. RETSINA, T. IAKOVLEV, M. VAN HEININGEN, A. DENG, Y. SHATKIN, J. A. MULYADI, A. Chapter 9 - **American process: production of low cost nanocellulose for renewable, advanced materials applications.** Materials Research for Manufacturing, Springer Series in Materials Science, v. 224, p. 267-302. Springer International Publishing Switzerland, Inc. 2016.

NG, H. M.; SIN, L. T.; TEE, T.T.; BEE, S.T.; HUI, D.; LOW, C.Y., RAHMAT, A. R. **Extraction of cellulose nanocrystals from plant sources for application as reinforcing agent in polymers.** Composites Part B: Engineering, v. 75, p. 176-200. Elsevier, Inc. 2015.

NIGRI, E. M. BARROS, A. C. ROCHA, S. D. F. ROMEIRO FILHO, E. **Assessing environmental impacts using a comparative LCA of industrial and artisanal production processes: “minas cheese” case.** Food Science and Technology, v. 34(3), p. 522-531. Sociedade Brasileira de Ciência e Tecnologia de Alimentos, Inc. 2014.

NIPPON PAPER GROUP. **Cellulose nanofiber manufacturing technology and application development.** Available in: <<https://www.nipponpapergroup.com/english/research/organize/cnf.html>>. Accessed on August 13, 2020.

NOVACANA. **Etanol hidratado sobe 7% nas usinas e remunera mais que anidro pela 1ª vez na safra.** Available in: <<https://www.novacana.com/n/etanol/mercado/precos/etanol-hidratado-sobe-anidro-avanca-usinas-180219>>. Accessed on October 26, 2020.

NOVACANA. **As usinas de Açúcar e Etanol do Brasil.** Available in <https://www.novacana.com/usinas_brasil>. Accessed on March 26, 2021.

NSOR-ATINDANA, J. GOFF, H. D. LIU, W. CHEN, M. ZHONG, F. **The resilience of nanocrystalline cellulose viscosity to simulated digestive processes and its influence on glucose diffusion.** Carbohydrate Polymers. v. 200, p. 436-445. Elsevier, Inc. 2018.

ÖGMUNDARSON, O. SUKUMARA, S. HERRGÅRD, M. J. FANTKE, P. **Combining environmental and economic performance for bioprocess optimization.** Trends in Biotechnology, v. 38(11), p. 1203-1214. Elsevier, Inc. 2020a.

ÖGMUNDARSON, O. HERRGÅRD, M. J. FORSTER, J. HAUSCHILD, M. Z. FANTKE, P. **Addressing environmental sustainability of biochemicals.** Nature Sustainability, v.3, p. 167–174. 2020b.

OLIET, M. GARCIA, J. RODRÍGUEZ, F. GILARRRANZ, M. A. **Solvent effects in autocatalyzed alcohol–water pulping - Comparative study between ethanol and**

methanol as delignifying agents. *Chemical Engineering Journal*, v. 87, p. 157–162. Elsevier, Inc. 2002.

OLIVEIRA, F. B. BRAS, J. PIMENTA, M. T. B. CURVELO, A. A. S. BELGACEM, M. N. **Production of cellulose nanocrystals from sugarcane bagasse fibers and pith.** *Industrial Crops and Products*, v. 93, p. 48-57. Elsevier, Inc. 2016.

ÖZÜDOĞRU, H. M. R. NIEDER-HEITMANN, M. HAIGH, K. F. GÖRGENS, J. F. **Techno-economic analysis of product biorefineries utilizing sugarcane lignocelluloses: Xylitol, citric acid and glutamic acid scenarios annexed to sugar mills with electricity co-production.** *Industrial Crops & Products*, v. 133, p. 259-268. Elsevier, Inc. 2019.

PEREIRA, S. C. MAEHARA, L. MACHADO, C. M. M. FARINAS, C. S. **2G ethanol from the whole sugarcane lignocellulosic biomass.** *Biotechnology for Biofuels*, v. 8, p. 44-60. BioMed Central, Inc. 2015.

PEREIRA, B. ARANTES, V. **Production of cellulose nanocrystals integrated into a biochemical sugar platform process via enzymatic hydrolysis at high solid loading.** *Industrial Crops & Products*, v. 152, p. 112377. Elsevier, Inc. 2020.

PERRY, R. H.; GREEN, D. W. **Perry's Chemical Engineers' handbook.** USA: McGraw-Hill. 2007.

PETERS, M. S. TIMMERHAUS, K. D. **Plant Design and Economics for Chemical Engineers.** 5th Edition. New York: McGraw-Hill, 2003.

PHANTHONG, P. REUBROYCHAROEN, P. HAO, X. XU, G. ABUDULA, A. GUAN, G. **Nanocellulose: Extraction and application.** *Carbon Resources Conversion*, v. 1, p. 32-43. KeAi Publishing, Inc. 2018.

PICCINNO, F. HISCHIER, R. SEEGER, S. SOM, C. **Life cycle assessment of a new technology to extract, functionalize and orient cellulose nanofibers from food waste.** *ACS Sustainable Chemistry and Engineering*, v. 3(6), p. 1047-1055. American Chemical Society, Inc. 2015.

PICCINNO, F. HISCHIER, R. SEEGER, S. SOM, C. **Predicting the environmental impact of a future nanocellulose production at industrial scale: Application of the life cycle assessment scale-up framework.** *Journal of Cleaner Production*, v. 174, p. 283-295. Elsevier, Inc. 2018.

PINTO, L. O. BERNARDES, J. S. REZENDE, C. A. **Low-energy preparation of cellulose nanofibers from sugarcane bagasse by modulating the surface charge density.** *Carbohydrate Polymers*, v. 218, p. 145-153. Elsevier, Inc. 2019.

PIRES, J. R. A. SOUZA, V. G. L. FERNANDO, A. L. **Valorization of energy crops as a source for nanocellulose production - Current knowledge and future prospects.** *Industrial Crops and Products*, v. 140, p. 111642. Elsevier, Inc. 2019.

- POTRICH, E. MIYOSHI, S. C. MACHADO, P. F. S. FURLAN, F. F. RIBEIRO, M. P. A. TARDIOLI, P. W. GIORDANO, R. L. C. CRUZ, A. J. G. GIORDANO, R. C. **Replacing hexane by ethanol for soybean oil extraction: Modeling, simulation, and techno-economic-environmental analysis.** *Journal of Cleaner Production*, v. 244, p. 118660. Elsevier, Inc. 2020.
- PRATTO, B. SOUZA, R. B. A. SOUSA JR, R. CRUZ, A. J. G. **Enzymatic hydrolysis of pretreated sugarcane straw: kinetic study and semi-mechanistic modeling.** *Applied Biochemistry and Biotechnology*, v. 178(7), p. 1430-1444. Springer Science+Business Media New York, Inc. 2015.
- REID, M. S. VILLALOBOS, M. CRANSTON, E. D. **Benchmarking Cellulose Nanocrystals: From the Laboratory to Industrial Production.** *Langmuir*, v. 33(7), p. 1583-1598. American Chemical Society, Inc. 2016.
- RESENDE, R. R. RODRIGUES, C. WOICIECHOWSKI, A. L. LETTI, L. A. J. KARP, S. G. GOELZER, F. D. SOLBRAL, K. C. A. CORAL, J. D. CAMPIONI, T. S. MACENO, M. A. C. SOCCOL, C. R. **Biotecnologia aplicada à agro&indústria: fundamentos e aplicações. Capítulo 8: Materiais lignocelulósicos como matéria-prima para a obtenção de biomoléculas de valor comercial.** Blucher, Inc. 2014.
- RESHMY, R. EAPEN, P. SHERELY, P. A. ARAVIND, M. RAVEENDRAN, S. PARAMESWARAN, B. ASHOK, P. **A green biorefinery platform for cost-effective nanocellulose production: investigation of hydrodynamic properties and biodegradability of thin films.** *Biomass Conversion and Biorefinery*, v. 11, p. 861-870. Springer-Verlag GmbH Germany, part of Springer Nature, Inc. 2021.
- REVISTA PESQUISA FAPESP. International Issue, January 2018. **Alternative uses for a plant fiber.** Available in: <<https://revistapesquisa.fapesp.br/en/alternative-uses-for-a-plant-fiber-2/>>. Accessed on July 28, 2020.
- RIBEIRO, R. S. A. POHLMANN, B. C. CALADO, V. BOJORGE, N. PEREIRA JR., N. **Production of nanocellulose by enzymatic hydrolysis: Trends and challenges.** *Engineering in Life Sciences*, v. 19, p. 279-291. Wiley-VCH Verlag GmbH & Co. KGaA, Inc. 2019.
- ROCHA, G. J. M. MARTÍN, C. SILVA, V. F. N. GÓMEZ, E. O. GONÇALVES, A. R. **Mass balance of pilot-scale pretreatment of sugarcane bagasse by steam explosion followed by alkaline delignification.** *Bioresource Technology*, v. 111, p. 447-452. Elsevier, Inc. 2012.
- ROJO, E. PERESIN, M. S. SAMPSON, W. W. HOEGER, I. C. VARTIAINEN, J. LAINE, J. ROJAS, O. J. **Comprehensive elucidation of the effect of residual lignin on the physical, barrier, mechanical and surface properties of nanocellulose films.** *Green Chemistry*, v. 17, p. 1853-1866. The Royal Society of Chemistry. 2015.
- ROSALES-CALDERON, O. PEREIRA, B. ARANTES, V. **Economic assessment of the conversion of bleached eucalyptus Kraft pulp into cellulose nanocrystals in a stand-**

alone facility via acid and enzymatic hydrolysis. Biofuels, Bioproducts and Biorefining. Society of Chemical Industry and John Wiley & Sons, Ltd. 2021.

ROVERA, C. GHAANI, M. SANTO, N. TRABATTONI, S. OLSSON, R. T. ROMANO, D. FARRIS, S. **Enzymatic hydrolysis in the green production of bacterial cellulose nanocrystals.** ACS Sustainable Chemistry and Engineering, v. 6(6), p. 7725-7734. American Chemical Society, Inc. 2018.

SAAD, M. B. W. OLIVEIRA, L. R. M. CÂNDIDO, R. G. QUINTANA, G. ROCHA, G. J. M. GONÇALVES, A. R. **Preliminary studies on fungal treatment of sugarcane straw for organosolv pulping.** Enzyme and Microbial Technology, v. 43, p. 220-225. Elsevier, Inc. 2008.

SAAE. **Tarifas da água por categoria – industrial 2019.** Available in: <https://www.saae.sp.gov.br/consumo_tarifas>. Accessed on April 17, 2021.

SAMIR, M. A. S. A. ALLOIN, F. DUFRESNE, A. **Review of recent research into cellulosic whiskers, their properties and their application in nanocomposite field.** Biomacromolecules, v. 6(2), p. 612-626. American Chemical Society, Inc. 2005.

SANTO, M. E. REZENDE, C. A. BERNARDINELLI, O. D. PEREIRA JR., N. CURVELO, A. A. S. AZEVEDO, E. R. GUIMARÃES, F. E. G. POLIKARPOV, I. **Structural and compositional changes in sugarcane bagasse subjected to hydrothermal and organosolv pretreatments and their impacts on enzymatic hydrolysis.** Industrial Crops & Products, v. 113, p. 64-74. Elsevier, Inc. 2018.

SAMCO. **How Much Do Microfiltration and Ultrafiltration Membrane Systems Cost?** Available in: <<https://www.samcotech.com/how-much-do-microfiltration-and-ultrafiltration-membrane-systems-cost/>>. Accessed on September 18, 2020.

SANTOS-ROCHA, M. S. R. PRATTO, B. SOUSA JR, R. ALMEIDA, R. M. S. G. CRUZ, A. J. G. **A kinetic model for hydrothermal pretreatment of sugarcane straw.** Bioresource Technology, v. 228, p. 176–185. Elsevier, Inc. 2017.

SCIENTIA. **Ácido Sulfúrico – Processo de Concentração.** Available in: <<https://sites.google.com/site/scientiaestpotentiaplus/acido-sulfurico/acido-sulfurico-processo-de-concentracao>>. Accessed on May 21, 2019.

SHATKIN, J. A. WEGNER, T. H. BILEK, E. M. COWIE, J. Market projections of cellulose nanomaterial-enabled products – Part 1: Applications. TAPPI Journal, v. 13(5), p. 9-16. 2014.

SHEN, R. XUE, S. XU, Y. LIU, Q. FENG, Z. REN, H. ZHAI, H. KONG, F. **Research progress and development demand of nanocellulose reinforced polymer composites.** Polymers, v. 12, p. 2113-2132. MDPI, Inc. 2020.

SHOW, P. L. OLADELE, K. O. SIEW, Q. Y. ZAKRY, F. A. A. LAN, J. C. W. LING, T. C. **Overview of citric acid production from *Aspergillus niger*.** Frontiers in Life Science, v. 8(3), p. 271-283. Taylor & Francis, Inc. 2015.

- SIQUEIRA, G.; BRAS, J.; DUFRESNE, A. **Cellulose whiskers versus microfibrils: influence of the nature of the nanoparticle and its surface functionalization on the thermal and mechanical properties of nanocomposites**. *Biomacromolecules*, v. 10(2), p. 425-432. American Chemical Society, Inc. 2009.
- SOFLA, M. R. K. BATCHELOR, W. KOSINKOVA, J. PEPPER, R. BROWN, R. RAINEY, T. **Cellulose nanofibres from bagasse using a high speed blender and acetylation as a pretreatment**. *Cellulose*, v. 26, p. 4799-4814. Springer Nature B.V., Inc. 2019.
- SONG, Q. WINTER, W. T. BUJANOVIC, B. M. AMIDON, T. E. **Nanofibrillated Cellulose (NFC): A High-Value Co-Product that Improves the Economics of Cellulosic Ethanol Production**. *Energies*, v. 7, p. 607-618. MDPI, Inc. 2014.
- SQUINCA, P. BILATTO, S. BADINO, A. C. FARINAS, C. S. **Nanocellulose Production in Future Biorefineries: An Integrated Approach Using Tailor-Made Enzymes**. *ACS Sustainable Chemical Engineering*, v. 8(5), p. 2277-2286. American Chemical Society, Inc. 2020.
- SUN, Y. CHENG, J. **Hydrolysis of lignocellulosic materials for ethanol production: A review**. *Bioresource Technology*, v. 83, p. 1-11. Elsevier, Inc. 2002.
- SUN, X. LU, H. WANG, J. **Recovery of citric acid from fermented liquid by bipolar membrane electrodialysis**. *Journal of Cleaner Production*, v. 143, p. 250-256. Elsevier, Inc. 2017.
- TAN, K. W. HEO, S. K. FOO, M. L. CHEW, I. M. L. YOO, C. K. **An insight into nanocellulose as soft condensed matter: Challenge and future prospective toward environmental sustainability**. *Science of The Total Environment*, v. 650, p. 1309-1326. Elsevier, Inc. 2019.
- TEIXEIRA, E. M. BONDANCIA, T. J. TEODORO, K. B. R. CORRÊA, A. C. MARCONCINI, J. M. MATTOSO, J. H. C. **Sugarcane bagasse whiskers: Extraction and characterizations**. *Industrial Crops and Products*, v. 33, p. 63-66. Elsevier, Inc. 2011.
- THAKRE, N. DATTA, D. PRAJAPATI, A. K. CHAUDHARI, P. K. PALD, D. **Reactive extraction of citric acid using different extractants: equilibrium, kinetics and modeling**. *Chemical and Biochemical Engineering Quarterly*, v. 31(4), p. 437-446. Croatian Society of Chemical Engineers, Inc. 2017.
- TONON FILHO, R. J. **Modelagem e simulação em plantas de etanol: uma abordagem técnico-econômica**. Masters Thesis. Departamento de Engenharia Química, Universidade Federal de São Carlos. 2013.
- TOWLER, G. SINNOTT, R. K. **Chemical Engineering Design: Principles, Practice and Economics of Plant and Process Design**. 5th Edition. UK: Butterworth-Heinemann, 2009.

TROVAGUNTA, R. ZOU, T. ÖSTERBERG, M. KELLEY, S. S. LAVOINE, N. **Design strategies, properties and applications of cellulose nanomaterials-enhanced products with residual, technical or nanoscale lignin — A review.** Carbohydrate Polymers, v. 254, p. 117480. Elsevier, Inc. 2021.

TURK, J. OVEN, P. POLJANŠEK, I. LEŠEK, A. KNEZ, F. REBEC, K. M. **Evaluation of an environmental profile comparison for nanocellulose production and supply chain by applying different life cycle assessment methods.** Journal of Cleaner Production, v. 247, p. 119107. Elsevier, Inc. 2020.

TURTON, R., BAILIE, R.C., WHITING, W.B., SHAEIWITZ, J.A. **Analysis, Synthesis, and Design of Chemical Processes.** 3rd Edition. New Jersey: Prentice Hall, 2009.

UNICA. União da Indústria de Cana-de-Açúcar. **A Bioeletricidade da Cana - Julho de 2019.** Available in <<https://www.unica.com.br/wp-content/uploads/2019/07/UNICA-Bioeletricidade-julho2019-1.pdf>>. Accessed on March 3, 2021.

USLU, H. **Extracion of citric acid in 2-octanol and 2-propanol solutions containing tomac: An equilibria and a LSER model.** Brazilian Journal of Chemical Engineering, v. 25(3), p. 553-561. Associação Brasileira de Engenharia Química, Inc. 2008.

U.S. GRAINS COUNCIL. **World fuel ethanol production liters.** Available in <<https://grains.org/infographic/world-fuel-ethanol-production-in-million-liters/world-fuel-ethanol-production-liters>>. Accessed on July 3, 2021.

VAN DEN BERGH, M. VAN DE VOORDE, B. DE VOS, D. **Adsorption and selective recovery of citric acid with poly(4-vinylpyridine).** ChemSusChem, v. 10(24), p. 4864-4871. Wiley-VCH, Inc. 2017.

VANDERFLEET, O. M. CRANSTON, E. D. **Production routes to tailor the performance of cellulose nanocrystals.** Nature Reviews Materials, v. 6, p. 124-144. 2021.

VANHATALO, K. M. PARVIAINEN, K. E. DAHL, O. P. **Techno-economic analysis of simplified microcrystalline cellulose process.** Bioresources, v. 9(3), p. 4741-4755. 2014.

VÁRNAI, K. PETRI, L. NAGY, L. **Prospective evaluation of spent sulfuric acid recovery by process simulation.** Periodica Polytechnica Chemical Engineering, v. 65(2), p. 243-250. 2021.

WANG, H. LI, D. ZHANG, R. **Preparation of ultralong cellulose nanofibers and optically transparent nanopapers derived from waste corrugated paper pulp.** BioResources, v. 8(1), p. 1374-1384. 2013.

WANG, Q. ZHAO, X. ZHU, J. Y. **Kinetics of strong acid hydrolysis of a bleached kraft pulp for producing cellulose nanocrystals (CNCs).** Industrial and Engineering Chemistry Research, v. 53, p. 11007-11014. American Chemical Society, Inc. 2014.

WANG, Z. MO. L. ZHAO, S. LI, J. ZHANG, S. HUANG, A. **Mechanically robust nacre-mimetic framework constructed polypyrrole-doped graphene/nanofiber nanocomposites with improved thermal electrical properties.** *Materials & Design*, v. 155, p. 278-287. Elsevier, Inc. 2018.

WEINWURM, F. DRLJO, A. SILVA, T. L. S. FRIEDL, A. **Principles of ethanol organosolv lignin precipitation: process simulation and energy demand.** *Chemical Engineering Transactions*, v. 39, p. 583-588. The Italian Association of Chemical Engineering, Inc. 2014.

WYMAN, C. E. DALE, B. E. ELANDER, R. T. HOLTZAPPLE, M. LADISCH, M. R. LEE, Y. Y. **Comparative sugar recovery data from laboratory scale application of leading pretreatment technologies to corn stover.** *Bioresource Technology*, v. 96(18), p. 2026-2032. Elsevier, Inc. 2005.

XIAO, Y. RONG, L. WNAG, B. MAO, Z. XU, H. ZHONG, YI. ZHANG, L. SUI, X. A **light-weight and high-efficacy antibacterial nanocellulose-based sponge via covalent immobilization of gentamicin.** *Carbohydrate Polymers*, v. 200, p. 595-601. Elsevier, Inc. 2018.

XIE, H. DU, H. YANG, X. SI, C. **Recent Strategies in Preparation of Cellulose Nanocrystals and Cellulose Nanofibrils Derived from Raw Cellulose Materials.** *International Journal of Polymer Science*. v. 2018, p. 7923068. Hindawi Publishing Corporation, Inc. 2018.

YANG, J. **Manufacturing of Nanocrystalline Cellulose.** Masters Thesis. Master's Programme in Chemical, Biochemical and Materials Engineering. School of Chemical Engineering, Aalto University. 2017.

YANG, N. ZHANG, W. YE, C. CHEN, X. LING, S. **Nanobiopolymers fabrication and their life cycle assessments.** *Biotechnology Journal*, v. 14(1), p. 1700754. WILEY-VCH Verlag GmbH & Co. KGaA, Inc. 2018.

YU, H. ABDALKARIM, S. Y. H. ZHANG, H. WANG, C. TAM, K. C. Simple process to produce high-yield cellulose nanocrystals using recyclable citric/hydrochloric acids. *ACS Sustainable Chemistry & Engineering*, v. 7, p. 4912-4923. American Chemical Society, Inc. 2019.

ZETTERHOLM, J. BRYNGEMARK, E. AHLSTRÖM, J. SÖDERHOLM, P. HARVEY, S. WETTERLUND, E. **Economic evaluation of large-scale biorefinery deployment: A framework integrating dynamic biomass market and techno-economic models.** *Sustainability*, v. 12, p. 7126-7153. MDPI, Inc. 2020.

ZHANG, Y. H. P. LYND, L. R. **Toward an aggregated understanding of enzymatic hydrolysis of cellulose: Non complexed systems.** *Biotechnology and Bioengineering*, v. 88, p. 797-824. Wiley Periodicals, Inc. 2004.

ZHANG, Y. H. P. HIMMEL, M. E. MIELENZ, J. R. **Outlook for cellulase improvement: Screening and selection strategies.** *Biotechnology Advances*, v. 24, p. 452-481. Elsevier, Inc. 2006.

ZHANG, N. TAO, P. LU, Y. NIE, S. **Effect of lignin on the thermal stability of cellulose nanofibrils produced from bagasse pulp.** *Cellulose*, v. 26, p. 7823-7835. Springer Nature B.V., Inc. 2019.

ZHANG, K. SU, Y. XIAO, H. **Preparation and Characterization of nanofibrillated cellulose from waste sugarcane bagasse by mechanical force.** *Bioresources*, v. 15(3), p. 6636-6647. 2020.

ZHONG, C. **Industrial-scale production and applications of bacterial cellulose.** *Frontiers in Bioengineering and Biotechnology*, v. 8, p. 605374. 2020.

ZION RESEARCH. **Nanocellulose (nano-crystalline cellulose, nano-fibrillated cellulose and bacterial nanocellulose) market for composites, oil & gas, paper processing, paints & coatings, and other applications: Global industry perspective, comprehensive analysis, size, share, growth, segment, trends and forecast, 2015 - 2021.** Available in: <<https://www.marketresearchstore.com/report/nanocellulose-market-z53869>>. Accessed on August 12, 2020.

ANNEXES

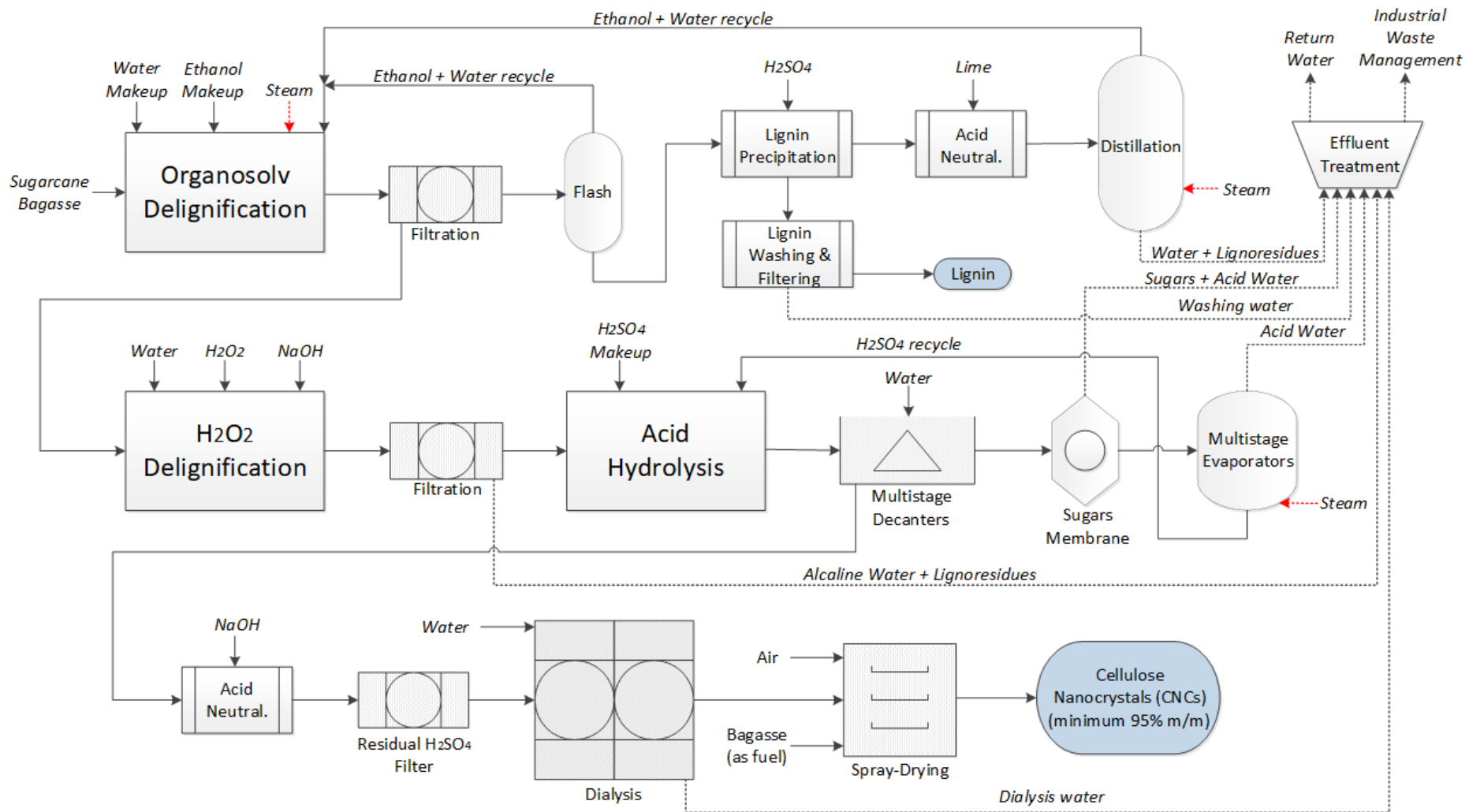


Figure A1 - Block diagram for the CNCs production methodology proposed in Case Study C1.

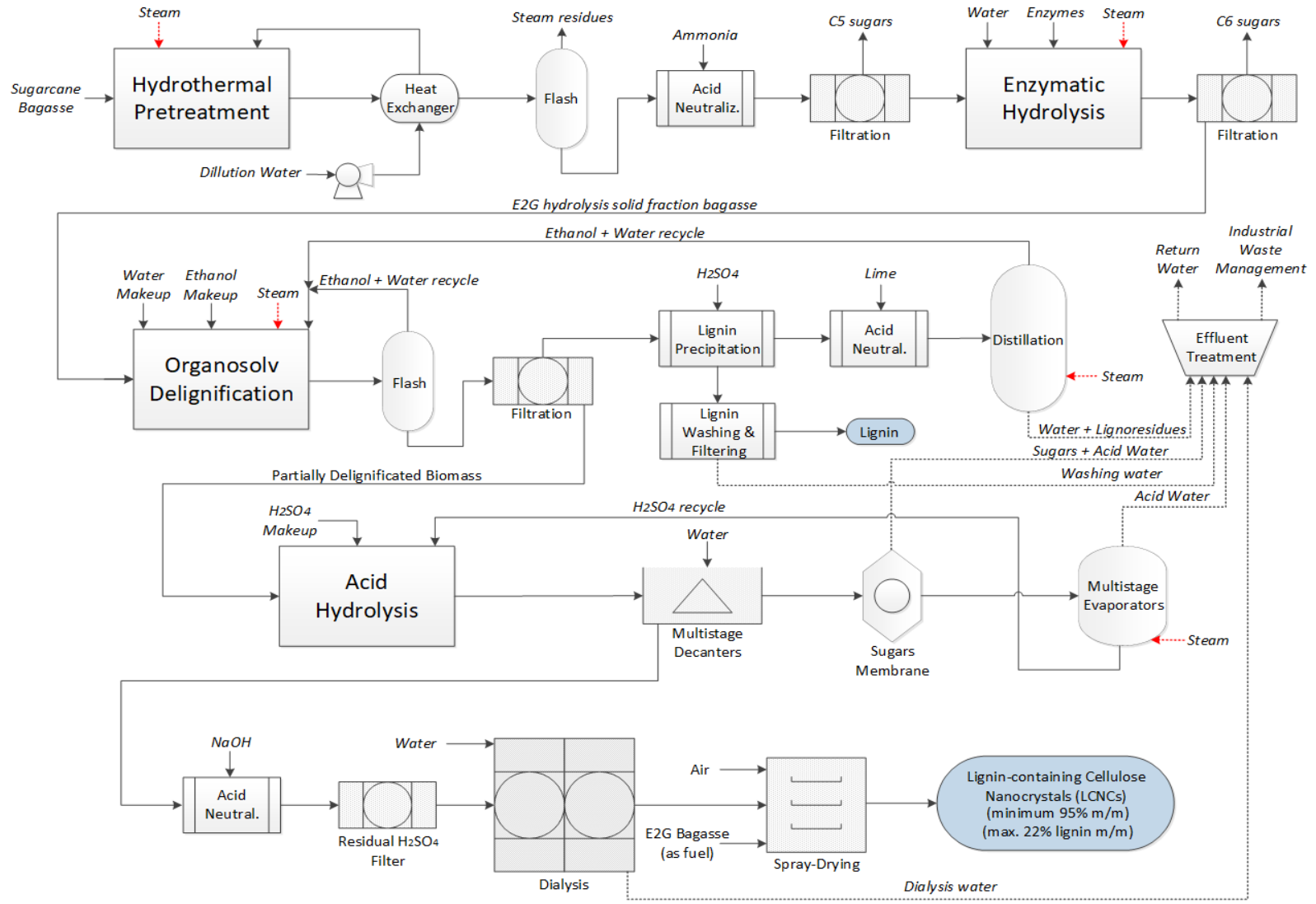


Figure A2 - Block diagram for the LCNCS production methodology proposed in Case Study C3.

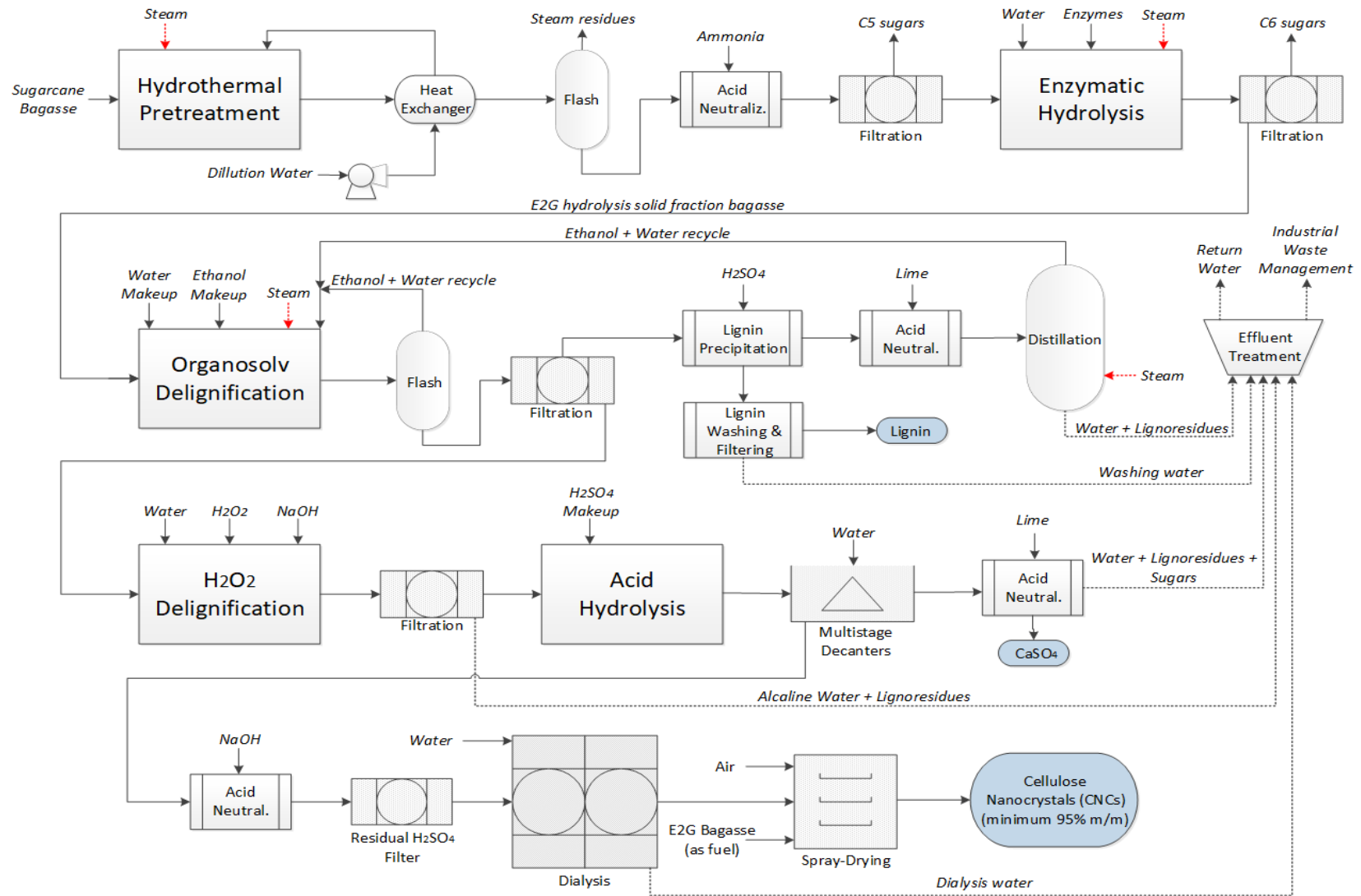


Figure A3 - Block diagram for the CNCs production methodology proposed in Case Study C4.

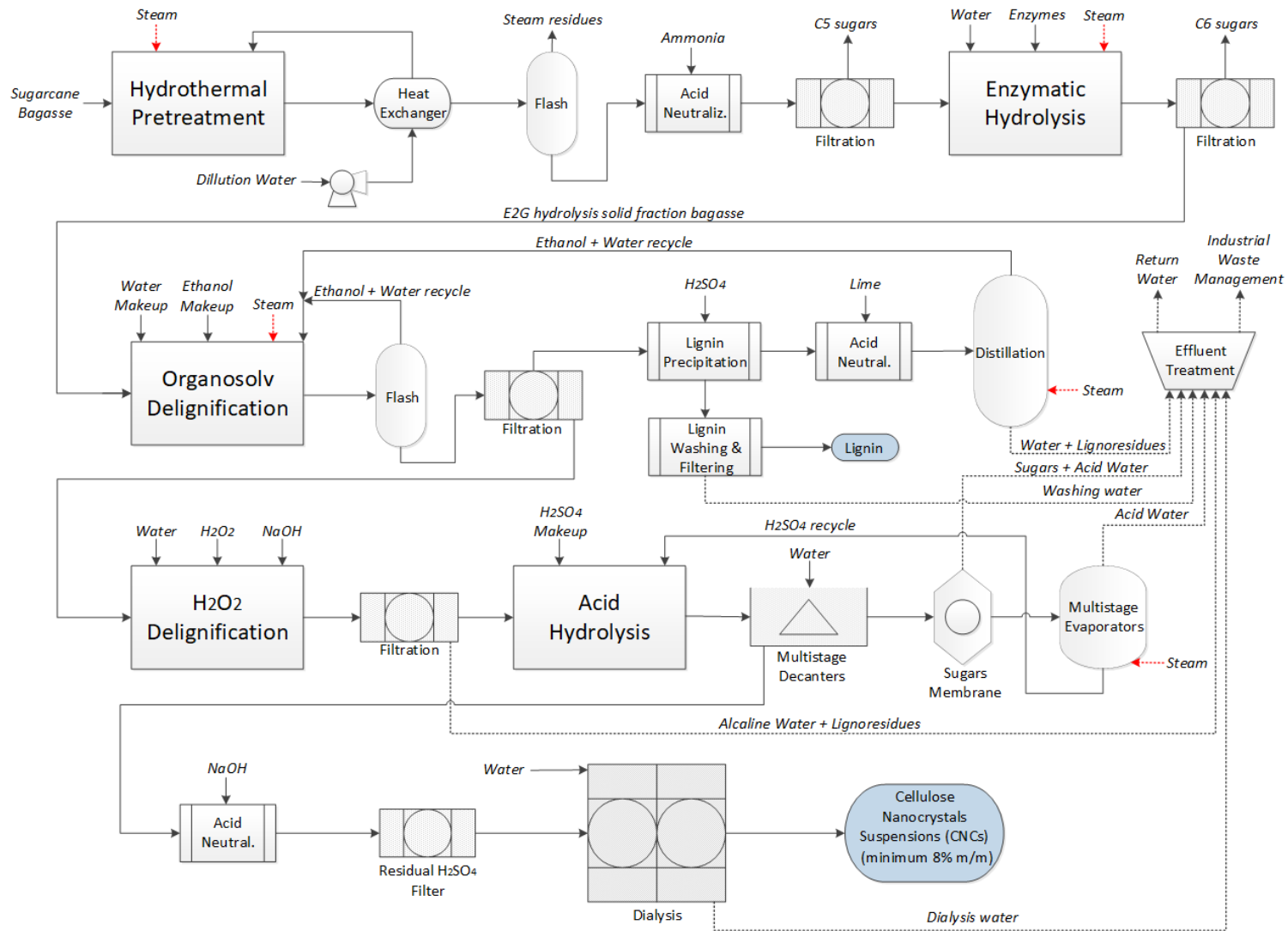


Figure A4 - Block diagram for the CNCs suspensions production methodology proposed in Case Study C5.

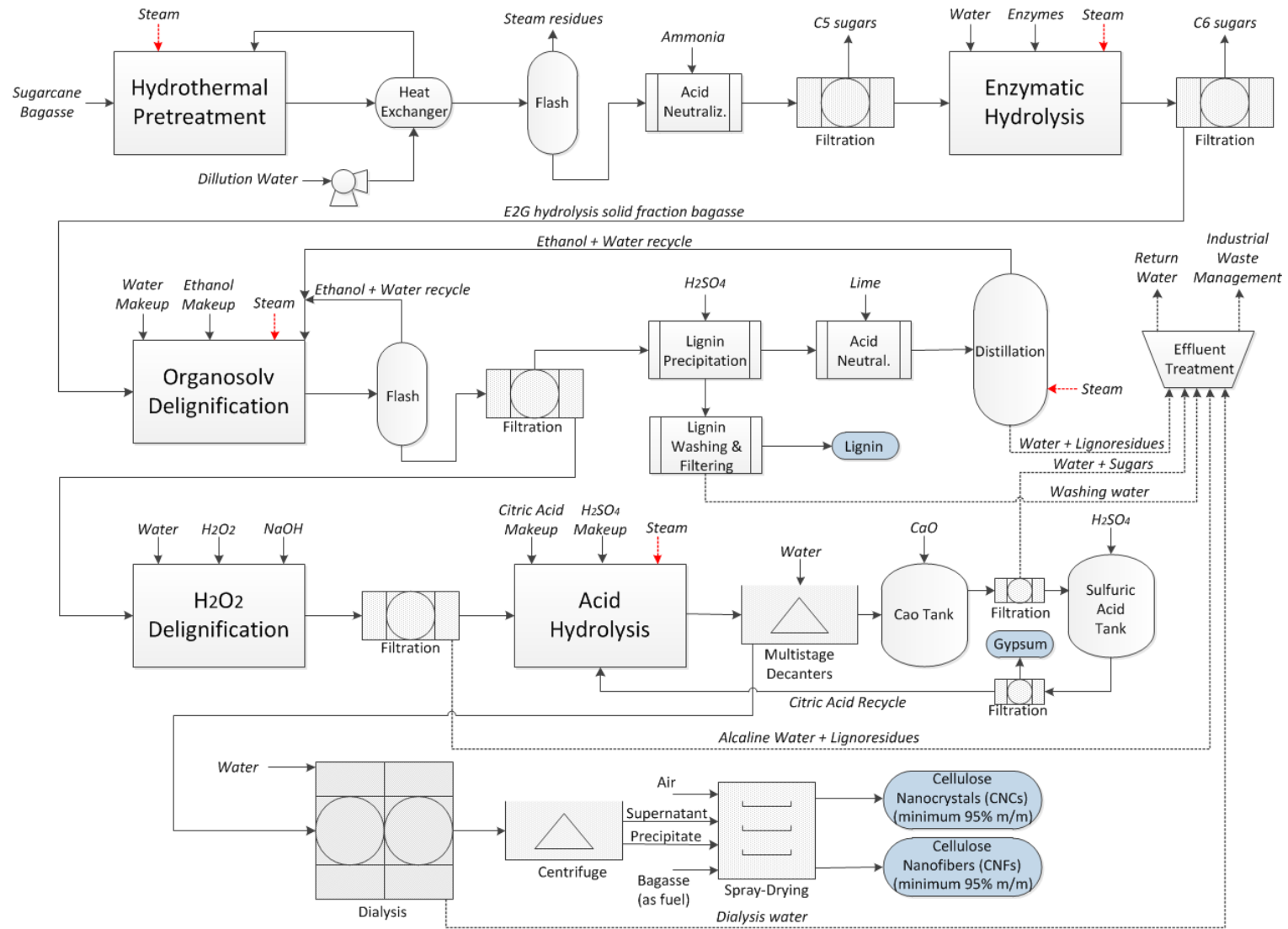


Figure A5 - Block diagram for the CNCs / CNFs production methodology proposed in Case Study C7.

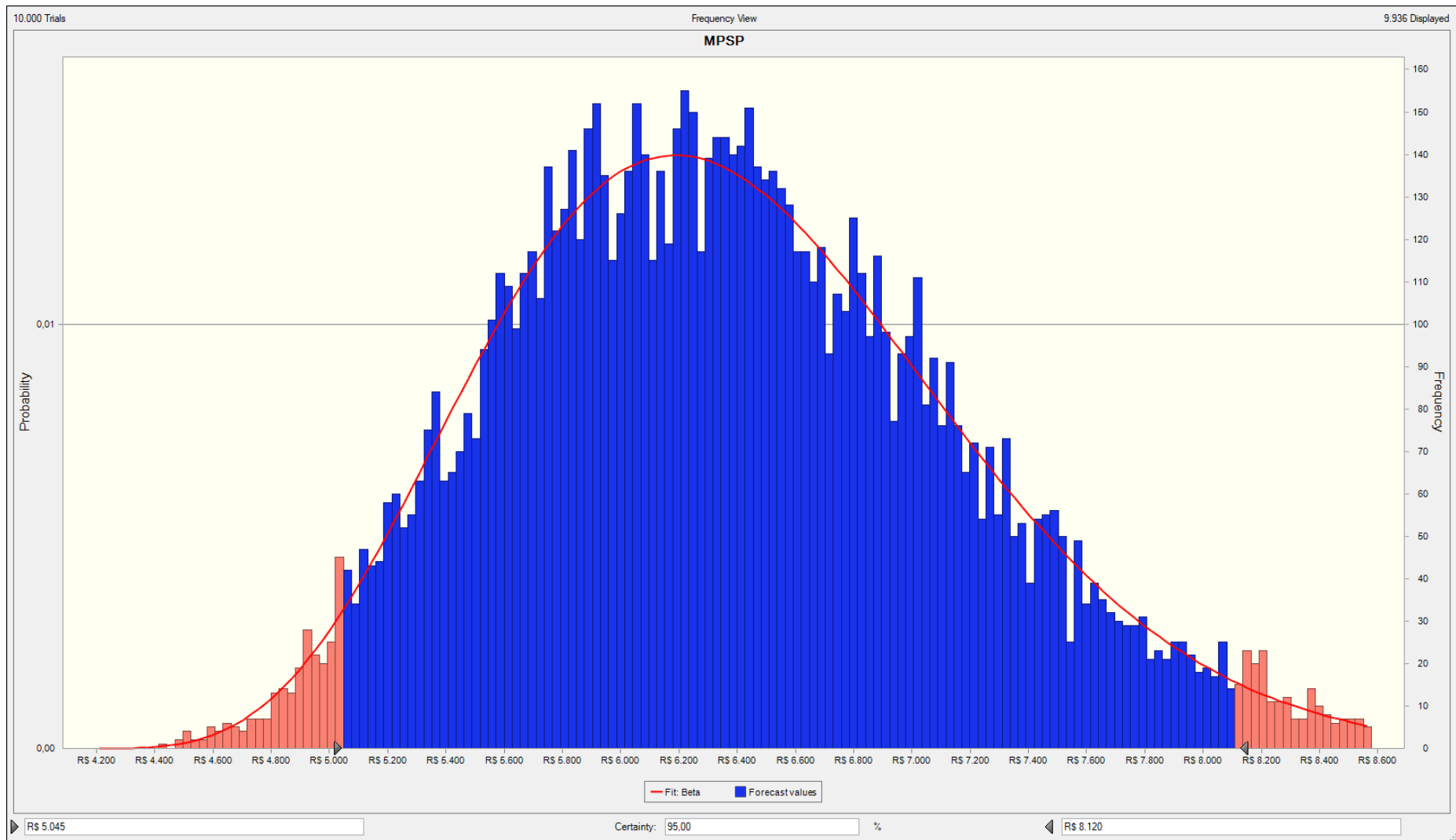


Figure A6 - Probabilistic Risk Assessment of Parameters by Monte-Carlo simulation for Case Study C1. Regions of the graph in blue denote ranges for which the MPSP can be expected with 95% statistical confidence.

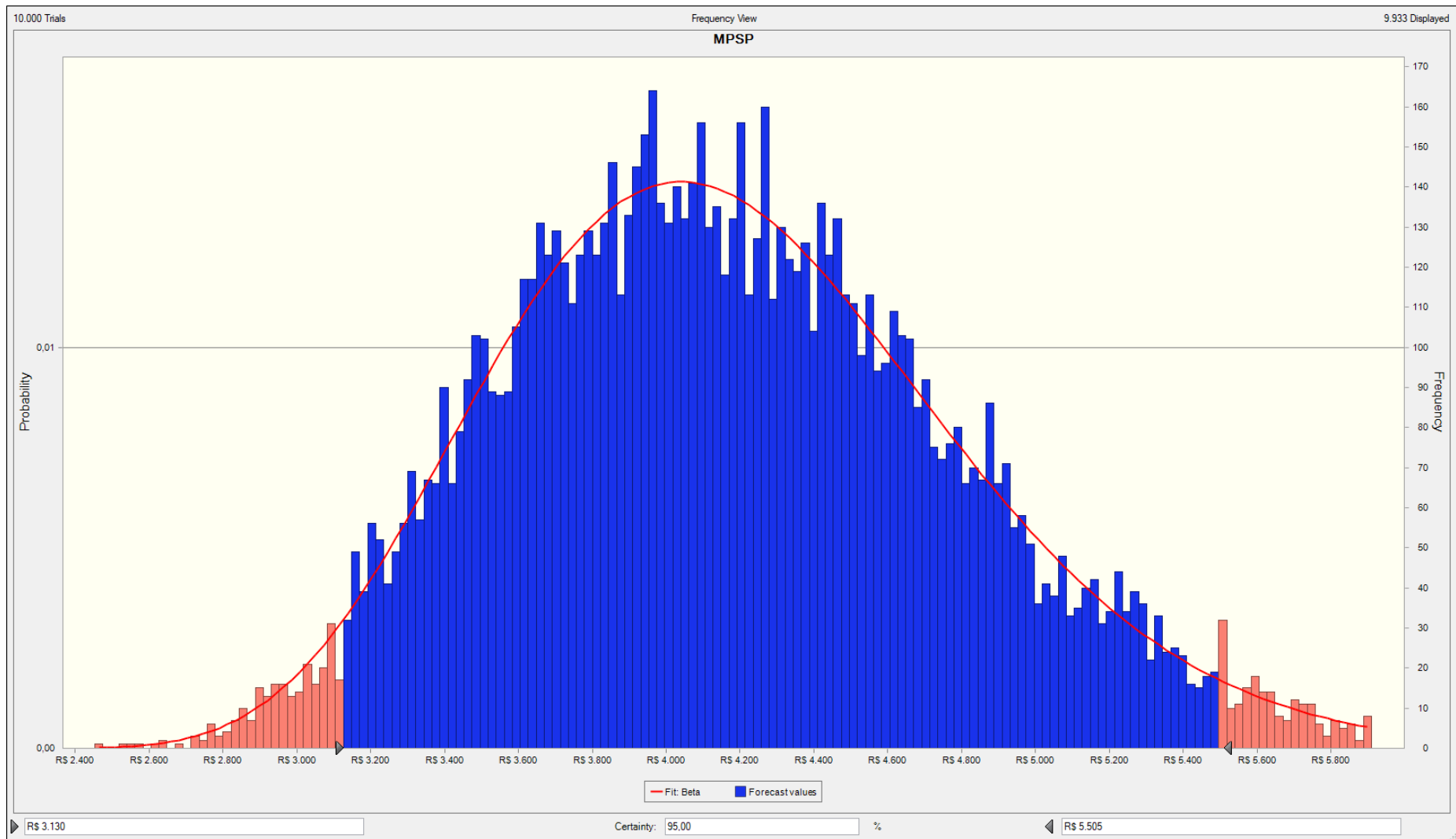


Figure A7 - Probabilistic Risk Assessment of Parameters by Monte-Carlo simulation for Case Study C3. Regions of the graph in blue denote ranges for which the MPSP can be expected with 95% statistical confidence.

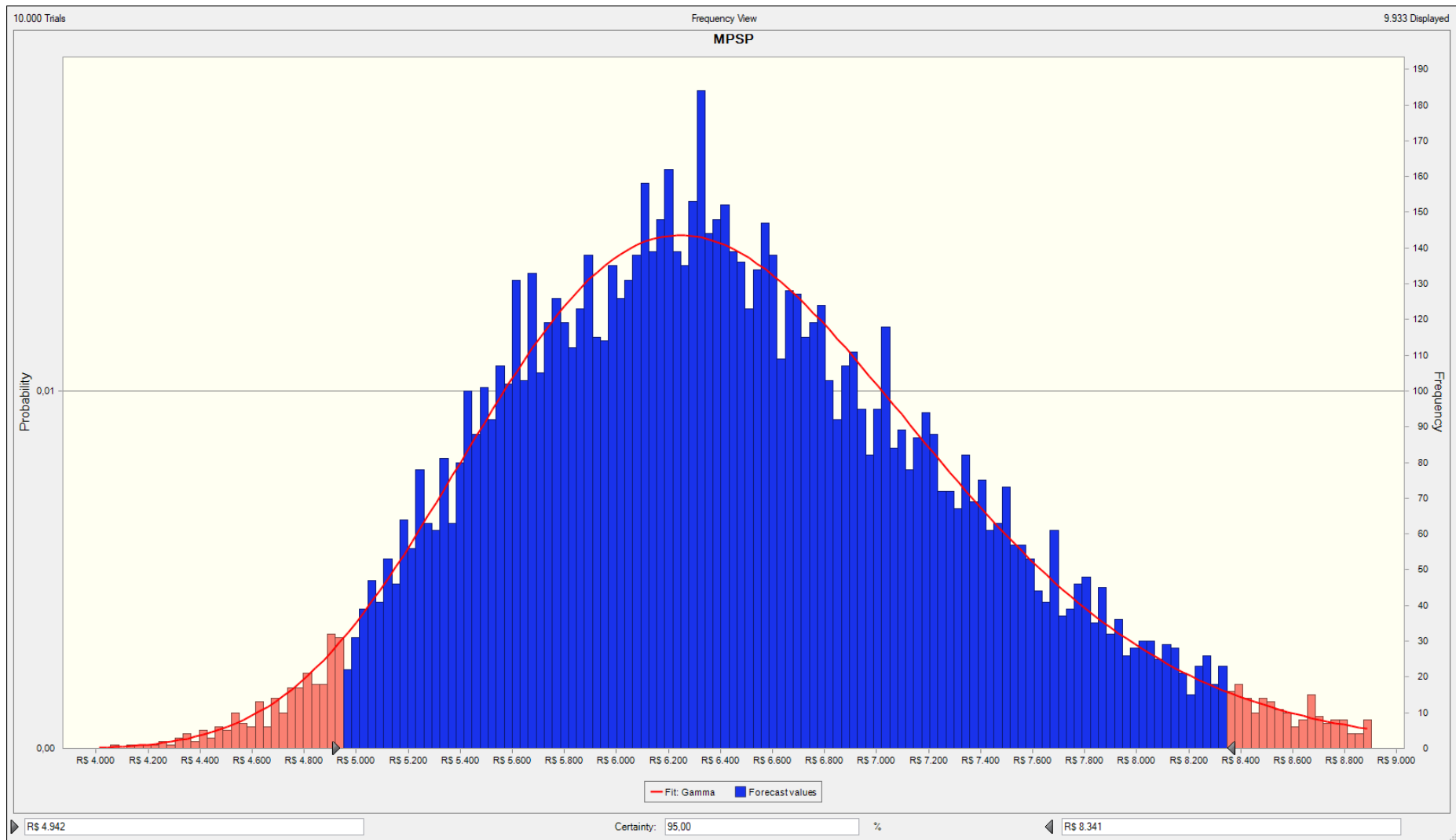


Figure A8 - Probabilistic Risk Assessment of Parameters by Monte-Carlo simulation for Case Study C4. Regions of the graph in blue denote ranges for which the MPSP can be expected with 95% statistical confidence.

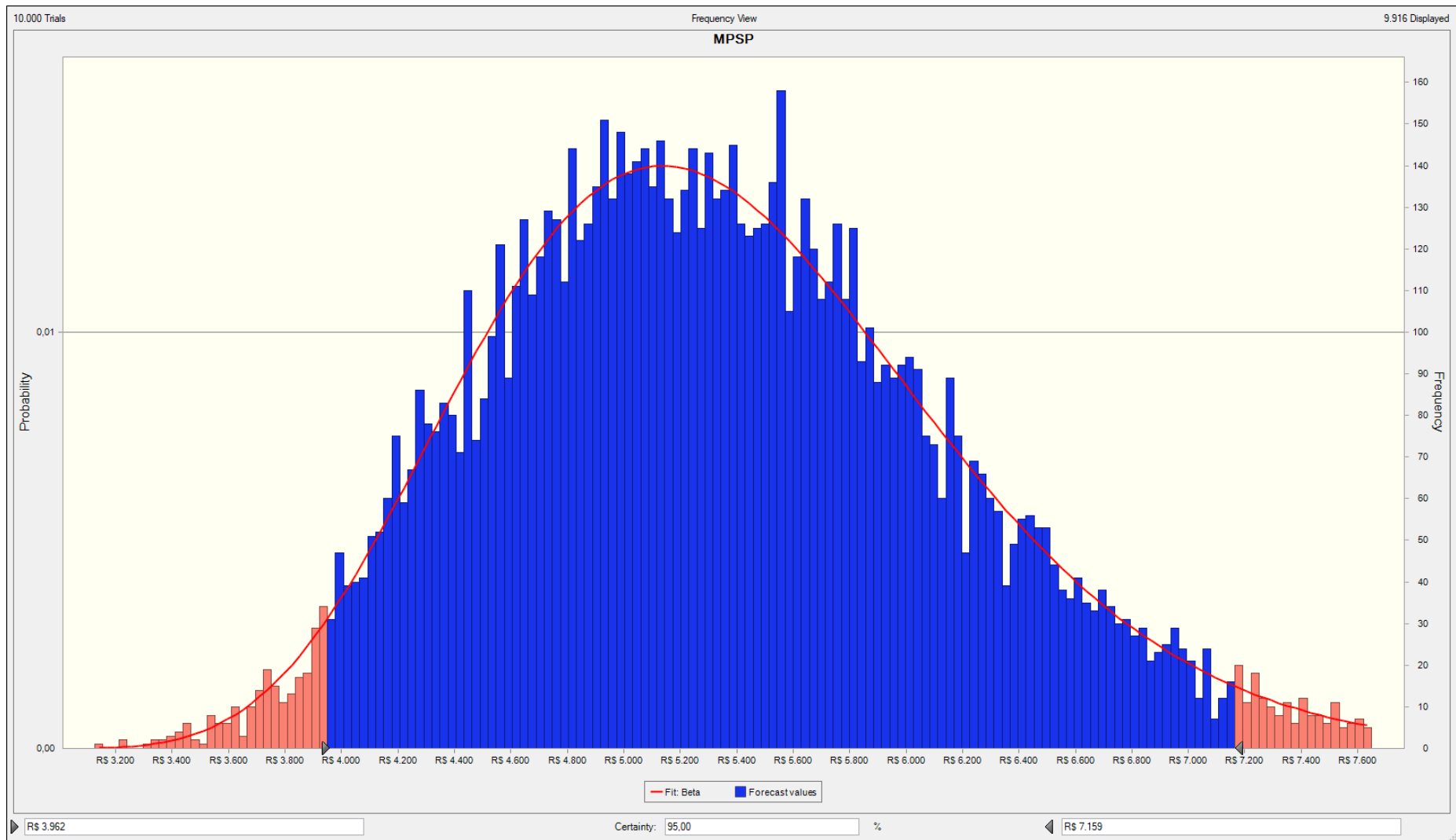


Figure A9 - Probabilistic Risk Assessment of Parameters by Monte-Carlo simulation for Case Study C5. Regions of the graph in blue denote ranges for which the MPSP can be expected with 95% statistical confidence.

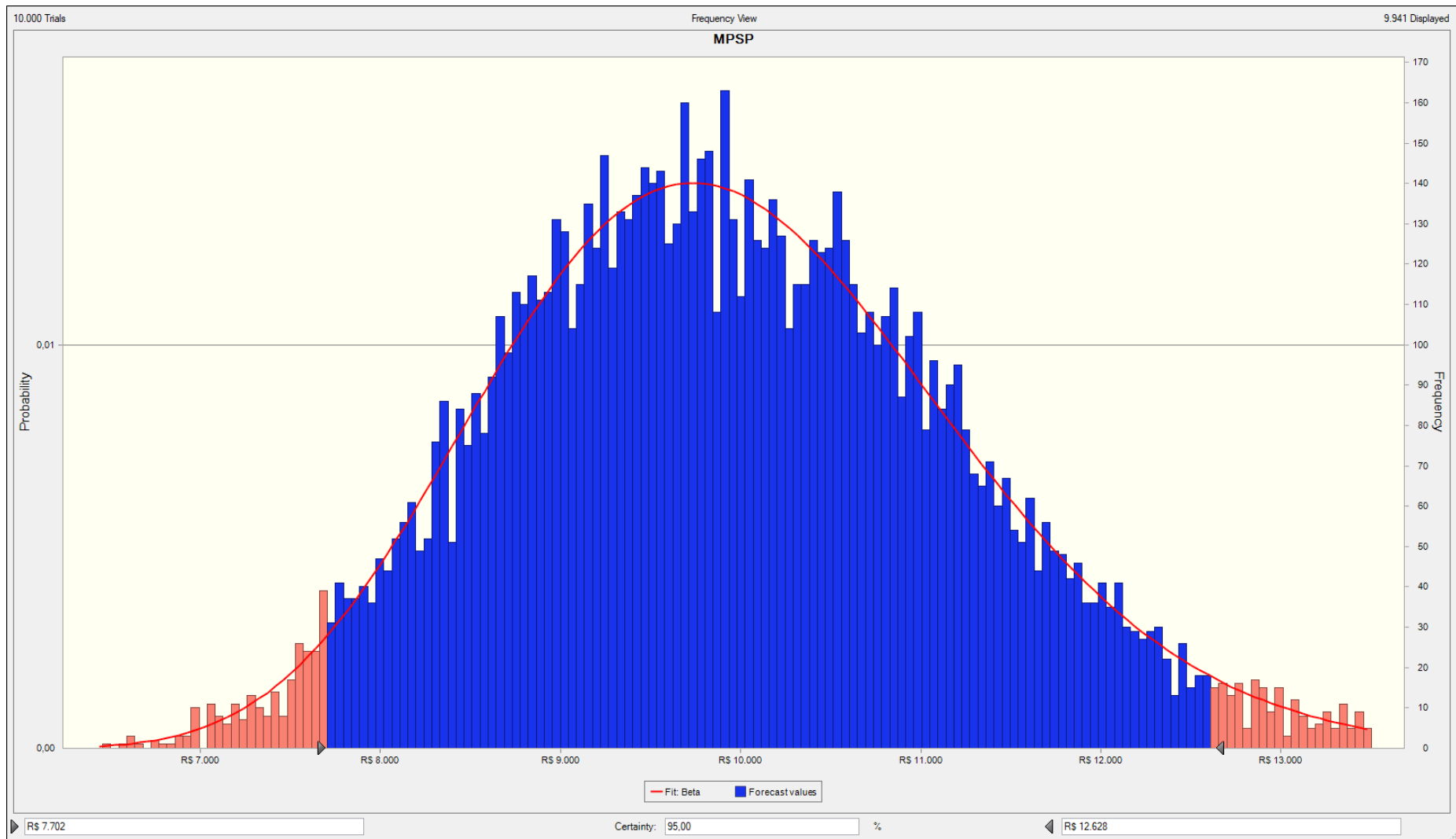


Figure A10 - Probabilistic Risk Assessment of Parameters by Monte-Carlo simulation for Case Study C6. Regions of the graph in blue denote ranges for which the MPSP can be expected with 95% statistical confidence.

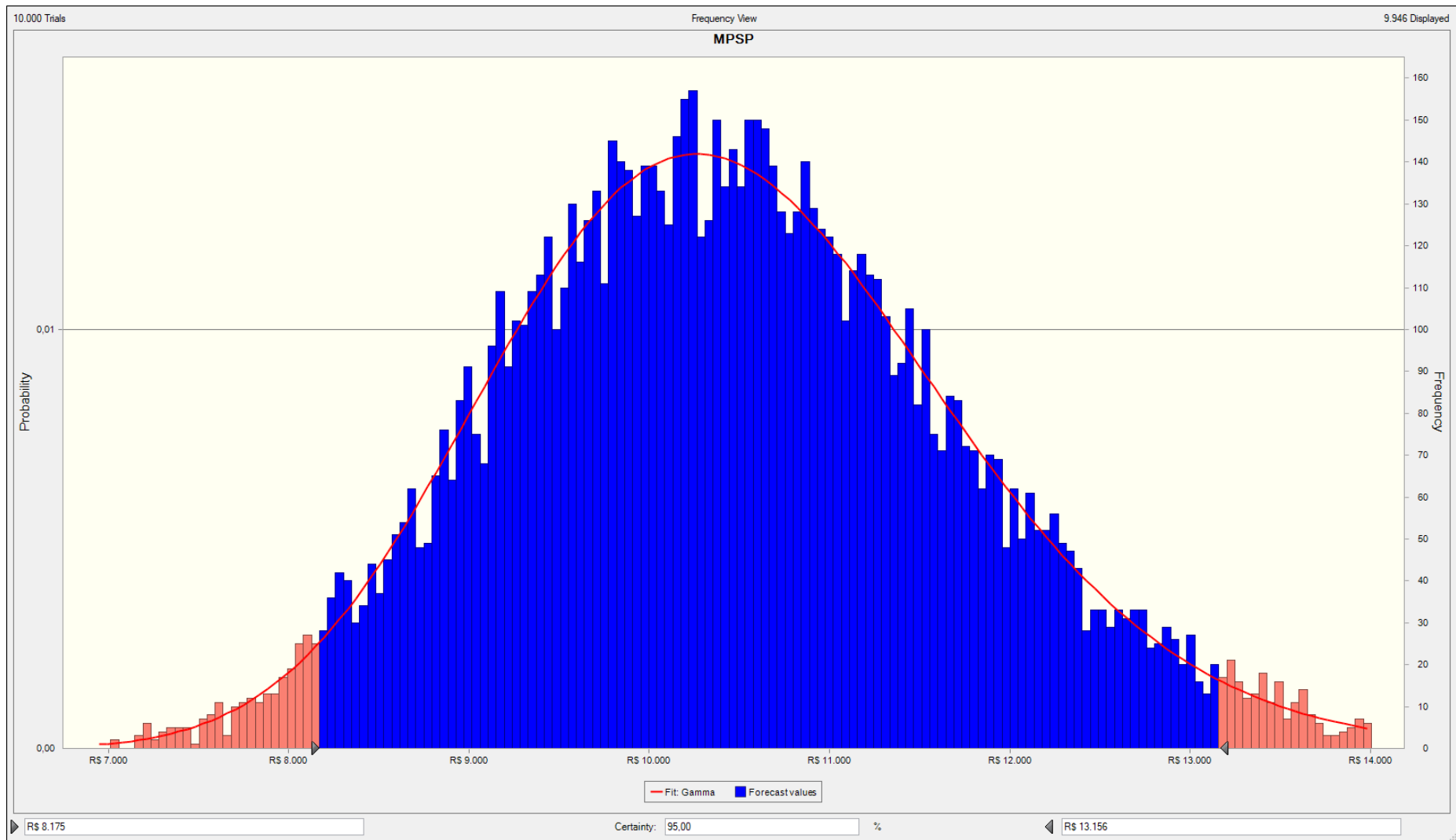


Figure A11 - Probabilistic Risk Assessment of Parameters by Monte-Carlo simulation for Case Study C7. Regions of the graph in blue denote ranges for which the MPSP can be expected with 95% statistical confidence.

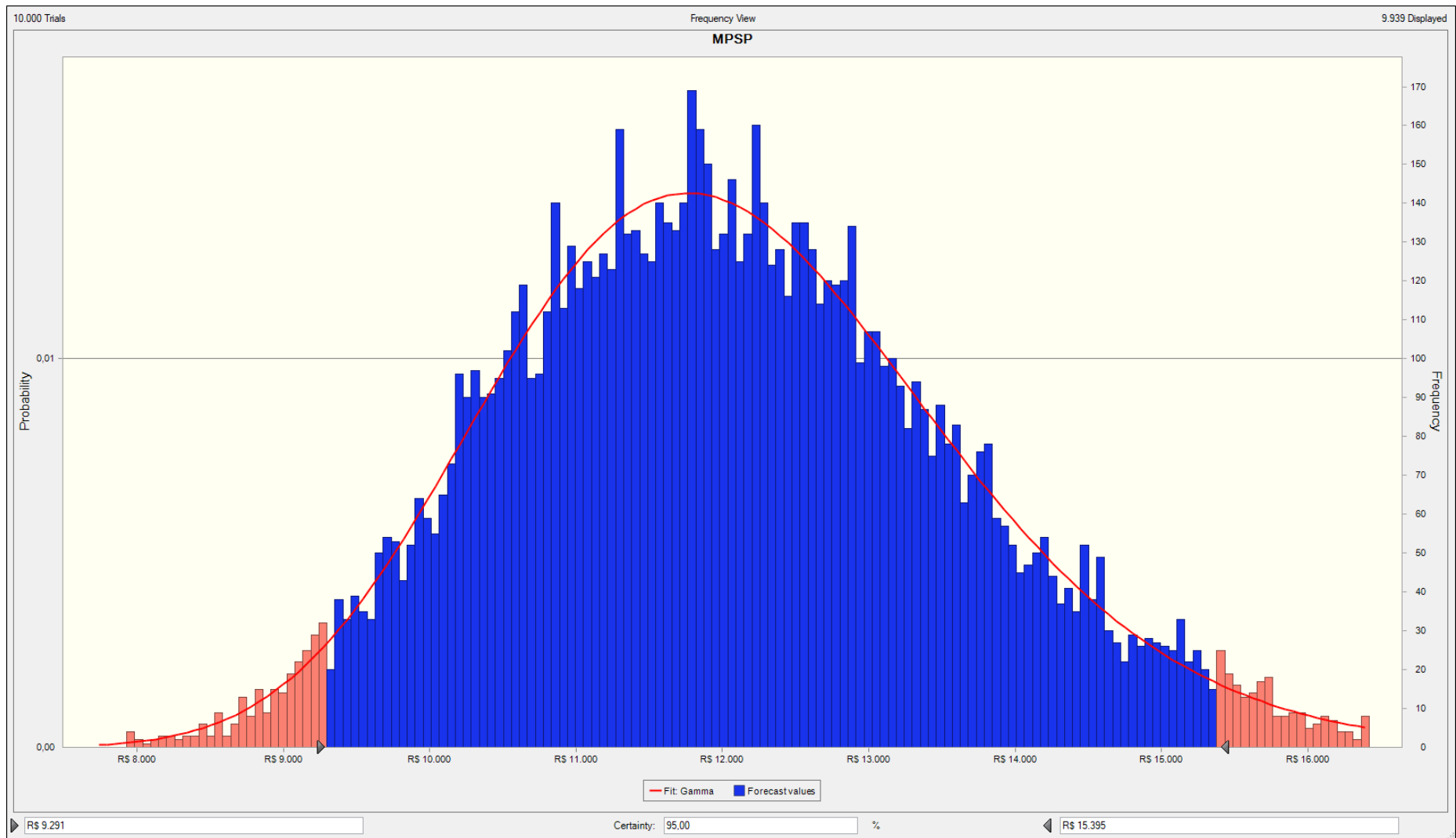


Figure A12 - Probabilistic Risk Assessment of Parameters by Monte-Carlo simulation for Case Study C8. Regions of the graph in blue denote ranges for which the MPSP can be expected with 95% statistical confidence.

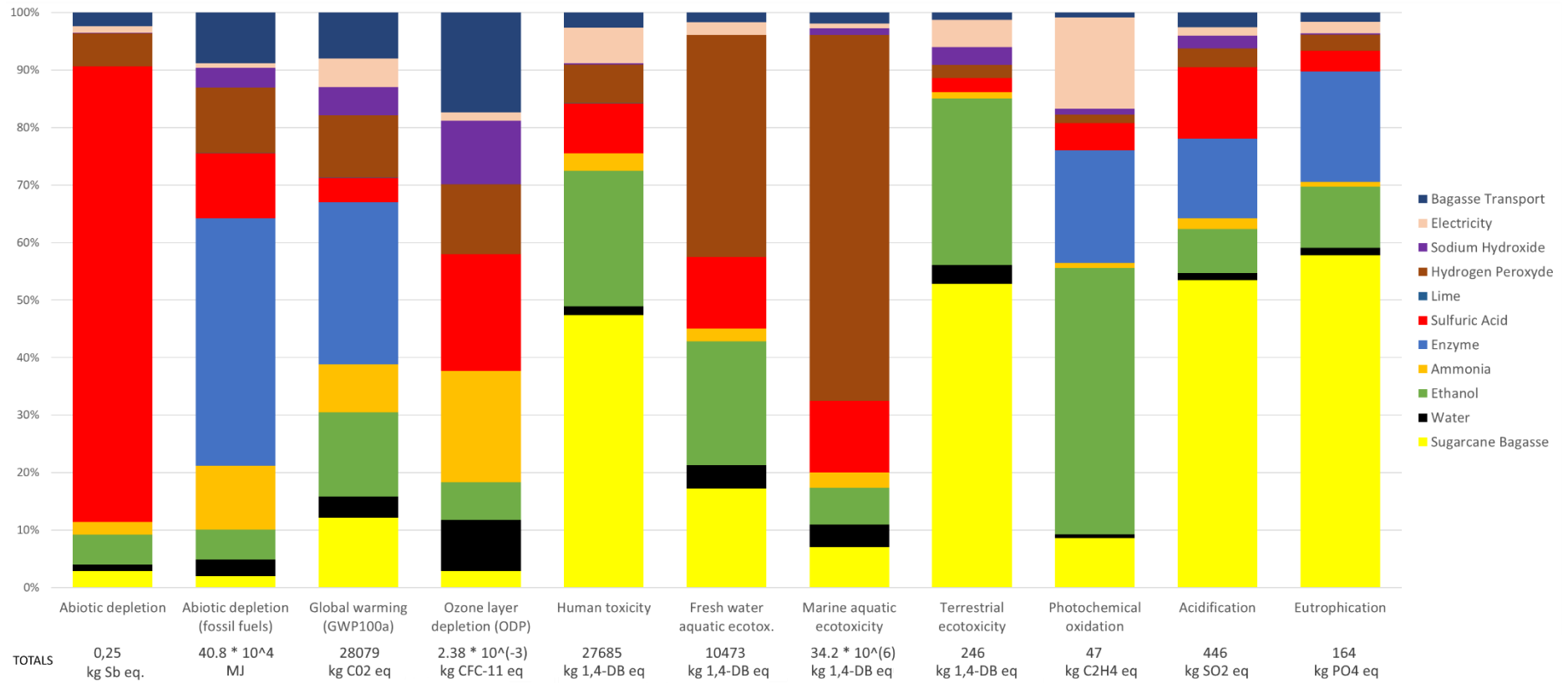


Figure A13 - Relative environmental impacts of each process input for Case Study C2 obtained through Life Cycle Assessment (CML-IA Baseline v3.04 2000 method, SimaPro[®] software). The absolute values for each impact category are also shown.

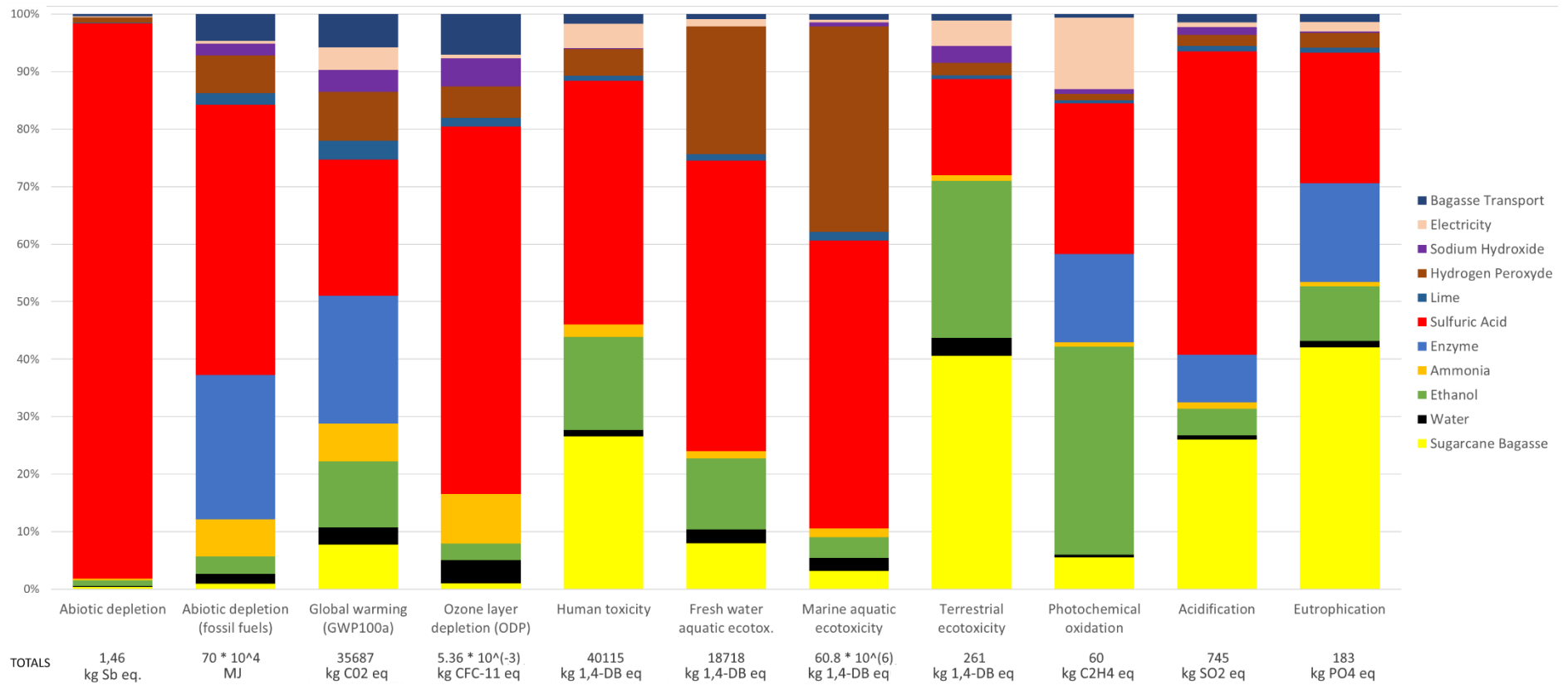


Figure A14 - Relative environmental impacts of each process input for Case Study C4 obtained through Life Cycle Assessment (CML-IA Baseline v3.04 2000 method, SimaPro® software). The absolute values for each impact category are also shown.

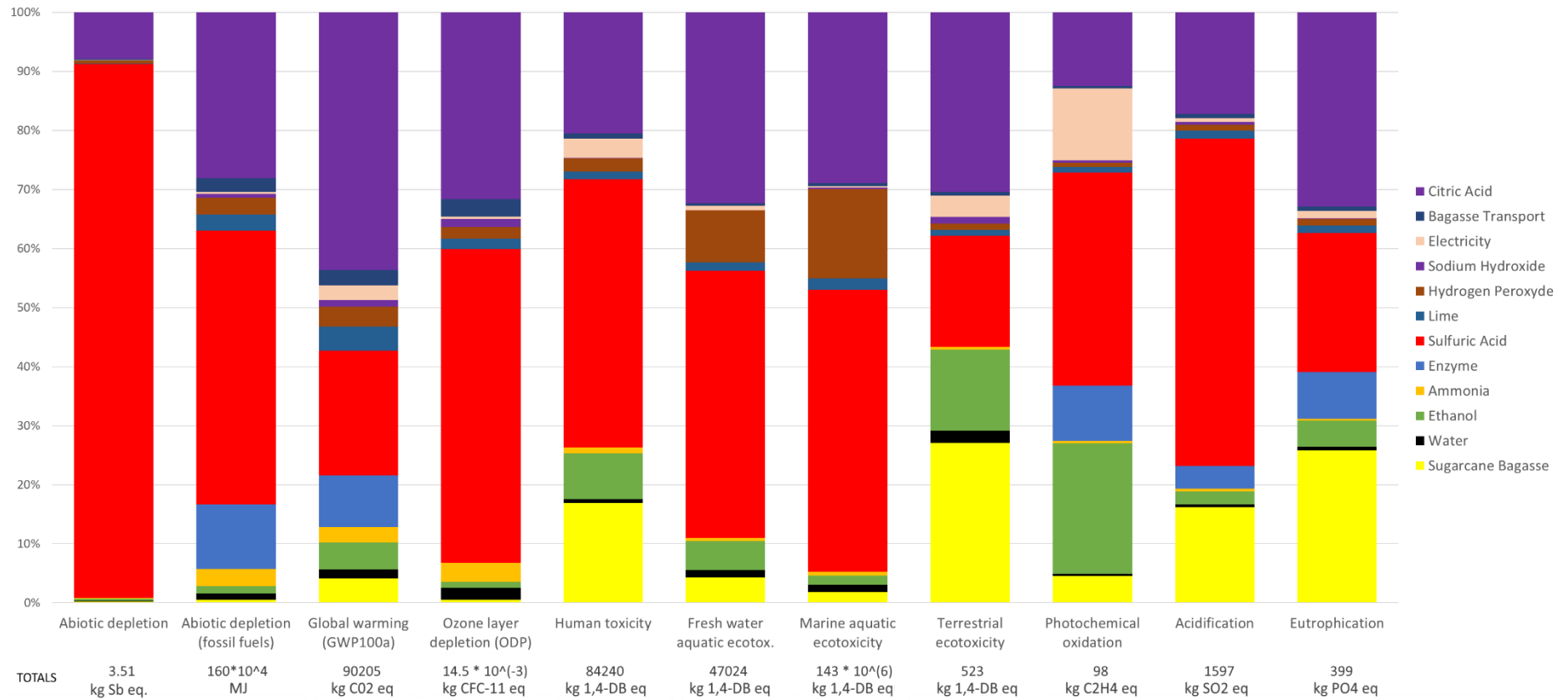


Figure A15 - Relative environmental impacts of each process input for Case Study C6 obtained through Life Cycle Assessment (CML-IA Baseline v3.04 2000 method, SimaPro® software). The absolute values for each impact category are also shown.

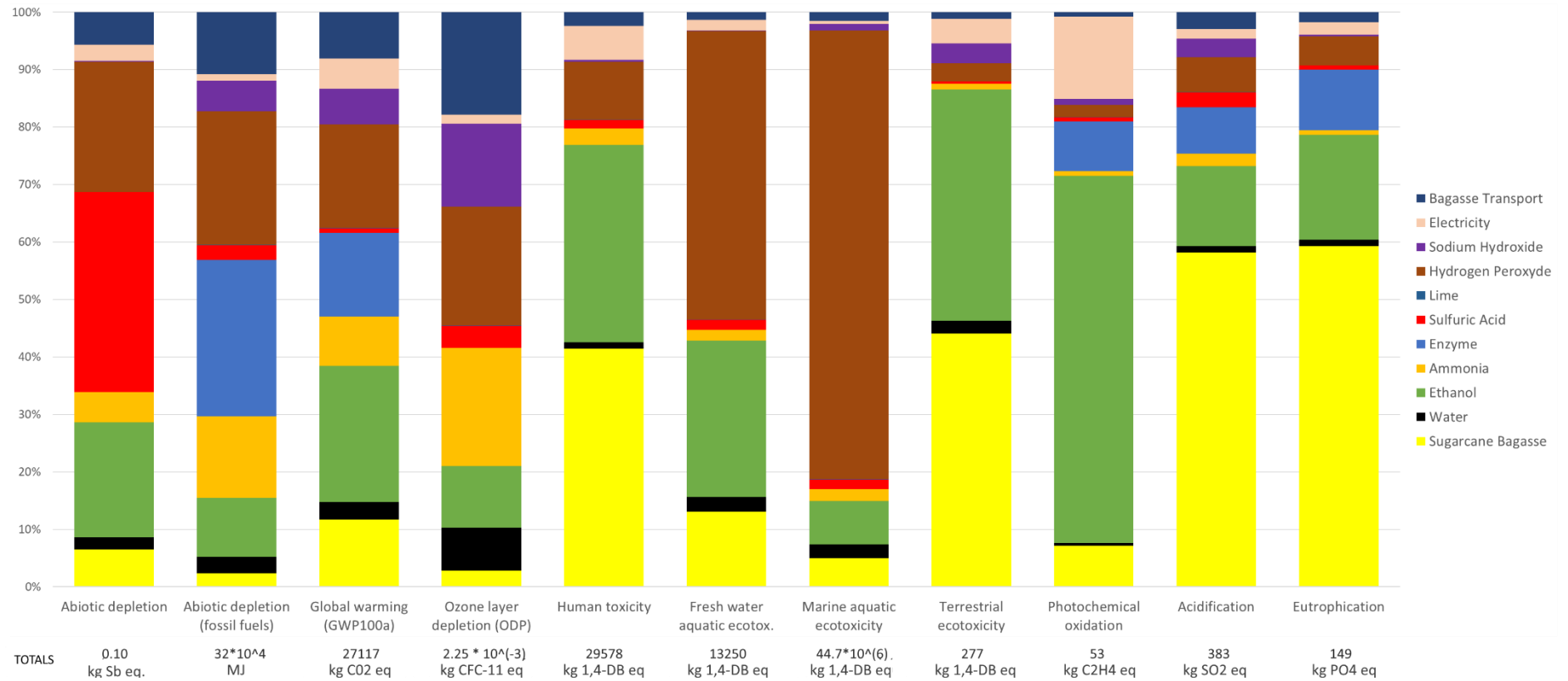


Figure A16 - Relative environmental impacts of each process input for Case Study C8 obtained through Life Cycle Assessment (CML-IA Baseline v3.04 2000 method, SimaPro® software). The absolute values for each impact category are also shown.