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Life cycle assessment as a tool for the industrialisation of chemical and mechanochemical processes

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This thesis represents a collaboration with Deasyl (https://www.deasyl.com/), a Swiss technology provider that relies on innovation and new horizons in mineral and organic chemistry, while upholding principles of green chemistry. The research has been conducted under the auspices of the UNESCO Chair in Life Cycle and Climate Change at Escola Superior de Comerç Internacional from the University Pompeu Fabra (ESCI-UPF) and the PhD Program in Environmental Engineering at the Department of Civil and Environmental Engineering at the Polytechnic University of Catalonia (UPC). Other institutions such as the University of Girona (UdG), the University of Malaga (UMA) the German company WAB-GROUP, and the French company EasylZinc have also collaborated in some of the papers in this thesis. The thesis has been supervised by Dr. Pere Fullana i Palmer, Director of the UNESCO Chair in Life Cycle and Climate Change ESCI-UPF, as well as Dra. Alba Bala Gala, a Executive Director at the same UNESCO Chair, and Dra. Irene Malpartida Garcia, Chief Technical Officer at Deasyl. One of the primary objectives of this thesis is to identify the environmental impacts of innovative syntheses for chemical production and compare them to those obtained for conventional processes. This has been accomplished using an enhanced and adapted methodology for Life Cycle Assessment (LCA).

This doctoral thesis is comprised of six scientific papers, beginning with two review papers that serve as the theoretical framework for the subsequent articles. Specifically, they provide a thorough examination and synthesis of existing research in the field, which is essential to understanding the contributions made by the following articles. By establishing a strong theoretical foundation, the review papers provide a solid basis for the empirical work that follows. In this way, the thesis builds on a cohesive and well-supported framework, allowing for a deeper exploration and analysis of the topics at hand:

I.   Life cycle assessment as a tool for evaluating chemical processes at industrial scale: a review [2].

II.   Linking Mechanochemistry with the Green Chemistry principles: Review article [3].

The following articles are LCAs of different production processes based on chemical and mechanochemical reactions. They are more specific and applied articles in which the environmental impact of different production routes is calculated, interpreted, and compared, helping to inform broader discussions about sustainable manufacturing practices:

III. Life cycle assessment on calcium zincate production methods for rechargeable batteries [4].

IV. Wood chips components separation with a new mechanochemical process compared to chemical depolymerization: a technical, economic and environmental comparison [5].

V. Sustainability of cellulose micro-/nanofibers: A comparative life cycle assessment of pathway technologies [6].

VI. Compared life cycle assessment for nicotine extraction from tobacco leaves according to processes and experimental conditions at lab scale *(Under review)*.

Finally, a detailed study using a similar methodology as for previous articles and implementing modelling and simulation tools such as AspenPlus and CosmoRS for a circular economy model of biodiesel production has been used for the industrialisation of a laboratory process to pilot scale. Based on mechanochemistry and waste management, divided into 3 parts corresponding to: i) production of biodiesel from used cooking oils (UCO), ii) valorisation of waste glycerol into calcium diglyceroxide (CaDG), catalyst to produce biodiesel from UCO, and iii) solketal, additive to improve the properties of biodiesel. This study has not been published due to third-party confidentiality issues at the completion date of the thesis but it is discussed in the chapter 10.

In addition, during the period of development of the thesis, several LCA articles have been published in which the author of the thesis appears as co-author:

- Life cycle assessment of PE and PP multi film compared with PLA and PLA reinforced with nanoclays film [7].
- Techno-economic and environmental evaluation of a market pulp reinforced with micro-/nanofibers as a strengthening agent in packaging paper [8].
- Short Communication: Biogenic Carbon in Fast-Moving Products: A deception or Real Contribution to Circularity? [9].

The publication of the above-mentioned studies contributed through oral and poster presentations at various scientific congresses of international reputation. For example:

- SETAC Europe 32nd Annual Meeting (https://europe2022.setac.org/) in Copenhagen (Denmark) from 15th to 19th of May 2022, presenting a poster about the calcium zincate article [4] and a short talk about the LCA in chemical reactions review [2].

- LCIC 2022 (https://fslci.org/lcic/lcic2022/) in Berlin (Germany) from 29th of June to 1st of July 2022, presenting an updated version of the poster about the calcium zincate article [4].
- CONAMA 2022 (https://2022.conama.org/) in Madrid (Spain) from 21st to 24th of November 2022, presenting a poster about the preliminar results on the circularity of a biodiesel framework based on the biodiesel production from UCO and valorisation of the glycerol waste into CaDG and solketal.
- GREN 2023 (https://www.elsevier.com/events/conferences/green-and-sustainable-chemistry-conference) in Dresden (Germany) from 22nd to 24th of May 2023, presenting an updated version of the poster about biodiesel and a short talk about all the different articles included in this thesis.
- MeCCE15 (https://www.mecce.org/) in Barcelona (Spain) from 30th of May to 2nd of June 2023, presenting an updated poster about all the different articles included in my thesis.

During the stay at UNESCO Chair in Life Cycle and Climate Change, I had the enriching opportunity to attend COP27 (https://cop27.eg/#/) as an observer, in Sharm el-Sheikh (Egypt) from 6th to 18th of November 2022. I was also able to participate as a professor in the brush-up course in Chemical Principles and in the Carbon Footprint subject at the Master of Science in Sustainability Management jointly offered by ESCI-UPF and UPF-BSM. As well as in the postgraduate course on Sustainability Transition and Climate Emergency at ESCI-UPF in the subjects of Organisation Carbon Footprint and Organisation Environmental Footprint. As part of my work with the UNESCO Chair, I also could apply the most important carbon footprint and life cycle assessment (LCA) methodologies in several consultancy projects for private institutions such as the following:

- Carbon footprint of a green hydrogen production plant in Las Palmas and Tenerife (Canary Islands).
- Life cycle assessment of an oxalic acid production facility in Spain.
- Environmental factor calculation of several energy production technologies for the Oficina Catalana de Canvi Climàtic (OCCC).
- Guidelines for small companies in climate change mitigation and adaptations for the Cambra de Comerç de la Comunitat Valenciana.
- Organisational carbon footprint (scope 1 and 2) of ports in Las Palmas (Canary Islands).
- EPD certification of the products of 2 steel production plants in Barcelona (Spain) and Huta (Poland).

- Organisational carbon footprint of a (bio)plastic company in Barcelona (Spain).
- Life cycle assessment of the products of a leather additives company in Barcelona (Spain).
- Organisational carbon footprint of several health institutes in Barcelona (Spain).

I also had the unvaluable experience of spending a 3 months-stage at the Pontificia Universidad Católica de Chile, because of a collaboration between this university and Deasyl. During this time, I participated in the development of their education in LCA and attended training in the use of different software for the modelling of chemical processes (AspenPlus v12 and CosmoRS) that were used for the study of the processes for biodiesel, calcium diglyceroxide and solketal production.

To conclude, and with the aim of disseminating my contributions in the scientific field, all the results I have obtained throughout this thesis, among others, have been promoted through social media in X (@SergiArfelis), LinkedIn (Sergi Arfelis Espinosa), and Instagram/Threads (@sergiarfelis).

IV. LIST OF ACRONYMS

AOP	Advanced Oxidation Processes
BHKP	Bleached Hardwood Kraft Pulp
BSM	Barcelona School of Management
CaDG	Calcium Diglyceroxide
CAZN	Calcium Zincate
CDP	Chemical Depolymerization Process
CED	Cumulative Energy Demand
CLP	Classification, Labelling and Packaging of hazardous substances
CMNF	Cellulose Micro- and NanoFibers
CNF	Cellulose NanoFibers
CSTR	Continuous Stirred Tank Reactor
EEA	European Economic Area
ELCD	European Reference Life Cycle Data System
EoL	End-of-Life
EPLCA	European Platform on Life Cycle Assessment
ESCI	Escola Superior de Comerç Internacional
EU	European Union
FU	Functional Unit
GC	Green Chemistry
GCO-II	Global Chemicals Outlook II
GO	Graphene Oxides
HCS	Hydro-Chemical-Synthesis
HMMS	Hydro-Micro-Mechanical-Synthesis
HMS	Hydro-Mechanical-Synthesis
HPH	High-Pressure Homogenizer
HTS	Hydro-Thermal-Synthesis
ICHEM	Impact (Induction) in Continuous-flow Heated Mechanochemistry
ILCD	International Reference Life Cycle Data System
ISO	International Organization for Standardization
IUPAC	International Union of Pure and Applied Chemistry
JRC	Joint Research Centre
LAG	Liquid-Assisted Grinding

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LCA	Life Cycle Assessment
LCC	Life Cycle Costing
LCDN	Life Cycle Data Network
LCI	Life Cycle Inventory
LCIA	Life Cycle Impact Assessment
LCSA	Life Cycle Sustainability Assessment
LCT	Life Cycle Thinking
LP	Low-Pressure
MOF	Metal-Organic Framework
NGO	Non-Governmental Organisation
OCCC	Oficina Catalana de Canvi Climàtic
PEF	Product Environmental Footprint
PV	Photovoltaics
REACH	Registration, Evaluation, Authorisation and Restriction of Chemicals
ROSES	RepOrting standards for Systematic Evidence Syntheses
SCP	Sustainable Consumption and Production
SDG	Sustainable Development Goals
SEM	Scanning Electron Microscopy
s-LCA	Social Life Cycle Assessment
SSE	Singles-Screw Extrusion
TAA	Triacetonamine
TEMP	2,2,6,6-tetramethylpiperidine
TEMPO	2,2,6,6-tetramethyl-1-piperidinyloxy radical
TSE	Twin-Screw Extrusion
UCO	Used Cooking Oils
UdG	University of Girona
UK	United Kingdom
UMA	University of Málaga
UN	United Nations
UPC	Polytechnic University of Catalonia
UPF	University Pompeu Fabra
WBCSD	World Business Council for Sustainable Development
WMP	Wet Milling Process
ZVI	Zero-Valent Iron

V. ABSTRACT

The chemical sector is a $4 trillion global business and a significant employer, with chemicals present in almost all manufactured goods. The increased investment and innovative capacity of the chemicals industry to provide safe and sustainable chemicals will be vital to offer new solutions and supporting the green transition of our economy and society. There have been multiple approaches and tools created to aid chemists in the development, design, and application of chemical products. The approach of the Life Cycle Assessment (LCA) applied to the design of chemicals and processes have helped scientists to look at environmental impacts with a life cycle perspective. It provides a comprehensive view of the environmental loads, covering a wide set of environmental performance indicators such as Global Warming Potential, Primary Energy Consumption, Water Use, Land Use or Depletion of resources. Despite this, their availability in scientific databases is scarce, especially within the chemical and industrial sectors. Much of the information is protected by confidentiality issues, the processes are presented as black boxes, and the data are at laboratory scale, so the results are not representative of the industrial scale.

The present thesis is related to the application of the LCA for the industrialisation of chemical and mechanochemical processes. The first article presents the literature review on how LCA has been applied to chemical processes. The second article is another literature review specifically focused on mechanochemistry processes in the frame of green chemistry. Chemistry and mechanochemistry are cutting edge LCA application sectors and its methodology is scarce. The development of review articles aims to bring a guide for the development of these topics. Furthermore, the thesis proceeds with the assessment of innovative technologies for different chemical and mechanochemical processes: production of calcium zincate as ingredient for rechargeable batteries, cellulose extraction from wood chips, or nicotine extraction from tobacco leaves, for instance.

It has been concluded that the choice of feedstock is typically the main source of environmental impact of a chemical process. In addition, the mass and energy balances as well as the type of energy supplied to feed the process are of great importance, as part of the life cycle inventory. When selecting the functional unit (FU) of processes from the chemical industry sector, where a quantity of product must be supplied in a given time, special attention must be paid. Although outside of the cradle-to-gate LCA practice, there are variables such as the residence time of the reaction which make the final product with more service units or more function. Therefore, this should be considered as valuable additional information when deciding among alternatives. The

result of the LCA with a FU depending only on mass does not take this into account. There are several chemical LCA papers that already perform the study with a flowrate as FU. Another example is the consideration of module D within the EN 15804:2012+A2:2019 for the consideration of information out of the cradle to gate scope in construction products LCAs [10], [11]. On the other hand, the scaling of material flows from laboratory scale, where the data are obtained, to pilot or industrial scale, where the process is to be applied, is of crucial importance. For this purpose, different frameworks based on thermodynamic equations, as well as process modelling, and simulation tools have been used during the thesis. For instance, it has been observed that the process integration from laboratory to industrial scale is about 20%, as average, reaching maximum values of 90% for some equipment such as the ball mill reactor used at Deasyl laboratories. Finally, in the LCA comparisons, a study of the evolution of the environmental impact is carried out considering the forecast of the electricity mixes in the following years according to the reports of the European green deal to interpret the results behaviour along next years.

Article 3, 4, 5 and 6 present different comparative studies based on LCA and technical and economic feasibility for different chemical processes. In general, the mechanochemical processes are favoured over solvothermal processes. Mainly, the advantages offered by mechanochemical and wet-milling are related to the ability to operate continuously, with milder conditions and reducing the use of solvent. As well as greater ease of scalability and operation of the process. Also playing an important role is the fact that while conventional processes require steam, traditionally produced from natural gas, propane or naphtha, to reach high temperatures, mechanochemical reactors require an electrical power supply to drive the motor and reactor discs, which generally has a smaller environmental footprint.

Keywords: LCA, Mechanochemistry, Chemical reaction, Industrialisation, Mass balance, Energy balance.

VI. RESUMEN

El sector químico es un negocio global de \$4 billones y un importante empleador, con sustancias químicas presentes en casi todos los productos manufacturados. El aumento de la inversión y de la capacidad innovadora de la industria química para proporcionar productos seguros y sostenibles será vital para ofrecer nuevas soluciones y apoyar la transición ecológica de nuestra economía y sociedad. Se han creado múltiples enfoques y herramientas para ayudar a los químicos en el desarrollo, diseño y aplicación de productos químicos. El enfoque del Análisis del Ciclo de Vida (ACV) aplicado al diseño de productos químicos y procesos ha ayudado a los científicos a examinar los impactos ambientales con una perspectiva de ciclo de vida. Proporciona una visión global de las cargas medioambientales, abarcando un amplio conjunto de indicadores medioambientales como el Calentamiento Global, el Consumo de Energía Primaria, el Uso del Agua, el Uso del Suelo o el Agotamiento de los Recursos. A pesar de eso, su disponibilidad en bases de datos científicas es escasa, especialmente dentro de los sectores químicos e industriales. Mucha de la información es protegida por temas de confidencialidad, los procesos se presentan como cajas negras, y los datos se encuentran a escala de laboratorio, con lo cual los resultados no son representativos de la escala industrial.

La presente tesis está relacionada con la aplicación del ACV a la industrialización de procesos químicos y mecanoquímicos. El primer artículo presenta la revisión bibliográfica de ACV aplicado a procesos químicos. El segundo artículo es otra revisión de procesos mecanoquímicos. La química y la mecanoquímica son sectores punteros en la aplicación del ACV y su metodología es escasa. El desarrollo de estos artículos pretende aportar una guía para el desarrollo de estos temas. Además, la tesis prosigue con la evaluación de tecnologías innovadoras para procesos químicos: producción de zincato cálcico como ingrediente para baterías recargables, extracción de celulosa a partir de astillas de madera o extracción de nicotina a partir de hojas de tabaco, por ejemplo.

Se ha concluido que la elección de la materia prima suele ser la principal fuente de impacto ambiental de un proceso químico. Además, los balances de masa y energía, así como el tipo de energía suministrada para alimentar el proceso, son de gran importancia, como parte del inventario del ciclo de vida. Al seleccionar la unidad funcional (UF) de procesos del sector industrial químico, donde se debe suministrar una cantidad de producto en un tiempo dado, se debe prestar especial atención. Aunque quede fuera de la práctica del ACV de la extracción de materias primas a la obtención del producto, hay variables como el tiempo de residencia de la reacción que hacen que el producto final tenga mayor calidad o funcionalidad. Por lo tanto, esto

debe considerarse como información adicional valiosa al decidir entre alternativas. El resultado del ACV con una UF que depende solo de la masa no tiene en cuenta esto. Hay varios documentos de ACV químico que ya realizan el estudio con un caudal como UF. Otro ejemplo es la consideración del módulo D dentro de la EN 15804:2012+A2:2019 para la consideración de información fuera del alcance de la cuna a la obtención del producto en los ACV de productos de construcción. Por otro lado, la escalabilidad de los flujos de materiales desde la escala de laboratorio, donde se obtienen los datos, hasta la escala piloto o industrial, donde se aplicará el proceso, es de crucial importancia. Para este propósito, se han utilizado diferentes marcos basados en ecuaciones termodinámicas, así como modelado de procesos y herramientas de simulación durante la tesis. Por ejemplo, se ha observado que la optimización energética desde la escala de laboratorio hasta la industrial es del 20%, en promedio, alcanzando valores máximos del 90% para algunos equipos como el reactor utilizado en los laboratorios de Deasyl. Finalmente, en las comparaciones de ACV, se lleva a cabo un estudio de la evolución del impacto ambiental teniendo en cuenta la previsión de las mezclas de electricidad en los próximos años según los informes del Pacto Verde Europeo para interpretar el comportamiento de los resultados en los próximos años.

En los resultados de los diferentes estudios comparativos basados en ACV y factibilidad técnica y económica, los procesos mecánico-químicos son favorecidos sobre los procesos convencionales. Principalmente, las ventajas ofrecidas por la mecano-química están relacionadas con la capacidad de operar de manera continua, con condiciones más suaves y reduciendo el uso de solventes. El uso de la mecanoquímica permite reducir problemas de transferencia de masa por ejemplo de procesos químicos donde los reactivos no son miscibles. Otras ventajas son una mayor facilidad de escalabilidad y operación del proceso. También juega un papel importante el hecho de que mientras los procesos convencionales requieren vapor, tradicionalmente producido a partir de gas natural, propano o nafta, para alcanzar altas temperaturas, los reactores mecánico-químicos requieren un suministro eléctrico para impulsar el motor y los discos del reactor, lo que generalmente tiene una huella ambiental más pequeña.

Palabras clave: ACV, Mecanoquímica, Reacción química, Industrialización, Balance de masa, Balance de energía

1. INTRODUCTION

1.1. BACKGROUND

In September 2015 the United Nations (UN) launched an ambitious plan for a better and more sustainable future for all people and the world by 2030. This framework, which is called the Sustainable Development Goals (SDGs), consists of 17 aspirational goals and 169 specific targets to measure, and achieve the goals. The SDGs have been embraced by governments, industry, and many other organizations worldwide [12]. The goals are designed to tackle the major global challenges we face, including poverty, inequality, climate change, environmental degradation, peace, and justice [13]. The SDGs were developed after extensive consultations and negotiations involving a wide range of stakeholders, including international businesses, non-governmental organizations (NGOs), policy makers, and civil society [14].

Chemistry and chemical industry play an essential role in helping society achieve the SDGs. The Global Chemicals Outlook-II (GCO-II) recognizes that advancements in chemistry contribute to the attainment of the SDGs. The chemical industry is a massive global business worth over four trillion dollars, providing direct and indirect employment opportunities to more than 20 million people worldwide and impacting over 95% of manufactured goods [15]. Chemicals are everywhere in our daily life and play a fundamental role in most of our activities, as they are present in almost every device we use. Chemicals are also the building blocks of low-carbon, zero pollution and energy- and resource-efficient technologies, materials, and products. The increased investment and innovative capacity of the chemicals industry to provide safe and sustainable chemicals will be vital to offer new solutions and support the green transition of our economy and society [16]. Many chemical companies, such as Dow Chemical and BASF, have already aligned their strategy with the SDG program. In addition, there are multiple examples of cases where green and sustainable chemistry contribute in some of these goals by innovations and the use of advanced materials.

For instance:

- To achieve SDG 2, which aims to eliminate hunger, chemicals are used to protect plants and crops from pest infestations, improving food production and distribution channels. Additionally, advances in packaging can help extend the life of food while ensuring its quality and safety. [17], [18], [19].
- SDG 3 aims to promote good health and well-being, and achieving this requires a deeper understanding of how diseases and hazardous chemicals in our food, water, and

environment affect human health. To address this, it is important to focus on medical diagnosis, pharmaceutical development and management, and the development of disinfectants that do not contribute to antimicrobial resistance [20], [21].

- SDG 6 aims to ensure access to clean water and sanitation for all, and there are several ways to achieve this goal. Developing new chemicals to enhance water purification and lower-cost desalination processes are crucial steps in achieving universal access to safe and affordable drinking water [22], [23].

- Achieving SDG 7, which aims to secure affordable and clean energy, and SDG 12, which promotes responsible consumption and production, requires the development of new materials for renewable energy, as well as more energy-efficient processes in the chemical industry. Additionally, advancing cleaner fuel technologies can contribute to achieving these goals [24], [25], [26], [27].

- SDG 13 aims to mitigate and adapt to climate change, and there are several ways to achieve this goal. For example, the development of advanced materials for renewable energy can reduce reliance on fossil fuels and lower carbon emissions. Additionally, improving treatments for diseases and developing high-yield seeds and fertilizers can increase food production and help reduce the environmental impact of agriculture [28], [29], [30].

The European Union (EU) has one of the most comprehensive and protective regulatory frameworks for chemicals globally, backed by advanced knowledge. This framework is increasingly recognized as a model for safety standards worldwide, consisting of around 40 legislative instruments. Key regulations include the Registration, Evaluation, Authorization, and Restriction of Chemicals (REACH) and the Classification, Labelling, and Packaging of hazardous substances (CLP). Additionally, legislation on the safety of toys, cosmetics, biocides, plant protection products, food, carcinogens in the workplace, and environmental protection are also part of the EU's regulatory framework [16]. The EU has achieved undeniable success in creating an efficient internal market for chemicals while reducing risks to human health and the environment posed by hazardous substances such as carcinogens and heavy metals. Furthermore, the predictable legislative framework provided by the EU allows companies to operate in a stable regulatory environment [16].

Even though, 84% of Europeans are worried about the impact of chemicals present in everyday products on their health, and 90% are worried about their impact on the environment [31]. To facilitate the green transition of the chemical industry and its value chains, innovation must be prioritized, and existing EU chemicals policy must evolve and respond more effectively to the

challenges posed by hazardous substances. This includes promoting the safe and sustainable use of all chemicals while minimizing and substituting chemicals with chronic effects on human health and the environment whenever possible. Furthermore, it is essential to phase out the most harmful substances used in non-essential consumer products. While legislative efforts are still necessary, it is important to educate citizens regarding the safe use of chemicals. In some cases, there is high concern for harmless materials. Promoting the safe and sustainable use of chemicals can help reduce public concern and improve confidence in chemical safety.

The development of Environmental Life Cycle Assessment (LCA) or Life Cycle Sustainability Assessment – which refers to the evaluation of environmental, social and economic impacts of products throughout their life cycle [32] – provide quantitative metrics in the design stage of chemical products. This helps making the most appropriate decisions from a sustainable point of view. Quantifying and communicating transparently the environmental and health impacts of chemical products could help alleviate public concerns.

For many years, the scientific community has advocated for a more circular economy with a life-cycle perspective to avoid rebound effects [33]. To aid chemists in the development, design, and application of chemical products, multiple approaches and tools have been created. Although these tools have not yet been directly aligned with the SDGs, the holistic approach of LCA has enabled scientists to evaluate environmental impacts throughout the life cycle of products, from raw material sourcing to end-of-life (EoL) disposal. As a result, LCA and other sustainability assessment methods can inform the development of chemical products that align with the principles of the circular economy and promote progress towards the SDGs.

The basis of this thesis is the use of LCA methodology to compare the environmental impact of innovative chemical processes with conventional processes used to manufacture the same product. Specifically, the study focuses on mechanochemical processes, as they are the primary type of reactor used by Deasyl, the principal company collaborating with the thesis.

1.2. LIFE CYCLE ASSESSMENT

The concept of LCA emerged in the 1960s in the United States when experts began to worry about the impact of energy sources and materials on the environment. By the 1970s, with projections of population growth and increased demand for resources, studies were conducted in greater detail, including material and energy balances of processes involving raw material consumption and waste generation [34].

Currently, Life Cycle Thinking (LCT) and LCA are scientific approaches behind a growing number of environmental policies and business decision support in the context of Sustainable Consumption and Production (SCP). It is standardized by ISO 14040:2006 Environmental management - Life cycle assessment - Principles and framework [35] and the ISO:14044:2006 Environmental management - Life cycle assessment - Requirements and guidelines [36], the International Reference Life Cycle Data System (ILCD) further developed it by providing a common basis for consistent, robust and quality-assured life cycle data, methods and assessments in guides such as the ILCD Handbook: General guide for Life Cycle Assessment [37]. Within these standards, the phases to be followed in the performance of a complete LCA study are defined as: 1) Goal and scope definition; 2) Inventory analysis; 3) Impact assessment and 4) Interpretation. Figure 1-1 depicts the previously named phases.
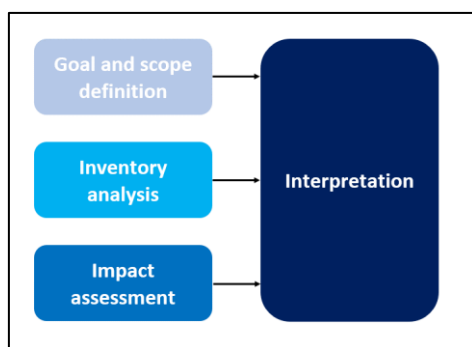
Figure 1-1 LCA phases [35], [36]

Goal and the scope involve setting the functional unit (FU), which serves as the basis for calculating the environmental impacts of the product, as well as defining the system boundaries and allocation factors. The midpoint and endpoint indicators, which will be quantified, should also be specified. The next step is to compile and document all the emissions to the atmosphere, soil, and water, the wastes, and the resources (raw material and energy) consumed during the life cycle of the product. This is typically done by creating a Life Cycle Inventory (LCI), which corresponds to the mass and energy balance of the chemical reactions involved in the process. To ensure the accuracy and reliability of the LCI data, the ISO standards recommend using primary data obtained from the studied processes through measurements and experiments [35], [36]. Finally, the Life Cycle Impact Assessment (LCIA) is performed, which considers three areas of protection: human health, natural environment, and natural resources use. The LCIA has three mandatory successive elements and three optional ones [38], described in Figure 1-2.
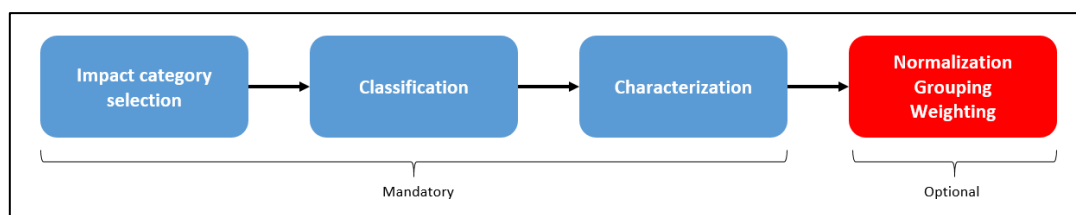
Figure 1-2 Steps in the impact assessment stage [35], [36]

The LCIA considers the data collected during the LCI phase and provides an assessment of the potential environmental impacts of the product. Depending on the objective of the study, impact categories typically covered in a LCIA include climate change, ozone depletion, eutrophication, acidification, human toxicity, ionizing radiation, ecotoxicity, photochemical ozone formation, land use and resource depletion, among others [38], [39], [40], [41].

The chapter 4 (Life cycle assessment as a tool for evaluating chemical processes at industrial scale: a review) of this thesis presents the state of the art of how LCA has been applied to chemical processes in scientific publications between 2011 and 2021 (Paper I).

1.3. MECHANOCHEMISTRY

Mechanochemistry is a scientific field that investigates chemical reactions resulting from the direct absorption of mechanical energy [42]. See Figure 1-3. While thermochemistry, electrochemistry, and photochemistry are commonly thought of as the main routes for providing activation energy for chemical reactions, mechanochemical activation is an environmentally friendlier alternative that avoids or reduces the use of solvents [43], [44]. Mechanochemistry offers advantages in terms of reaction conversion, selectivity, and times due to an increase in surface area, leading to better contact between reactants and an enhanced reaction rate [45], [46]. Positioned between chemistry and mechanical engineering, mechanochemistry is a crucial tool for a broad range of sustainable chemistry applications.
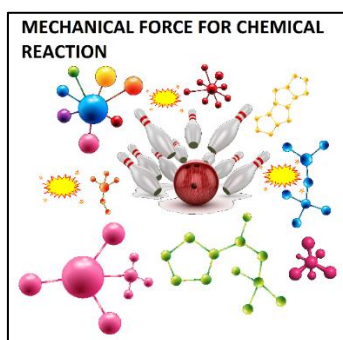
Figure 1-3 Mechanochemistry representation [47]

Mechanochemistry is a field that has been known and used for many years but has yet to be fully utilized on an industrial scale. Despite an increasing number of publications on mechanochemistry, there is a lack of literature on LCAs related to this topic. In fact, only one article was found in a search of various scientific databases (Scopus, Science Direct, and Web of Science) [48]. This deficiency in research highlights the need to expand the knowledge and literature available in this area. The goal of this thesis is to address this gap by exploring the potential of mechanochemistry compared to conventional industrial processes and paving the way for wider adoption of these processes on a larger scale.

The chapter 5 (Linking mechanochemistry with the green chemistry principles: review article) of this thesis presents the state of the art of the most recent mechanochemistry applications in green chemistry (Paper II).

2. OBJECTIVES

The overarching goal of this thesis is to use LCA methodology to compare the environmental impact of innovative mechanochemical processes with conventional processes used in the manufacturing of the same product. As the potential of mechanochemistry remains largely unexplored in comparison to conventional industrial processes, the primary objective of this doctoral thesis is to investigate and emphasize the environmental benefits of mechanochemistry through LCA. Additionally, this thesis aims to apply LCA as a tool to enhance the decision making on the industrialisation of these processes.

To achieve these objectives, the thesis will pursue the following specific objectives:

1) **Conduct comprehensive literature review of existing research in the principal fields of the thesis**: Given the scarcity of literature on LCA for mechanochemical processes, this is divided into two critical reviews. One focus on LCA applied to chemical processes (chapter 4), and the other explores mechanochemistry applications (chapter 5).

2) **Develop an LCA framework for chemical and mechanochemical processes**: This objective involves establishing a systematic approach for conducting LCA for chemical and mechanochemical processes, developing an appropriate method for data collection, analysis, and interpretation. This method is described in chapter 3 and subsequently tested and validated through the articles from chapters 6 to 9.

3) **Explore the integration of social and economic assessments in the LCA framework**: This objective aims to identify and incorporate relevant social and economic indicators, in order to provide a more holistic perspective on the sustainability of chemical processes. This involve reviewing existing methodologies and adapting them to fit the context of mechanochemical processes. This is presented in chapters 7 and 9.

4) **Investigate the application of modelling and simulation tools for LCA**: This objective aims to explore the use of existing and emerging modelling and simulation tools in LCA for chemical and mechanochemical processes. This involves evaluating the accuracy and efficiency of these tools, as well as identifying potential areas of improvement to better inform decision-making in the field. This is implemented transversally in all the chapters from 6 to 9.

The present research emerges in response to the increasing demand for more sustainable chemical processes, reducing emissions and wastes, closing the loop of various chemicals, and

promoting circular economy and the accomplishment of the SDGs. LCA has been identified as the most suitable tool for measuring these objectives, as it encompasses all stages from raw material extraction and processing to product disposal or recycling at the end of its useful life.

3. METHODOLOGICAL APPROACH AND WORKFLOW TO CONDUCT LCA OF CHEMICAL REACTIONS

A first step in this research is to conduct a state-of-the-art review of the existing LCA studies on chemical processes to identify the methods and tools most used by LCA practitioners, as well as to recognize gaps and potential areas for improvement (chapter 4). The outputs of this review established the basis and the methodological criteria of the LCAs presented in the chapters 6 to 9.

- When comparing different routes to obtain the same chemical product, LCA practitioners employ a cradle-to-gate analysis. The EoL stage is often assumed to be the same for both processes, as the chemical products obtained through different processes are presumed to have similar functional properties, unless significant differences are known and validated. If not, these differences must be accounted for using the FU or allocation factors.

- Environmental impacts are usually calculated by: 1) determining the impacts of input material flows, 2) adding the impacts of output flow treatment, 3) including the impacts of energy used for heating and cooling, and 4) incorporating the impacts of energy used for stirring, pumping, milling, and other mechanical processes applied to the material flows. Consequently, the key factors affecting midpoint and endpoint indicators include the reaction yield, mass proportion of the reactant, reaction time, and energy demand for the processes, among others.

- Additional studies may be conducted depending on each case, such as pedigree matrix analysis to identify parameter uncertainties, sensitivity analysis for the most uncertain parameters, and forecasting electricity mix evolution for 2030 and 2050 according to the green deal [49], among others.

This information, in conjunction with the standardized ISO 14040:2006 [35], ISO:14044:2006 [36], and the ILCD Handbook [37], serves as a guide for the specific LCA studies presented in chapters 6 to 9. The modus operandi and logical consequential process of the research work is illustrated in Figure 3-1.
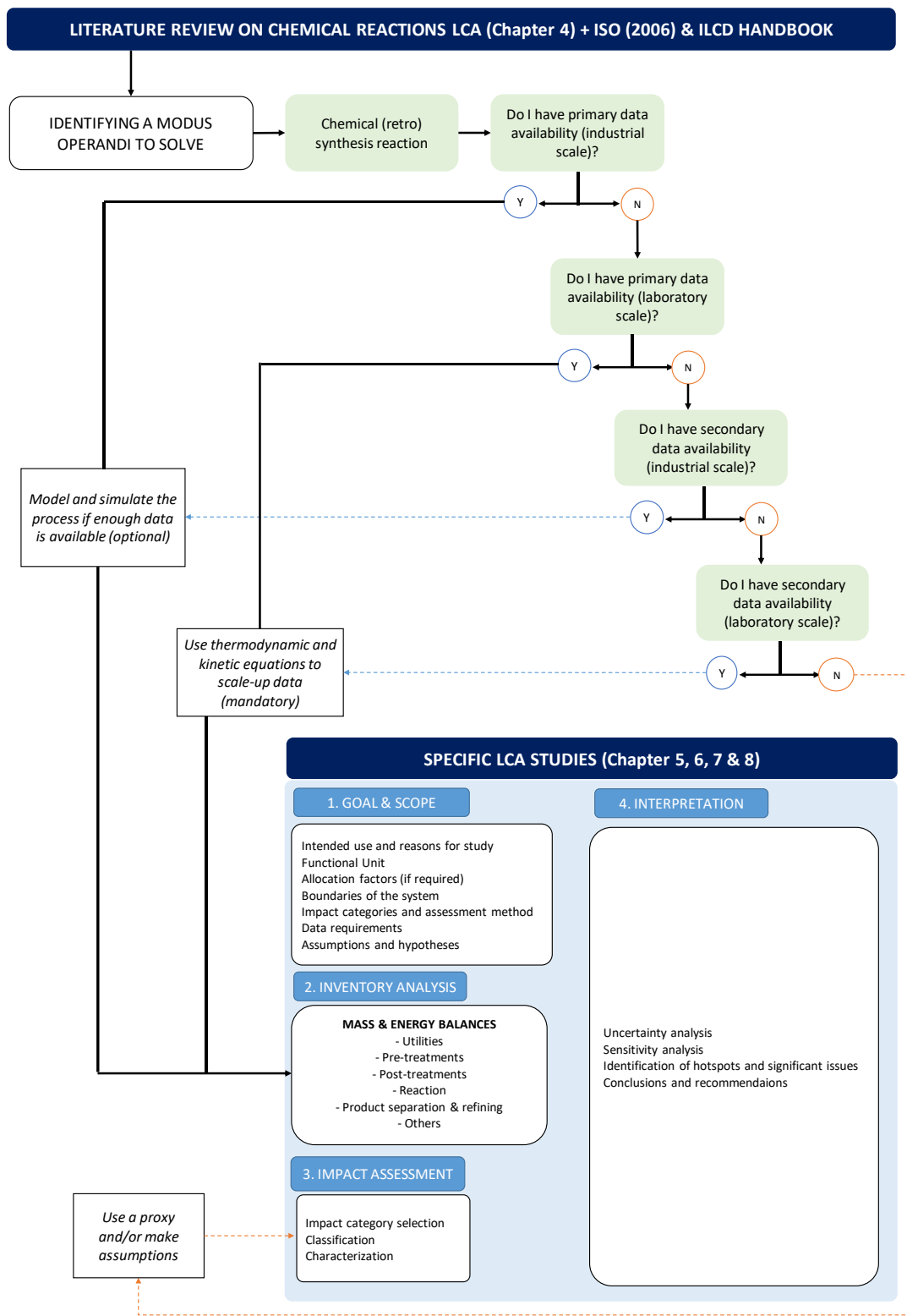
Figure 3-1 Modus Operandi and research logic

In summary, the research prioritizes the use of primary data from industrial-scale processes. If unavailable, primary data at the laboratory scale can be utilized after scaling up, either through

simulation software or fundamental thermodynamic and kinetic equations. Secondary data is only employed when primary data is unattainable, typically for conventional processes used as benchmarks in this thesis. To minimize uncertainty and inaccuracy, proxies have been avoided.

4. LIFE CYCLE ASSESSMENT AS A TOOL FOR EVALUATING CHEMICAL PROCESSES AT INDUSTRIAL SCALE: A REVIEW

4.1. ABSTRACT

The present paper reviews 47 LCAs applied to green chemical reactions. The selection of the evaluated articles was conducted with a systematic literature review methodology. The review arises from the need to define the best methods for developing LCAs of chemical processes, this is the basis of the author's doctoral thesis in collaboration with a Swiss start-up in the green chemistry sector, Deasyl. The authors go through the stages defined in ISO 14040 and 14044, identifying both the gaps and the best techniques used in all the reviewed papers. The main difficulty observed when developing LCAs of chemical reactions is the lack of data due to confidentiality issues in chemical companies. In addition, this data is commonly only available at the laboratory scale. Laboratory data is sometimes directly upscaled without further consideration. Even though, simulation software, advanced calculations benchmarks, pinch analysis and retrosynthetic analysis are the best methods to estimate and scale up the mass and energy balances in the LCI stage. From the LCIA methodologies, they should be standardized to enable the comparability between LCAs of the same product. Both the European Commission and the Life Cycle Initiative are making progress in this regard. Eventually, the ReCiPe is the most used methodology among the reviewed papers. Finally, the article proposes different analyses to be performed in the interpretation phase: i.e., projecting the energy mix foreseen for the years 2030 and 2050 in energy-intensive processes or including other sustainability vectors (economic and social) in cross-cutting projects.
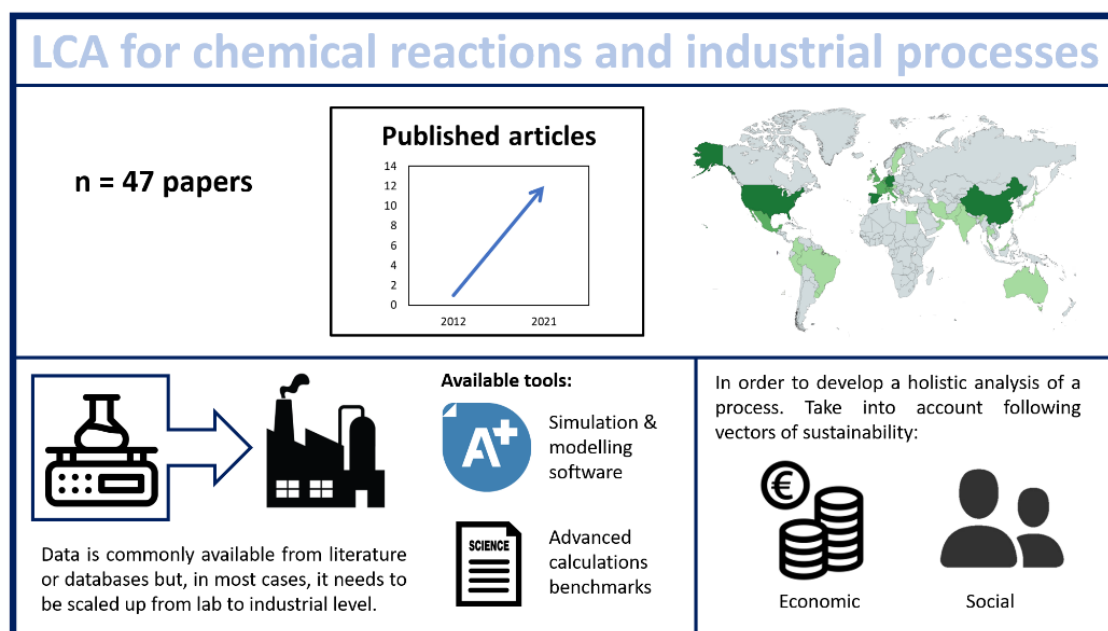
Figure 4-1 Graphical abstract of the Chem-LCA literature review paper

4.2. INTRODUCTION

This review paper presents the state of the art of LCA in the field of green chemistry. It stems from the author's doctoral thesis in collaboration with the Swiss company, Deasyl, with the aim of finding the best techniques to measure the environmental impact of chemical reactions obtained in a pilot plant, scaling up the results to an industrial scale.

There have been multiple approaches and tools created to aid chemists in the development, design, and application of chemical products. The LCA methodology can be applied to the design of chemical reactions to evaluate their environmental impacts, from the extraction of the raw material to the EoL of the final product. LCA is standardized by ISO 14040:2006 [35] and ISO 14044:2006 [36]. It covers a wide set of environmental performance indicators such as Global Warming Potential, Acidification Potential, Eutrophication Potential, Ozone Layer Depletion Potential, Human Toxicity Potential, Water Use, Land Use or Ecotoxicity Potential, among others [38], [39], [40].

In 2014, the World Business Council for Sustainable Development (WBCSD) presented a guideline for the chemical sector to assess and report on the environmental footprint of products based on LCA and, in 2016, a guideline for the chemical sector to assess and report on the social impact of chemical products, based on a life cycle approach [50], [51].

The present literature research paper reviews and compares the publications on 47 LCAs of chemical processes from 2012 to 2021, indexed in three of the most common scientific

databases (Science Direct, Scopus, and Web of Science). With the search methodology presented by Sazdovski et al., (2021) [52], search strings and further screening of results have been carried out to mine the research papers systematically. The year 2012 has been selected as the starting point of the collection of papers since the last literature review paper about LCA of chemical reactions dated from that year [53].

The review by Jacquemin et al., (2012) [53] is a broad review from the 1970s to 2000s that focuses also on the theoretical aspects of LCA. It does not go into detail on aspects such as the characterization techniques or the modelling software, for example. The present paper aims to: update the state of the art in this field; identify gaps and propose improvements or refinements; evaluate which methods are most used and which methods, which may not be so widely used, could potentially be used; and contribute through findings and suggestions to increase the methodological reliability and practicality of the use of LCA in chemical processes.

4.3. METHODOLOGY

The review was conducted according to the principles of systematic reviews [54] and avoiding common biases which may affect traditional literature reviews [55]. The study was conducted in the following three steps:

1) **Searching scientific papers developed as LCA studies for chemical processes at an industrial scale:** Three scientific databases, Science Direct, Scopus, and Web of Science, were the main sources for searching the relevant bibliography. The searches were performed in July 2021 with English search terms applied to titles, abstracts, and keywords. Mainly, two search strings were used:

    i.   "("Life cycle") AND (LCIA OR inventory) AND (chemical OR reaction OR synthesis) AND (reactant OR solvent OR catalyst)"

    ii. "("Life cycle analysis" OR "Life cycle assessment") AND ("Life Cycle Impact Assessment" OR "Life cycle inventory") AND reaction AND reactant".

    The strings were formulated using "AND" terms which are responsible for narrowing the scope to a complete LCA which must include all the stages of this methodology, especially the LCI and the LCIA. The selected LCAs must measure the environmental impacts of a chemical reaction, taking into consideration its material and energy flows and not assessing it as a black box.

2) **Screening results under the pre-defined selection criteria for the scope of the study:** The preliminary number of results filtered for chemistry or chemical engineering subject areas

were 527. After removing duplicates there were 400 research articles left. They were manually screened at progressively greater levels of detail (i.e., titles, then abstracts, and finally the full text) [55].

The applied eligibility criteria were the fitness of the articles with the scope and goal of the study. Only scientific papers published in the English language from peer-reviewed scientific journals were considered.

9 pre-screened research papers that were encountered in the bibliography section of the already screened papers and that matched the criteria requirements were added to the study. Then, 47 scientific papers were finally used for detailed study and analysis. The ROSES flow diagram [56] shows the process followed in the screening and synthesizing of the scientific articles (Figure 4-2).

3) **Compiling results in an Excel table for the analysis of the selected papers and relating them with the pre-defined indicators and variables selected in the scope of the study:** The information presented in Table 4-1 were compiled and organised in an Excel file for each of the 47 scientific papers reviewed. This was used to calculate the indicators and findings descripted along the next sections of the paper.

Table 4-1. Information collected from the research articles

General data	Scope and purpose	Quality of data	Categorization data	Interpretation and results data
Author/s	Functional unit	Sources of the data used in the mass balance	Methodology used in midpoint / endpoint indicators	Do they perform an economic analysis?
Title	Product/s of the reaction	Sources of the data used in the energy balance	Software used for process simulation	Do they perform a social analysis?
Year of publication	Type of process	Sources of the data of the chemical compounds	Software used for LCA simulation	Do they perform an uncertainty analysis?
Journal	Objective of the LCA	How do they scale up the data?		Do they perform a sensitivity analysis?
Number of pages	System boundaries			Allocation rules used
Location				Environmental impact categories calculated

ROSES Flow Diagram for Systematic Reviews. Version 1.0
1- ("Life cycle") AND (LCIA OR inventory) AND (chemical OR reaction OR synthesis) AND (reactant OR solvent OR catalyst)"
2- ("Life cycle analysis" OR "Life cycle assessment") AND ("Life Cycle Impact Assessment" OR "Life cycle inventory") AND reaction AND reactant

Searching

Records identified (*Chemistry & Chemical Engineering areas*) through ScienceDirect database searching (2012-2021) (n = 393)

Records identified through Web of Science database searching (2012-2021) (n = 99)

Records identified through Scopus database searching (2012-2021) (n = 35)

Screening

Records after duplicates removed (n = 400) → Duplicates (n = 127)

Records after title screening (n = 239) → Excluded titles (n = 161)

Records after abstract screening (n = 57) → Excluded abstracts (n = 182)

Articles after full text screening (n = 38) → Excluded full texts, with reasons (n = 19)
Excluded on:
• Study type (not LCAs) (n = 13)
• Study type (literature review) (n = 3)
• Study type (others) (n = 3)

Pre-screened articles from other sources (n = 9)

Articles
Studies

Articles / Studies included in the review (n = 47 / n = 47)

Synthesis

Studies included after critical appraisal (n = 47)

Figure 4-2 ROSES flow diagram for this systematic review [56]

4.4. RESULTS AND DISCUSSION

OVERVIEW OF THE SELECTED ARTICLES

The 47 reviewed LCAs are chronologically ordered. As shown in Figure 4-3, around 23% of the articles reviewed were published between 2013 and 2014 [57], [58], [59], [60], [61], [62], [63], [64], [65], [66], just after the World Bank Group published a report warning on the track of a world with a temperature increase of 4 °C scenario [67]. Around 45% of the articles reviewed have been recently published, between 2020 and 2021 [68], [69], [70], [71], [72], [73], [74], [75], [76], [77], [78], [79], [80], [81], [82], [83], [84], [85], [86], [87], [88]. It seems that in the following years more LCAs will be performed to understand and optimize the chemical processes.

Figure 4-3 Number of articles taken into consideration

The location of LCAs included in the review is presented in Country (number of LCAs included in the review paper): Spain (10), Germany (6), China (5), United States (5), Italy (4), United Kingdom (4), Netherlands (3), Belgium (2), France (2), Israel (2), Mexico (2), Australia (1), Austria (1), Brazil (1), Colombia (1), Egypt (1), India (1), Iran (1), Ireland (1), Israel (1), Japan (1), Malaysia (1), Oman (1), Pakistan (1), Peru (1), Serbia (1), Sweden (1), Switzerland (1), Taiwan (1), Thailand (1), Trinidad & Tobago (1), United Arab Emirates (1), Uruguay (1)

Figure 4-4. The location has been selected according to the institutions developing the LCA. In the case of LCAs developed between institutions of two or more countries, the LCA has been attributed to both countries.

Country (number of LCAs included in the review paper): Spain (10), Germany (6), China (5), United States (5), Italy (4), United Kingdom (4), Netherlands (3), Belgium (2), France (2), Israel (2), Mexico (2), Australia (1), Austria (1), Brazil (1), Colombia (1), Egypt (1), India (1), Iran (1), Ireland (1), Israel (1), Japan (1), Malaysia (1), Oman (1), Pakistan (1), Peru (1), Serbia (1), Sweden (1), Switzerland (1), Taiwan (1), Thailand (1), Trinidad & Tobago (1), United Arab Emirates (1), Uruguay (1)

Figure 4-4 Principal location of the LCAs and its main products

Most of the studies (55%) were performed in European countries [57], [58], [59], [60], [63], [65], [66], [69], [70], [74], [75], [82], [84], [86], [89], [90], [91], [92], [93], [94], [95], [96], [97], [98], [99]. This is an expected result given that LCA is an official and standardized tool for assessing the environmental impacts in the EU, mostly since its Communication on Integrated Product Policy (COM (2003)302) [100]. About the rest of the papers, 24% of the studies were performed in Asia [62], [64], [72], [76], [77], [78], [79], [80], [87], [88], [101], [102], [103], 11% in Central or South America [61], [81], [86], [88], [89], [104], [105], 8% in North America [74], [79], [86], [103], [106], and 2% in Africa and Oceania [68], [101]. LCA has become a widely acknowledged tool and its use has also been encouraged by governments all over the world (i.e., United States, Japan, or China) [41], [107], [108].

The selection of the LCAs used as a sample for the review paper aims to present a varied spectrum of different types of chemical reactions that also corresponds in percentage to the studies reported in the literature. From the 47 papers reviewed, 17 LCAs studied biomass, bioplastics, or biofuels materials [58], [61], [62], [64], [65], [68], [69], [70], [76], [78], [82], [84], [86], [87], [88], [92], [93]; 8 assessed hydrogen production [59], [63], [94], [95], [96], [97], [98], [105]; 7 considered chemical commodities such as ammonia, methanol, adipic acid, acrylonitrile, hydrocarbons, or solvents [60], [66], [73], [77], [79], [81], [89]; 5 LCAs were pharmaceutical or new advanced materials related [57], [83], [99], [104], [106]; 2 analyzed carbon capture and storage processes [71], [74]; 1 focused on desalination water treatment [102]; 1 studied energy storage with Li-S batteries [103] and 6 assessed another type of chemical processes or products [75], [80], [85], [90], [91], [101].

Most of the LCAs were addressed to the impacts from cradle-to-gate (57%) since they are comparisons between processes with a similar EoL stage [60], [64], [65], [68], [70], [71], [73], [77], [79], [80], [81], [82], [86], [87], [88], [92], [94], [95], [96], [97], [98], [99], [101], [104], [105], [106]. Chemical products usually can have a lot of different uses. The EoL stage may change depending on the final use given to the chemical product, as well as the location where it is being used. This uncertainty presents complexities in the EoL LCIA, especially if chemicals are used by third companies. LCA practitioners usually focus the study on the activities which are under the control of the company. There was a 20% of gate-to-gate studies associated with the study of one or two steps of the chemical process [58], [61], [63], [66], [75], [78], [85], [91], [93]. For example, there is one case [57] comparing conventional reactions against eco-efficient catalytic reactions, which are still at laboratory scale. This case study focuses only on the reaction stage, excluding the extraction of raw material, transport, use, and EoL stages. Even though the uncertainties about the application of the chemical product may drive the LCA practitioner to select a gate-

to-gate approach, whenever possible, is recommended to study the whole cradle-to-grave (only 21% of the evaluated papers selected this boundary system [59], [62], [69], [74], [76], [83], [84], [90], [102], [103]). The uncertainties may be faced using allocation rules for the cradle-to-feed and gate-to-grave stages. For example, according to market data percentages assigned to the main applications related to the chemical product under evaluation [35], [36], [109]. Finally, there are 2% of the papers that used a gate-to-grave boundary system to focus the study on selecting the best waste treatment procedure for a specific case study [89].

Figure 4-5 presents the number of the evaluated papers that selected each type of boundary system, as well as a brief scheme describing the different steps which are commonly evaluated from cradle to grave.
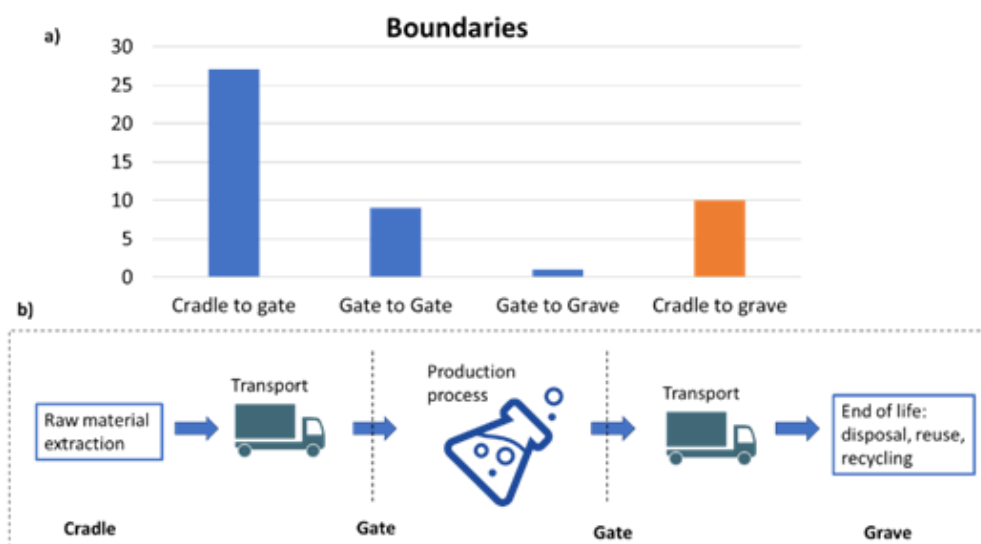
Figure 4-5. a) Number of papers selecting each type of boundary system b) Steps included in each system from cradle to grave

QUALITY OF DATA

Regarding the quality of data, most of the papers (57%) mainly used secondary data for the mass and energy balances in the LCI [61], [62], [63], [65], [71], [74], [75], [76], [79], [81], [82], [84], [86], [88], [91], [92], [93], [95], [97], [98], [101], [104], [105], [106]. This data is usually available from literature or databases but, in most cases, it needs to be scaled up from laboratory to industrial level.

Some of the studies [83], [101], [104] have used the retrosynthetic analysis to get the environmental impact of the compounds from its chemical predecessors or substances with similar functional groups and chemical composition. However, this only solves the upscaling requirements in case that we have industrially available data of the chemical predecessors.

40

When scaling up processes from the laboratory scale to the industry scale there are factors which are to be considered: energy efficiency, material and energy recycling or process integration [71], [92], [110]. The mass balance scaling shall correspond to the difference between the conversion obtained in the laboratory and in the industrial unit. In many cases, this depends on the type of process under study and the type of equipment to be used. There is no consensus on a best method for this purpose. While none of the articles reviewed have considered differences in the mass balance from laboratory to industry scale, we recommend applying one of the following alternatives: i) using pilot plant data instead of laboratory data, ii) consulting an expert opinion on the process under study, or iii) opting for a conservative approach by multiplying the conversion obtained in the laboratory by a factor of 80-90%. For the energy balance, one of the studies assumed a 20% energy efficiency increase when scaling up data and compared its results based on standard refineries in the country [61]. This seems a good approach since it is dealing with the uncertainty of the assumption comparing it with primary data from companies and industry experts. Other researchers without access to primary data dealt with the same issue by mapping the heating and cooling flows, and applying a small Pinch analysis [71].

About 30% of the studies used entirely primary data, which avoids a lot of issues related to scaling up and its associated uncertainty [58], [68], [70], [73], [77], [78], [80], [85], [89], [94], [99], [102], [103]. Unfortunately, most literature and patents do not include detailed descriptions of the required equipment, and confidentiality issues do not allow chemical companies to share relevant information [57], [83]. This may drive, in some cases, to the need of using less accurate or older data [59].

Finally, 13% of the LCAs used a mixed approach, combining primary and secondary data [57], [59], [60], [64], [69], [83], [87], [90], [96]. The open innovation philosophy precisely consists of sharing data and knowledge among private companies and research centres. One of the LCAs [64] gets its primary data from demonstrated enterprise investigation, interviews with farmers from the area of study, open LCI databases, and public references. In this case, farmers shared the information of the quantities of fertilizers they used, which decreased the uncertainty of the LCA study. The LCA practitioners developed a precise analysis, which served the farms in the decision-making task.

Open Innovation, a term coined by Professor Henry Chesbrough from the University of California, is a business innovation strategy that takes the concept of innovation beyond the internal boundaries of the organization itself so that cooperation with external professionals plays a fundamental role in the organization's innovation strategy [111]. Open Eco-innovation research is experiencing fast growth in research centres and companies [112].

The first step before starting the LCI is to define a FU that will be the basis for the calculation and must account for all conditions affecting the intended use of the outcome. From the 45% of the articles that compare the environmental impacts of different processes, the 71% use *kg*, *ton* or *mol* as a FU [57], [58], [63], [70], [74], [79], [88], [89], [91], [96], [97], [99], [101], [104]. We recommend considering the possibility of using kg/h or ton/year in these cases. Especially if the chemical processes to be compared have different residence times. In this way, we believe that the comparison of both processes is more faithful to reality, where the production of the companies is subject to an annual demand. From the 45% of the articles comparing different processes, the 19% selected a FU that considers the reaction time [73], [78], [84], [94].

The 68% of the evaluated papers obtained the LCI data from the Ecoinvent databases [58], [59], [60], [63], [65], [69], [70], [71], [74], [75], [78], [80], [81], [82], [85], [88], [90], [93], [94], [97], [99], [102], [105], [106], which are integrated into the most commonly used LCA software: GaBi (https://gabi.sphera.com/) and SimaPro (https://simapro.com/). Other data sources which have been also widely used are AspenTech databases (11%) [61], [76], [77] or research publications from scientific literature (9%) [73], [86], [87], [101].

AspenTech (https://www.aspentech.com/) is one of the leading process simulation software providers in the chemical, plastics, and life sciences industries. Moreover, it counts with massive databanks, which allow the LCA practitioner to deal with the uncertainty of data in the scaling-up process. Their software, AspenPlus, is the main tool used for the scaling up purpose among all the reviewed papers (43%) [59], [60], [63], [71], [76], [77], [78], [79], [84], [85], [86].

Other research articles are using more specific simulation software tools, depending on the field of each case study. The main drawback of simulation software is the large data requirements to design reliable software simulations. Some papers combine these software simulations with advanced process calculations benchmarks [82], proxies [88], [93], [95], [97], or shared primary data from companies located in the area of the study [81].

Around 23% scaled up their data using only proxies [61], [65], [75], [91], [96], [98], [103], [105], and 17% of the LCA used only the advanced process calculations benchmarks [62], [68], [69], [74], [83], [92], [101]. The most widely used benchmark among the evaluated articles [69], [83], [92] is a publication from 2016 which only requires the input of the mass of reactants, specific heats, density, the temperature of the reaction and residence time to estimate the scaled LCI data [110]. This is a useful approach to energy balance scaling. However, we recommend the instructions described in the previous section to add consideration for mass balance scaling.

Finally, another 17% did not use special consideration for the scaling up from laboratory to industrial data, and they directly proportionally scaled the values [57], [66], [87], [90], [104]. This leads to uncertainty which, in our view, is not acceptable. As discussed in the previous section, there are factors that do not allow us to consider the same behavior of a chemical process in the laboratory as in an industrial unit. Moreover, as previously described, we have tools to estimate these differences and reduce uncertainty.

LIFE CYCLE IMPACT ASSESSMENT (LCIA)

ReCiPe 2008 and 2016 [113] which have been authored by RIVM, CML, PRé Consultants, Radboud Universiteit Nijmegen and CE Delft is used in 55% of the LCAs reviewed [58], [69], [70], [71], [72], [74], [75], [78], [88], [89], [93], [96], [101], [105], [106]. Some of the authors of this methodology are also the developers of the CML 2001 and Ecoindicator 99 methodologies. So, it can be seen as a mix of the two methodologies, implementing the 18 midpoint indicators from CML and the 3 endpoint indicators from Ecoindicator 99.

CML 2001 is used in 33% of the evaluated studies [61], [65], [68], [81], [82], [87], [92], [102]. In this methodology, results are grouped in midpoint categories according to common mechanisms (i.e., climate change or ecotoxicity). CML-IA is a database developed by the Institute of Environmental Sciences from Leiden University (Netherlands) that contains characterisation factors for LCIA [114].

Ecoindicator 99 has been used in 8% of the analyzed papers [84], [85]. In this methodology, the results are grouped in endpoint categories with a damage-oriented approach.

IMPACT 2002+ is only used at a 4% rate [90]. It combines 14 midpoint categories adapted from existing characterizing methods (Eco-Indicator 99 and CML 2001) and relates them to 4 damage categories (human health, ecosystem quality, climate change, and resources) [115].

The Cumulative Energy Demand (CED) has been considered in 10 of the 47 research papers but in all the cases it has been combined with other indicators [57], [58], [59], [66], [70], [74], [97], [98]. It represents the energy use throughout the life cycle, including the energy consumption along the raw materials extraction, manufacturing, and disposal stages. The usefulness of CED as a stand-alone indicator for environmental impact is limited by its large uncertainty in the results. A major reason for this high uncertainty is non-fossil energy-related emissions and land use, such as landfill leachates, radionuclide emissions, and land use in agriculture and forestry [116].

The most measured midpoint impact categories along the evaluated LCAs are: Global Warming Potential (in 100% of the LCA), Acidification potential (in 62% of the LCA), Eutrophication

potential (in 60% of the LCA), Human health and Ozone depletion (both in 55% of the LCA), Ecotoxicity and Photochemical oxidant formation (both in 45% of the LCA); Fossil resource use (in 40% of the LCA), Land use (in 34% of the LCA), Water use (in 30% of the LCA); Minerals or metals resource use and Particulate matter (both in 26% of the LCA) and Abiotic depletion (in 15% of the LCA).

Selecting the appropriate LCIA methodologies is crucial to obtain reliable, consistent, and representative results. ReCiPe 2016 is the most recent and the one that brings together the most authors. In addition, its authors have participated in the development of other methodologies. This makes it a good option for evaluating the impacts of a chemical process.

MODELLING AND SIMULATION SOFTWARES

The LCI is carried out through the combined use of mass and energy balances. Lack of data and uncertainty of results are two of the main limitations when studying chemical or industrial processes. Therefore, tools that provide reliable databanks, and accurate results will upgrade the confidence in the LCI data and LCA results.

The 68% of the research articles under the evaluation have used simulation process software to carry out the mass and energy balances in the LCI elaboration [59], [60], [61], [62], [63], [65], [66], [68], [70], [71], [72], [75], [76], [77], [78], [79], [81], [82], [84], [85], [86], [90], [91], [92], [93], [95], [105], [106]. This provides reliable information both on the physical properties of chemical components and the thermodynamic and kinetic behaviour of the process. From this 68% articles, 84% have used the AspenPlus software [59], [60], [61], [62], [65], [70], [71], [75], [76], [77], [78], [79], [81], [82], [84], [85], [86], [90], [92], [93], [95], [97], [104].

The LCIA relates LCI results with environmental impact categories and indicators. Simulation software programs in LCA compile most of the LCIA methodologies, this facilitates the LCIA process by increasing the reliability and accuracy of the results. The 89% of the studies have explicitly mentioned the software used for their LCA. From this 89%, 67% have worked with SimaPro [57], [58], [61], [63], [65], [69], [70], [71], [73], [75], [78], [80], [81], [82], [84], [86], [88], [89], [91], [92], [93], [94], [95], [97], [102], [105], 19% have used GaBi [62], [83], [87], [96], [98], [106], 10% used Umberto LCA+ [60], [99], [101], [104], 2% worked with OpenLCA [85], and another 2% with CMLCA [68].

Dealing with uncertainty in data and results might be the most important issue when performing an LCA. From all the studies which form the systematic literature review, only 17% have explicitly presented an uncertainty analysis [59], [60], [64], [66], [74], [81], [88], [92]. On the other hand, 57% of them have presented a sensitivity analysis [57], [58], [59], [60], [64], [68], [71], [74], [75], [76], [77], [78], [79], [81], [82], [83], [85], [86], [87], [88], [89], [92], [96], [98], [101], [103], [105]. Allocation procedures [117] have been also used when required to assign the correct emissions according to the products, co-products, waste products, and FU under study. They have been selected depending on the causality of the allocation, being mass and economic ratio the most used methods.

Dynamic LCA characterization models with varying time horizons are recommended as a measure of the robustness for LCAs in comparative assessments. Several LCI and LCIA methodologies already consider this, for example, the Intergovernmental Panel on Climate Change (IPCC) model which gives direct Global Warming Potential values of greenhouse gases under different time-horizons (20, 100, 500 years), or the USEtox method for toxicity related impact categories [118]. Dynamic endpoint models (termed as a 'damage oriented approach' defined at the level of protection area) [119] have also been developed, such as the time-dependent Ecoindicators 99.

At the LCI level, a pedigree matrix approach is recommended for estimating data inaccuracy to literature-based data. This matrix is a qualitative evaluation of the data taken from the literature. It uses 5 indicators: i) reliability, ii) completeness, iii) temporal correlation, iv) geographical correlation, and v) further technological correlation [120], [121]. From the LCAs studied, two of them[88], [99], use this methodology to assess the uncertainty of their data.

Statistical methods may also be introduced as in the case of Sadeek et al., (2020) [81], who compares the coefficient variance between AspenPlus LCI results and results from primary data of a company in the area of study. Some studies compare the LCA results for a different number of scenarios. Luo et al., (2021) [74] compares 9 different scenarios with different hypotheses. Zhao et al., (2021) [76] presents a complete techno-economic analysis developed with Aspen Process Economic Analyzer for operating labour costs in the life cycle of bio-ethylene glycol production for oil, coal, and biomass energy production scenarios.

At the LCIA level, Monte Carlo simulation is the most recommended methodology [122], [123] and it is included in the main LCA software programs. Even though, it is still applied in a few LCA. Monte Carlo or other statistical simulation methods can randomly sample the values of uncertain variables based on probabilistic analysis, and combine them with the LCIA methods to

simulate, statistically significant environmental impact evaluation results, which can reflect the influence of uncertain factors more accurately [124]. Regarding the documents under study, Luo et al., (2021) [74] performed a Monte Carlo simulation with algorithms coded with the programming language R, Morales-Mora et al., (2012) [89] performed the Monte Carlo simulation with the SimaPro module.

LIFE CYCLE-SUSTAINABILITY ASSESSMENT (LCSA)

The impacts of a product should be considered in a holistic and integrated manner. Many and varied factors affect us and must be considered: social, ecological, and economic [32], [125], [126], [127].

Several methodological developments [128], [129], [130] have aimed at extending life cycle thinking to evaluate social and economic issues. However, they are not being widely used in the literature. Among all the articles reviewed only 32% included a Life Cycle Costing (LCC) or other economic analysis [68], [71], [73], [74], [75], [76], [77], [79], [81], [84], [86], [89], [90], [93], [106]; only 2% included a Social Life Cycle Assessment (s-LCA) or other social analysis [77].

To ensure quality, reliability, and comparability of different LCA results for the same product, it is necessary to use standardized methods.

The Life Cycle Initiative (https://www.lifecycleinitiative.org/) is a public-private, multi-stakeholder partnership hosted by UN Environment which facilitates the implementation of life cycle knowledge in the global sustainable development agenda.

In addition, the European Commission established the European Platform on Life Cycle Assessment (EPLCA, https://eplca.jrc.ec.europa.eu/). This platform, developed by the Joint Research Centre (JRC), together with DG-Environment, represents the reference point for essential data and methods to implement Life Cycle based approaches. Through the EPLCA, the ILCD Handbook was launched [131]. It provides a series of guidance documents for different types of LCA applications. More recently, this has been complemented by the launch of the Life Cycle Data Network (LCDN), which aims to provide an international basis for inter-operable, quality-assured life cycle inventory data while it equally supports the European Reference Life Cycle Database (ELCD).

4.5.   CONCLUSIONS

The present systematic literature review paper has evaluated the contribution of 47 scientific papers on life cycle assessments of chemical reactions at an industrial scale carried out from 2012 to 2021, filtering from an initial total of 527 papers.

We found that the LCA in chemistry is commonly used to analyse the environmental impacts of an innovative process of a product in a comparison with a conventional process for the same product. This comparison usually facilitates the LCA, as we have an equivalent EoL stage in both cases, which can be simplified. The feedstocks are also generally the same in both cases, however, an allocation factor must be applied depending on the conversion and selectivity of each process. Reaction time is also often a key difference when comparing different chemical processes. So, a good approach might be to use kg/h instead of kg as a FU.

Usually, the chemical product obtained is assumed to have similar functional properties and to be used for the same purposes regardless of the chemical synthesis pathway. The environmental impacts are commonly calculated by:

1) Working out the impacts of the input material flows
2) Adding the impacts of the output flow treatment
3) Adding the impact of the energy used heating up and cooling down
4) Adding the impacts of the energy used stirring, pumping, milling and other mechanical processes applied to the material flows.

The most cited inconvenience when applying LCA for a chemical reaction is the lack of data and the uncertainty when scaling up a process from the laboratory to the industry level. The main solutions reported to face this challenge consist in:

1) Using process simulation software
2) Using advanced process calculation benchmarks to work out the LCI
3) Using retrosynthetic breakdown to get the environmental impact of a substance from its chemical predecessors from substances with similar functional groups and chemical composition.

Once the LCI is completed, selecting the appropriate LCIA methodology is crucial to obtain reliable, consistent, and representative results. Standards and common approaches are necessary to get aligned results among the research communities. Eventually, there is not an

officially preferred method to perform the LCIA. But organisations such as the European Commission and the Life Cycle Initiative are making efforts to standardise these methodologies. Concerning the scenarios analyses that can be performed after the LCIA, none of the reviewed articles carries out a study of the evolution of the impact calculated assuming the new energy mix foreseen in the European Union for the years 2030 and 2050 according to the European green deal [49], [132]. This would be highly interesting considering that it may have a direct effect on the environmental impacts of the most energy-intensive processes in the coming years.

To conclude, LCA is a holistic analysis methodology that works out the environmental impacts of a product in an integrated manner. It is found advisable to apply it in the design stage of new chemical processes, where if the LCA practitioner deals well with the lack of data, it will be a key asset in the decision making.

5. LINKING MECHANOCHEMISTRY WITH THE GREEN CHEMISTRY PRINCIPLES: REVIEW ARTICLE

Published article:

5.1. ABSTRACT

The need to explore contemporary alternatives for industrial production has driven the development of innovative techniques that address critical limitations linked to traditional batch mechanochemistry. One particularly promising strategy involves the integration of flow processes with mechanochemistry. Three noteworthy technologies in this domain are single-screw extrusion (SSE) and twin-screw extrusion (TSE) and Impact (Induction) in Continuous-flow Heated Mechanochemistry (ICHeM). These technologies go beyond the industrial production of polymers, extending to the synthesis of active pharmaceutical ingredients, the fabrication of (nano)materials, and the extraction of high-added value products through the valorization of biomass and waste materials. In accordance with the principles of green chemistry, ball milling processes are generally considered greener compared to conventional solvothermal processes. In fact, ball milling processes require less solvent, enhance reaction rates and reaction conversion by increasing surface area and substituting thermal energy with mechanochemical energy, among others. Special attention will be given to the types of products, reactants, size of the milling balls and reaction conditions, selecting 60 articles after applying a screening methodology during the period 2020-2022. This paper aims to compile and analyse the cutting edge of research in utilizing mechanochemistry for green chemistry applications.
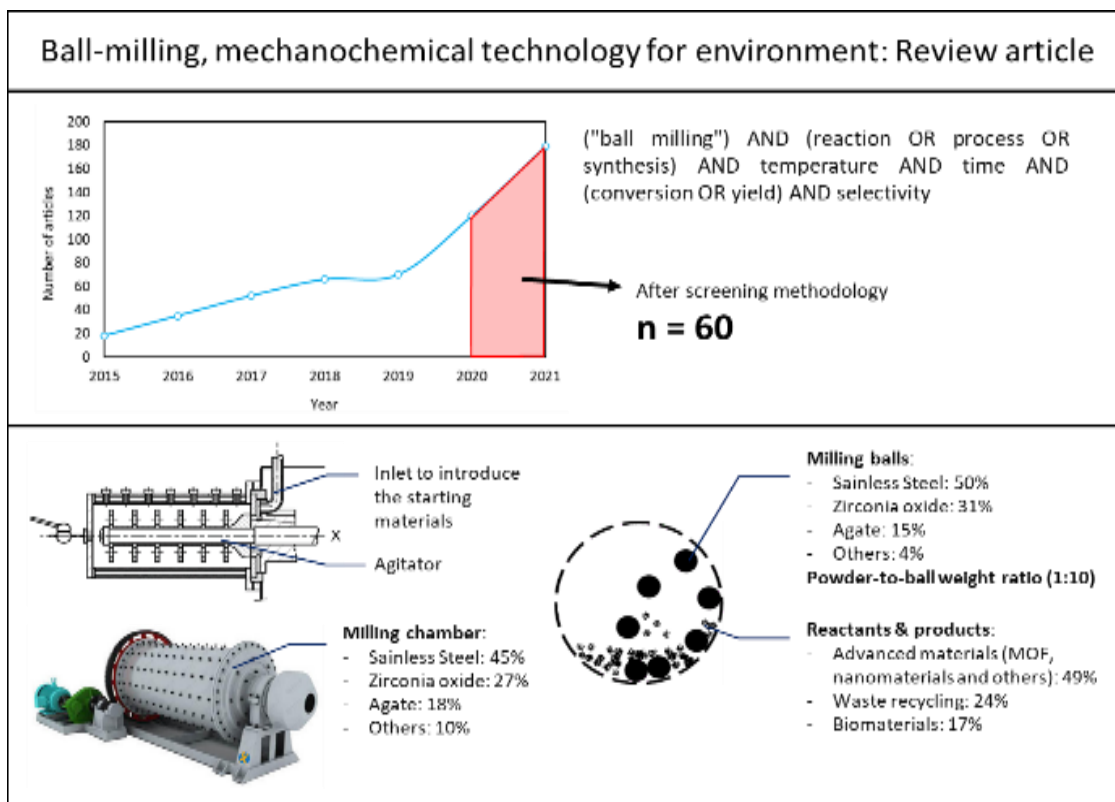
Figure 5-1 Graphical abstract of the green mechanochemistry literature review paper

5.2. INTRODUCTION

In recent decades, both the scientific community and society have heightened awareness regarding the impact of human activities on the environment. This increased awareness has exerted pressure on authorities and spurred efforts to find solutions to environmental challenges. Chemistry has emerged as a focal point of concern, given that many traditional chemical processes are not sustainable in the long term, leading to detrimental effects on the environment and overall quality of life, leading to well-known problematics such as climate change. As defined by International Union of Pure and Applied Chemistry (IUPAC), mechanochemistry involves chemical reactions induced by the direct absorption of mechanical energy. This mechanical energy can be applied through various means such as by shearing, stretching, grinding, or milling [42]. Impact is typically achieved through processes such as a jet mill, a falling hammer, and a disintegrator, while shear occurs in a mortar and pestle as well as in an extruder. Simultaneous application of both impact and shear forces is achieved in devices like a vibrating mill, an attritor, and a planetary mill (Figure 5-2).
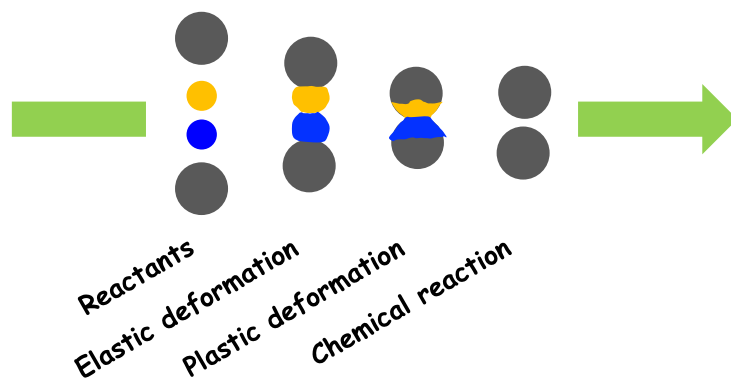
Figure 5-2 Basic concept for ball impact energy in mechanochemical synthesis

Mechanochemistry has been established, as a part of the chemistry, since the 1880s [133]. But it was not until 1990s that it has become a recognized field [134], with examples of such reactions occurring in commonplace devices like pestles or mortars. However, more comprehensive devices were developed, both at the laboratories or pilot level, such as ball milling, SSE or TSE [134]. Recent advancements in synthetic and purification techniques have elevated mechanochemistry's potential as a promising avenue for clean production processes [135], [136], [137], [138], [139]. Noteworthy examples include patents such as WO2016156749A1 "Method for manufacturing calcium zincate crystals, and the uses thereof" for the so-called IMPAºCT reactor, a ball milling reactor employing micro-sized zirconia oxide beads, which has been utilized in diverse applications and products development [4], [140], [141].

Mechanochemistry constitutes one of the four primary fields of chemistry, alongside thermochemistry, electrochemistry, and photochemistry. However, its applications have garnered increased attention from the scientific community in recent decades, owing to its numerous advantages. Notably, these advantages include the environmentally friendly nature of mechanochemical processes, the significant reduction or complete elimination of hazardous solvents, the ability to configure the reactor under milder conditions without requiring external heat, and the achievement of high yields in less time compared to other technologies [43], [44], [135], [138]. This is attributed to the reduction in particle size, resulting in an increased surface area, enhanced contact between reactants, minimized mass transfer limitations, and accelerated reaction rate [45], [46], [138]. Despite the notable progress, mechanochemistry's development is still in its early stages when compared to its potential in advanced chemical synthesis [135], [142]. Positioned between chemistry and mechanical engineering, mechanochemistry emerges as an indispensable tool for various applications within sustainable chemistry. Mechanochemical technologies are employed either independently of in conjunction

with other technologies – such as when its used to help activating the reaction before a conventional solvothermal reactor – to design and synthesize advanced chemical materials with added value [143].

For instance, metal-organic frameworks (MOFs) have received special interest due to their properties, including extraordinary porosity, adjustable pore sizes, and extensive possibilities for varying organic-inorganic compositions. Extensive studies of MOFs thus far underscore their significant potential, particularly in catalysis, gas adsorption, drug delivery, water treatment, and energy storage. However, the large-scale production of MOFs faces limitations primarily due to uneconomical, environmentally unfriendly, and complex synthesis methods. Mechanochemistry is an alternative solution for the efficient and environmentally friendly synthesis of various MOFs [4], [135], [144], [145]. Regarding thermoplastics recycling, the mechanical forces generated in mechanochemical processes can induce chain scission and the formation of free radicals [146], [147], [148]. Furthermore, mechanochemistry proves capable of synthesizing chalcogenides in the form of nanoparticles, such as sulfides and selenides. These materials are significant contenders for application in thermoelectric and photovoltaic systems, transforming thermal and solar energy into electrical energy without generating hazardous by-products [149], [150], [151]. Furthermore, the application of mechanochemical treatment in biomass research has drawn significant attention from researchers. This method effectively reduces the particle size, crystallinity, and degree of polymerization of lignocellulosic materials, influencing the structural characteristics of lignin, cellulose, and hemicellulose [6]. A major advantage is that this process is physical, meaning that, as the degree of polymerization decreases, toxic compounds typical of chemical depolymerizations are not produced [152]. Consequently, the ultimate objective of employing these mechanochemical processes is to facilitate the separation of components within lignocellulosic waste, leading to their valorization. This involves producing chemical compounds with high added value using enzymes or heterogeneous catalysts [153], [154].

Other relevant areas of research has garnered significant attention in recent years. For instance, the development of asymmetric organocatalysis and the mechanoenzymology under ball milling activation. Avila-Ortiz et al. (2019) highlight this trend in their study, "Recent Applications of Mechanochemistry in Enantioselective Synthesis," where they emphasize advantages such as the elimination of solvents from reaction media. The study presents the application of small dipeptides as chiral organocatalysts under solvent-free and high-speed ball milling conditions, with a focus on the asymmetric aldol addition reaction. Pérez-Venegas et al. (2020 and 2021) discuss the use of mechanochemistry in the synthesis of pharmacology active compounds [156], [157]. Their work emphasizes the evaluation of biocatalytic protocols mediated by the combination of mechanical activation and enzymatic catalysis, representing an innovative and

promising "green" approach in chemical synthesis in a high carbon emitting sector such as pharmacology.

Micro-ball-milling (beads) is widely used in mechanochemistry to grind powders into tiny particles. In these processes, mechanical forces are generated by the impact of the micro-milling balls (0.5-1 mm of diameter) with the reactants. Solvent-free processes or those using catalytic quantities of solvent, such as in the case of liquid-assisted grinding (LAG), are relatively uncommon in chemical synthesis. However, in the past decade, this approach has gained popularity with the use of ball milling because of its ease of use, low cost, environmental friendliness, and potential to yield extremely high yields [138], [158].

The objective of this paper is to compile and analyze the cutting edge of research in the utilization of ball milling for green chemical syntheses. For the sake of clarity, special attention will be given to the types of products and reactants, the material of the milling balls, and the utilized reaction conditions, among others.

5.3. METHODOLOGY

The present review follows the principles of systematic reviews [159] to avoid common biases affecting traditional literature reviews [160]. Initially, we conducted a search for papers on mechanochemical ball milling reactions that provided information on reaction conditions, materials, yield, and selectivity. The search string was applied to titles, abstracts, and keywords on the ScienceDirect scientific database: *("ball milling") AND (reaction OR synthesis) AND temperature AND time AND (conversion OR yield) AND selectivity AND flow*. Only paper in English, published in peer-reviewed journals, were considered. The search yielded 9,797 articles, which were screened for publications from January 2020 to February 2022 within the Environmental Science category. The remaining 354 articles underwent a manual screening process at progressively greater levels of detail (e.g., titles, abstracts, and full text) [160]. Eligibility criteria were applied to ensure alignment with the scope and goal of the present study. Additionally, 7 articles meeting the specified criteria were identified during the course of this work. These articles came to the authors' attention through references of other papers, in the preparation of unrelated studies, or through papers related to the work of the present review. The resulting set of scientific papers (60 articles) underwent detailed study and analysis. They were compiled and summarized in an Excel table, which included information such as the corresponding authors, title, keywords, year of publication, journal, number of pages, location, details on chemicals, and reaction conditions, and the materials used. The ROSES flow diagram

[161] illustrates the process followed in screening and synthesizing the scientific articles (Figure 5-3).

ROSES Flow Diagram for Systematic Reviews

("ball milling") AND (reaction OR process OR synthesis) AND temperature AND time AND (conversion OR yield) AND selectivity

Searching

Records identified (*Environmental Science area*) through ScienceDirect database searching (2020-2021-2022)
(n = 354)

Screening

Records after title, abstract and full text screening
(n = 53)

Excluded titles, abstracts or full text
(n = 301)

Articles from other sources
(n = 7)

Articles included in the review
(n = 60)

Figure 5-3 ROSES flow diagram for this systematic review [56]

The ScienceDirect database has been used as one of the leading and prominent scientific repositories worldwide. However, the authors of the present article wish to caution that certain works dealing with innovative reactions, mechanisms, and system development may be absent in this review, especially if they have been published in other scientific databases.

To address this potential gap, the authors suggest complementing the present review with additional research from reputable sources comparable to ScienceDirect in reliability and comprehensiveness. For instance, we wish to acknowledge the recent relevant review from Juaristi and Ávila-Ortiz (2023).

5.4. ARTICLES REVIEW RESULTS AND DISCUSSION

GENERALITIES AND PRINCIPLES

Publications on ball-milling processes exhibit a year-by-year growth (Figure 5-4), reflecting a rising interest in this field. For instance, the number of articles published in the first month of 2022 accounts for 31% of those published throughout the entirety of 2021, surpassing the total number of articles published in 2017.

("ball milling") AND (reaction OR process OR synthesis) AND temperature AND time AND (conversion OR yield) AND selectivity
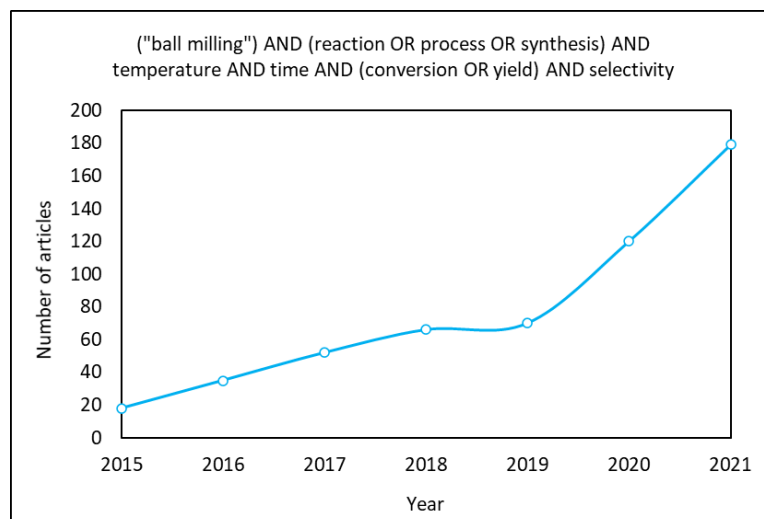
Figure 5-4 Articles published yearly related to the search string

Grinding, in a general context, refers to a mechanical action involving hard surfaces on a material, with the primary goal of disintegration and size reduction. The commonly used pestle and mortar represent a straightforward approach to this process. In contrast, non-manual methods often utilize ball milling, a well-established technique in materials processing. A ball mill, a type of grinder, typically possesses a cylindrical shape extending along a longitudinal axis where the stationary milling chamber is located. This method relies on the transfer of mechanical energy to solids being comminuted by the collisions with the milling agents, which typically are beads in a ball mill. While solid-state processes are prevalent in ball milling applications, there are instances of liquid-assisted grinding (LAG) reactions, such as glycerol valorization [163].

In general, mechanochemistry commonly categorizes methods into ball milling and extrusion techniques, each with distinct advantages and drawbacks. Ball milling, known for producing finer particle size (<10 microns), proves versatile across a wide array of applications, even for toxic and abrasive materials. However, a potential downside lies in the risk of product contamination due to wear and tear from the milling agents and the casing. In contrast, extrusion, while having certain limitations on the types of products it can handle, scalability and energy demands boasts notable advantages. These include operational flexibility, easy integration into production lines, high mixing efficiency, a continuous operation setup and the ability to handle large product volumes, among other benefits [163].

Based on the papers reviewed in this study – provided in the references of this paper and in the summary table from the supplementary materials –, the materials employed in this chamber consist of metals and ceramics, including the milling balls, which are frequently crafted from the same material as the stationary chamber. This design choice aims to prevent galvanic corrosion

and wear-related concerns. Although steel is the most used material, it poses the risk of metal contamination. To address this issue, zirconia, characterized by similar density and comparable impact to steel, can be utilized as an alternative to avoid such contamination (Figure 5-5) [135].
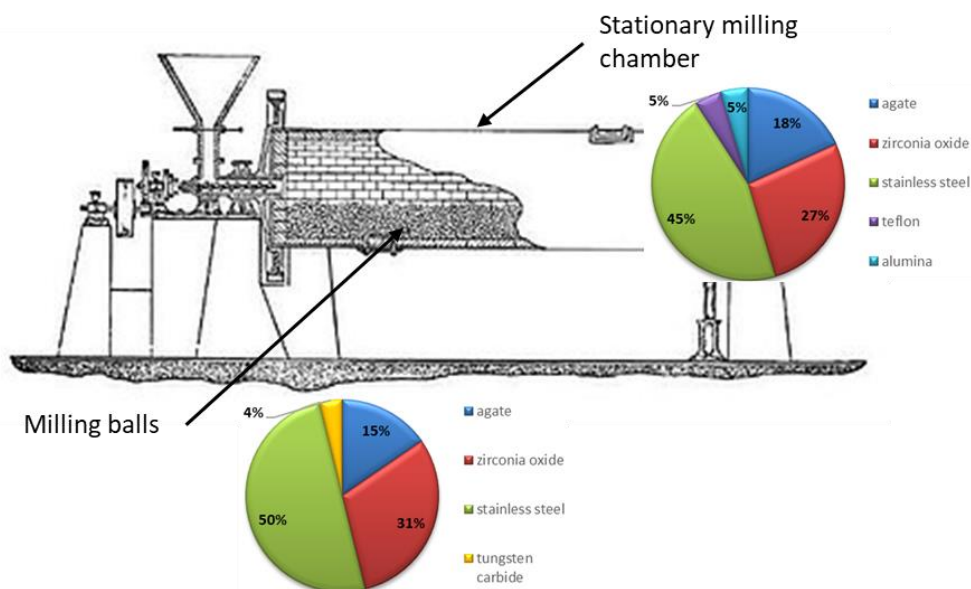
Figure 5-5 Ball mill scheme and nature of the milling chamber and balls

For the reviewed articles, the volume proportion between the reactants, typically in powder form, and the milling balls range from 1:3 to 1:30, being the most used the 1:10. There are different shapes and dimensions of agitators. Typically, an agitator shaped in an elongated rod form, where this chamber rotates on its longitudinal axis, providing mechanical energy to the system. The reactants and the milling agents are placed inside the chamber into motion, being prone to collision in this process. On a laboratory scale, the planetary ball mill is the most used technique or equipment, explicitly mentioned in 24 out of the 60 research papers included in the present study. This equipment consists in a jar filled with reactants and balls that vibrates and/or oscillates with a motor.

Of the 60 papers constituting the entire study, 49% are related to the synthesis of advanced materials such as composites, MOF, nanomaterials, and others. Examples include MIL-101 and ZIF-8 [164], MIL-100(Fe) and CoS [165], MIL-100(Fe) and WO_3 [166] for contaminant removal from water with advanced oxidation processes (AOP); carbon nanotubes [167], UiO-66-NH_2 and Bi_5O_7I composite [168], nano-FeS_2 for pharmaceutical industry wastewater treatment and enhanced degradation of ciprofloxacin [169]; zero-valent iron (ZVI) composites for organic pollutants [170] and chromium removal from water [171]; graphene oxides (GO) and other graphite derivatives for applications such as water treatment [172], [173], [174], supercapacitor

[175], lithium-ion batteries [176] or bone tissue engineering [177]; and Rh/meso-Al$_2$O$_3$ for chemical storage of hydrogen [178]. About 24% of the papers employ ball-milled materials for waste recycling, water remediation, or soil remediation, using raw material such as blast-furnace slag [179], [180], coal and fly ash landfilled in ash ponds [181], [182], halogenated organic pollutants [183], lithium-ion batteries [184], [185], cardboard waste [186], or heavy metals [187], [188], [189].Approximately 17% of the papers utilise biomaterials as starting reactants, including distiller grains [190], peanut shell for biochar production [191]; corn stover and SnO2 for bio-H2 production [192]; Sn-functionalised biochar catalyst for glucose isomeration to fructose and food waste valorisation [193]; natural cellulosic fiber–an abundant, low-cost renewable material with a wide variety of applications, serving as a crucial component for building a sustainable and green society– activation [194]; tannin, which is intensively explored due to its unique properties (e.g., wide pore size, high surface area, large pore volume, excellent chemical stability and adjustable channel structure), with different nitrogen source compounds [195]; milled waste biomass tar as a catalyst for H$_2$O$_2$ decomposition and subsequent methylene blue degradation in aqueous solution [196].The remaining 10% are articles that do not fit into the 3 theme described above.

BALL MILLING PROCESSES PARAMETRIZATION

While some studies has explored real time monitoring techniques, such as using highly penetrating synchrotron radiation to monitor mechanochemical transformations by X-ray powder diffraction (XRPD) through the walls of the milling jar [197], or employing Raman spectroscopy [198], and the combination of both [199], the current scientific community lacks the understanding on the operating conditions of reactions done using mechanochemistry, hence most of the published works employing ball milling or other mechanochemical processes do not mention information about the reaction, and kinetics and thermodynamics. This omission arises from the inherent difficulty of monitoring the operating conditions during these processes, treating the reaction as a "black box". This lack of detailed information makes it challenging to replicate experiments from one laboratory to another. Additionally, mechanochemical reactors generating extreme hotspots along reactions further complicate the control the operating conditions.

Out of the 60-research article evaluated in this study, 10% do not specify the requiring milling time for completing the reaction, 67% omit the information on the necessity of thermal input, approximately 22% fail to present the rotation speed of the miller, and about 78% do not

disclose the maximum yield achieved. Regarding milling equipment details, 80% do not provide the ball-to-powder weight ratio, 45% do not mention the milling ball or chamber material, around 55% do not specify the size of the milling balls used, and 60% do not offer information on the size of the chamber where the reaction takes place.

Despite the environmental advantages of mechanochemical processes, their optimization requires consideration of a substantial number of parameters, particularly those highlighted into the previous paragraphs. A comprehensive understanding of how mechanochemical processes function, how mechanical energy transforms into chemical energy, and how enhancements can be made is crucial for establishing mechanochemistry as a standard in the field of materials science. In January 2021, Gil-González et al. (2021) published a research article presenting a kinematic-kinetic approach for the parametrization and prediction of mechanically induced reactions. In this study, Gil-González et al. (2021) explored various experimental parameters such as the dimensions of the milling chamber, the grinding medium, and the rotational speed. They utilized the procedure outlined in previous works for the mechanochemical synthesis of $CoSb_3$ [201], [202] in two different planetary mills – the Micro Mill Pulverisette 7 Premium Line and the PM100 – modified to control gas atmosphere with a gas cylinder throughout the milling process [203], [204]. The authors proposed an equation to estimate the input power, accumulated energy and impact energy applied to the reactants. These were parametrized by combining theoretical-empirical equations proposed by Burgio et al. (1991) and the most widely used kinetic models for solid state reactions.

Specifically, the impact energy (J hit^{-1}) was calculated using equation 5-1:

$$\Delta E = \frac{1}{2} m_b W_p^2 \left[\left(\frac{W_v}{W_p}\right)^2 \left(\frac{D_v - d_b}{2}\right)^2 \left(1 - 2\frac{W_v}{W_p}\right) - 2R_p \left(\frac{W_v}{W_p}\right)\left(\frac{D_v - d_b}{2}\right) \right.$$

$$\left. - \left(\frac{W_v}{W_p}\right)^2 \left(\frac{D_v - d_b}{2}\right)^2 \right]$$

(5-1)

m_b: mass of a ball

d_b: diameter of a ball

D_v: diameter of the jars

R_p: distance from the center of the mill to the center of the vial

W_p: angular velocity of the supporting disk

W_v: angular velocity of the jars

Gil-González et al. (2021) introduce a correction factor to account for the hindering effect when employing multiple balls simultaneously in the milling process, which leads to a reduction in

impact energy. By taking into account the total number of balls utilized and the frequency with which balls are propelled against the opposite wall of the jars, it becomes feasible to estimate the total energy transferred per unit weight of powder.

TYPES OF MILLING

Neat milling, also known as dry milling, is a mechanical milling technique where solid materials are subjected to milling without the use of any additional liquid or solvent. In this process, milling balls or media impact and compress the material, resulting in size reduction and sometimes chemical transformations. Neat milling is often applied in situations where introducing liquids may adversely affect the desired product or where dry conditions are essential. It is commonly used in pharmaceuticals, ceramics, and materials science for producing fine powders and modifying material properties [172], [189], [206].

The term LAG was initially used in 2006 and involves the addition of small amounts of liquid to enhance the reaction kinetics, optimize yields and mitigate issues of product amorphization found in some neat grinding applications [136]. This technique enhances the milling process by facilitating reactions, improving particle size reduction, and providing a medium for heat dissipation. LAG is particularly useful when a reaction or transformation is promoted by the presence of a liquid medium. It is frequently employed in organic synthesis, pharmaceuticals, and materials research where enhanced reactivity and control over reaction conditions are desired.

Slurry milling involves milling a solid material in the presence of a liquid to create a slurry. The mixture of solid particles and liquid is then subjected to mechanical forces to achieve size reduction and other desired effects. Slurry milling is commonly used in industries such as mining and minerals processing, where the milling of ores is performed in the presence of water or other liquids. It helps in achieving efficient particle size reduction and liberating valuable components from the ore matrix [207].

Solution or wet milling involves milling a solid material in a liquid solution, typically using a solvent. This technique is employed to promote reactions between the solid material and the solvent, leading to the formation of new products. Solution milling is widely utilized in chemistry, particularly in the synthesis of nanoparticles, pharmaceuticals, and fine chemicals. It provides a controlled environment for reactions and allows for the generation of products with specific properties [176], [179], [189].

The Deasyl group has pioneered the development of various processes utilizing cutting-edge technology from WAB-Group. Among these innovations is the deployment of a highly efficient bead mill, equipped with ZrO_2 micro-milling beads stabilized with 20% CeO. Specifically, the DYNO®-MILL MULTI LAB, designed for continuous flow wet-milling applications, stands out. This state-of-the-art equipment operates on the principle of leveraging the collision between zirconia microbeads and reactants to activate reactions. Notably, the mechanical energy required for this process is achieved indirectly through the utilization of electricity, which powers the motor responsible for the motion of the rotor and discs within the machine [140]. The milling chamber accommodates microbeads, constituting 55% to 70% of the chamber's volume relative to its total stationary volume. These microbeads, exhibiting a substantially spherical shape, possess a mean diameter ranging from 0.5 to 1 mm and a Vickers hardness measured in accordance with standard EN ISO 6507-1, typically falling within the range of 1000 to 1400 HV1 [140]. Despite being an outstanding technique for diverse procedures as already commented, no methodology is perfect. Some limitations that have been encountered involve the use of hazardous solvents, including acids such as HCl or H_2SO_4, or even N,N-dimethyl formamide. Limitations rely on the composition of certain parts of the instrument. Furthermore, not full-continuous flow processes can be carried out, since some crucial stages in organic chemistry as purification have to be carried out in batch.

GREEN CHEMISTRY PRINCIPLES IN BALL MILLING PROCESSES

The environmental situation of the last decades has eased the advancement of Green Chemistry (GC), emphasizing the reduction of: i) reaction times, ii) use of solvents, and iii) energy demand. This approach is progressively assimilated and implemented in diverse scientific investigations [142]. The twelve principles of GC provide a framework for evaluating the effectiveness of this implementation in various chemical processes. These principles, as outlined by [208] and reiterated by Ardila-Fierro (2021), include: GC1) prevention, GC2) atom economy, GC3) less hazardous chemical syntheses, GC4) designing safer chemicals, GC5) safer solvents and auxiliaries, GC6) design for energy efficiency, GC7) use of renewable feedstocks, GC8) reduce derivatives, GC9) catalysis, GC10) design for degradation, GC11) real-time analysis for pollution prevention, and GC12) inherently safer chemistry for accident prevention [142], [208]. Specifically, addressing GC1) prevention, GC5) safer solvents and auxiliaries and GC8) reduce derivatives, ball milling can be conducted with little or no solvent. This is attributed to the fact that the activation energy of the reaction is achieved mechanically, with the milling balls. The

impact of the beads with those reactants can reduce the mass transfer limitations and enhance the mixing of them. In contrast, solvothermal processes rely on solvents as heat sinks in exothermic reactions or as heat suppliers in endothermic processes [43], [44]. Solvents are sometimes employed to enhance the mixing of reactants, especially when they are immiscible or highly viscous. The milling balls, with a lifespan of approximately 10,000 hours, can be continuously reused without experiencing wear or affecting the efficiency of the process [210]. Ball milling reactions often achieve high yields in a short time, mitigating the environmental impact associated with the milling balls. This assumption was notably considered by Arfelis et al. (2023) in their LCA comparing different processes for producing CAZN for zinc batteries.

For GC2) atom economy, some mechanochemical-aided reactions [211], [212], [213] have demonstrated superior yields and selectivity compared to conventional processes, resulting in a reduction in waste and by-products. For instance, Miranda Júnior et al. (2021) investigated, for first time via mechanochemistry, the copolymerization reaction of the biodegradable monomers urea and citric acid, achieving a yield of 82% compared to the solution condition, which yielded only 70% Wu et al. (2020). For GC3) less hazardous chemical syntheses and GC11) real-time analysis for pollution prevention, using fewer or even avoiding solvents helps reducing toxic or hazardous by-products. Moreover, ball milling is employed for pollution prevention or remediation of hazardous products. Examples include the use of landfilled coal ash in ball milling processes to produce cement binders [181], mechanochemical processes for stabilizing heavy metals in fly ash from municipal solid waste incineration plants [188], [189], conversion of furnace waste slag into building material through ball milling [216], mechanochemistry for the pre-treatment of arsenic selective leaching from copper smelter flue dusts [217], and the operation of a high-energy ball miller [218] for synthesizing magnetite nanoparticles with amino-phosphonic functionalized poly(-glycidyl methacrylate) polymer as a sorbent for U(VI) from aqueous solutions. Mechanochemistry is commonly employed in the fabrication of the manufacturing of MOFs for wastewater treatment. MOF are useful for water treatment advanced oxidation processes (AOP) like , such as the Fenton process [164], [165], [166], [167], [168], [171], [172], [174], [187], [196], [219], [220], as well as the remediation of organic pollutants [170], [183], [221], [222].

The majority of mechanochemical reactions take place without external heat input, aligning with the principle of GC6) design for energy efficiency. Although electricity is required to induce the mechanical forces activating the reaction – here, renewable, or nuclear (not preferred) can be used to reduce the environmental impact of these processes – the environmental impacts of electricity production are generally lower than those associated with steam production for thermal energy. This comparison may vary based on the electricity mix of each country.

Considering the European Union Green Deal, it is anticipated that the energy mixes of electricity will become greener over time [49]. Additionally, several applications for energy storage have been observed, such as the manufacturing of electrode materials for batteries [223], [224], [225], [226], [227] or MOFs for chemical storage of hydrogen or other gases [228], [229].

For the GC7) use of renewable feedstocks, several studies in the field of biomass valorisation have demonstrated the advantages of mechanochemistry [190], [192], [194], particularly when working with materials such as cellulosic fibers [194], corn stover [192], rice straw, distillers grains and Eupatorium adenophorum [190]. This topic is expanded in the section 3.5. Mechanochemical treatments in biomass valorisation. For GC9) catalysis, ball milling serves as a valuable tool in catalyst manufacturing [166], [191], [230], [231]. This method facilitates the production of smaller particle sizes and increased surface area [4], enhancing the catalyst's activity by maximizing contact between catalyst and reactants. Moreover, it introduces rich defects and oxygen-containing functional groups [191]. Notably, catalyst manufacturing can be achieved using biomass wastes such as walnut shell [232]. Addressing GC10) design for degradation involves finding a balance between long lifespan and (bio)degradability capacity. For instance, the prolonged stability of plastics has led to their undesirable accumulation in the environment. Recent efforts have focused on designing functional polymers with adaptable degradability [142]. Additionally, mechanochemical processes have emerged as a new avenue for degrading or recycling existing polymer-based products [169], [182], [190], [211]. Regarding GC12) inherently safer chemistry for accident prevention, some of the risks associated with mechanochemical processes can be easily mitigated: i) certain reactions are conducted under nitrogen or argon atmospheres to avoid prevent the risk of explosion risks [164], [233], ii) some authors introduce a small amount of solvent, typically water or ethanol, to decompose the residue of the reaction for the same purpose [187], iii) other intermittently pause the reaction to cool it down, preventing excessive temperature increases [176], [183], [188], [189], [196], [211], [218], [234].

Motivated by the principles of GC and mechanochemistry, innovative strategies and technologies are being developed. In this context, a sophisticated and sustainable high-throughput reaction platform has been created through collaboration between Bachofen AG (WAB-Group) and Deasyl S.A. (Patent No. 20220152621). This platform integrates the advantages of mechanical energy, thermal, and pressure activation within a continuous flow system, complemented by an in-situ heating mechanism. The tool employs the cutting-edge I-CHeM (Impact/Induction in Continuous flow Heated Mechanochemistry) technology [235].

Biomass represents one of the largest waste source globally, estimated at 130 million tonnes per year [154]. Lignin is the most abundant biopolymer after cellulose. The wood industry alone discarded, in 2022, between 50 to 70 million tons of lignin waste worldwide [236]. Typically composed of lignocellulosic, and lignin, biomass waste also includes proteins and extractable compounds like lipids, prompting the international energy agency to target 10% of the world's energy from biomass by 2050 [237]. The diverse processes biomass can undergo, owing to its complex composition, open up numerous applications, including the production of activated carbons through pyrolysis [237], [238], hydrogen production with heterogeneous catalysts [239], nanocellulose generation [6], [240], and the synthesis of biodiesel and platform molecules like 5-hydroxymethylfurfural and furfural (HMF) [241], [242].

The challenge with many of these processes lies in the energy-intensive reactors they employ, necessitated by high temperatures and pressures. However, mechanochemical pre-treatment has emerged as a solution, enhancing reaction yields and often allowing milder reaction conditions, thereby increasing productivity [243], [244], [245]. While many of these processes are dry or slightly wetted by inorganic acids, inorganic bases or solvents, there is a growing trend towards LAG processes for valorisation of biomass-derived products [246].

In the past decade, mechanochemical pre-treatment has gain significant attention, particularly for depolymerizing lignocellulosic materials, leading to improved subsequent treatments [247]. These treatments can yield nanocellulose, primarily nanofibrils (NFC), which, being less crystalline, offer advantages in various applications such as hydrolysis, pharmaceutical, and adsorbents [248], [249], [250]. Yu and Wu (2011) conducted ball milling experiments on microcellulose, observing significant changes in cellulose microstructure with just 1 hour of milling, reducing particle size. Extended milling (7 hours) led to particle agglomeration, proving less effective for further size reduction [251]. This cellulose pretreatment has been utilized by various research groups to enhance yields for various target compounds, including methyl lactate, ethylene glycol, HMF, and even H_2 as detailed in Table 5-1.

While most studies employ microcrystalline cellulose (MCC), Table 5-1 showcases results where biomass undergoes direct treatment using acid or mineral bases. The utilization of these acids/bases significantly enhances the hydrolysis processes of the hemicellulosic and cellulosic fractions. Furthermore, subsequent treatments enable the separation of lignin for individual recovery [252], [253].

Table 5-1. Pretreatment of biomass for diferents reactions of biomass valorisation under ball milling.

Biomass	Reaction	Time (h)	Temp. (ºC)	Yield (%)	Pression (Mpa)	Ref.
MCC	Cellulose → Methyl lactate	10	200	45	0,5	[254]
MCC	Cellulose → Glycerine	5	205	41	5	[255]
MCC	Cellulose → Glucose	1	200	76.3	-	[256]
MCC	Cellulose → HMF	2	170	45.4	-	[257]
MCC	Cellulose → H_2	24	40	-	-	[258]

Catalyst	Biomass	Reaction	Time (h)	Temp. (ºC)	Yield (%)	Ref.
NaOH/NH$_3$ (5%w/w)	Wheat straw	Wheat straw → Glucose	72	50	91,9 %	[259]
KOH	Rice straw	Rice Straw → Glucose + xylose	1	200	52.1% glucose 66.5% xylose	[256]
Ca(OH)$_2$	Eucalyptus wood chips	Eucalyptus wood chips → glucose	48	170	90	[260]
H$_2$SO$_4$	Eucalyptus loxophleba	Eucalyptus loxophleba → sugars monomers	0.5	150	94	[261]
HCl	Eucalyptus wood	Eucalyptus Wood → glucose	48	50	95.7	[262]

MCC: Microcrystalline cellulose

However, these processes typically involve two stages: an initial impregnation stage with acid or mineral base and a subsequent integration stage in a hydrothermal or continuous flow reactor. Nonetheless, LAG and ICHEM processes could potentially address these challenges and streamline the process into a single step. Biomass is immersed in a liquid medium, where the mechanochemical system reduces particle size, crystallinity, and enhances the reactivity of exposed hemicellulose chains. This is attributed to the reduction in monomers forming the chains and the increased number of chains in solution, rendering them more easily accessible [152], [153], [154].

To mitigate the current global warming trend and diversify energy sources, the transformation of biomass into fuels and chemicals is becoming increasingly popular. Traditionally, the industrial production of high-added value products such as vanillin involve non-environmentally friendly processes like the Riedel process [263]. In this regard, when combining mechanochemistry with continuous flow approaches, greener strategies to obtain the desired products can be reached. As reported by Martín-Perales et al. (2023), high yields of vanillin were obtained in the oxidation of biomass-derived platform molecules, such as isoeugenol and vanillyl alcohol. The novelty of this study is that no catalyst is needed, high temperatures are not required and in short times of

reaction, with optimal results at 25 ºC during 19 min of residence time and 30 mL of H_2O_2 (35% v/v) when using isoeugenol as precursor, and 80 ºC during 19 min of residence time and 10 mL of H2O2 (35% v/v) for vanillyl alcohol oxidation.

LCA IN BALL MILLING PROCESSES

When assessing the entire life cycle of products, it is crucial to acknowledge that the precursors used in some cases are obtained through contaminating or less eco-friendly processes. While numerous papers compare innovative ball milling processes with the conventional synthesis methods for producing identical products, highlighting the typically lower environmental impact of mechanical processes [165], [167], [175], [176], [178], [191], [212], [264], [265], [266], there is limited literature that quantifies these impacts throughout the entire life cycle of the products [4], [6], [48]. In conducting an overall environmental study, it is essential to consider whether the operation unit for milling balls requires additional pre-treatment or post-treatment processes, such as drying, calcination, size reduction, or other energy-intensive procedures that are not needed in conventional processes.

Morfino et al. (2022), conducted an LCA comparison between zircon and alumina sand applied in the production of ceramic tiles, including the milling processes required for its manufacture. The study results indicated that the main differences between the two processes were influenced by the energy mix used in each process. Mechanochemical processes rely on electricity as an energy supply, whereas solvothermal processes typically use steam (often produced from natural gas) for heat. Arfelis et al. (2023a) conducted an LCA comparing different pre-treatments for cellulose extraction from wood chips. The pre-treatments assessed are: i) mechanical, ii) enzymatic, and iii) TEMPO-mediated oxidation routes. The results of their LCA were allocated considering the different tensile strength obtained for each pre-treatment. This property affects the functionality of the product under comparison and, therefore, the LCA methodology itself obliges to take it into account in the FU of the study. The main output of their study is that both, mechanical and TEMPO-mediated oxidation routes, present lower impacts than the enzymatic pre-treatment. Being the mechanical pre-treatment the one presenting slightly milder contributions to climate change, acidification, eutrophication, and other indicators. Even though, Arfelis et al. (2023a) argued that the fact that TEMPO-mediated oxidation is environmentally unfeasible should be put under question. After all, and despite being disregarded in most assessment publications up to date, it is the only well-known way to selectively oxidize primary hydroxyl groups and thus producing kinds of CNFs that are

unthinkable by other ways. Arfelis et al. (2023b) conducted a LCA for the CAZN production for zinc batteries. The study consists in comparing the environmental impact of the wet milling production of CAZN crystals with the traditional production process named hydro-thermal synthesis. In this case, the results were allocated according to the activation rate of the batteries which depended on the particle size of the crystals. Arfelis et al. (2023b) also identified that, in LCAs dedicated to continuous industrial processes, the author must pay attention to the selection of the FU. Despite falling beyond the scope of cradle-to-gate LCA practices, factors such as the particle size of the ultimate product or the residence time of the reaction introduce variability, resulting in the final product having a higher number of service units or functions. Hence, it is crucial to recognize these aspects as valuable supplementary information when evaluating alternative options. Utilizing a functional unit dependent solely on mass in LCA results fails to account for these nuances. Notably, there exist numerous chemical LCA studies that already incorporate flowrate as the functional unit, addressing these intricacies in their analyses [73], [78], [84], [94]. Similar approach is taken in the incorporation of Module D within the framework of EN 15804:2012 + A2:2019, which serves to account for information beyond the cradle-to-gate scope in LCAs of construction products [10], [11].

In other LCAs conducted by the authors of this paper, it has been demonstrated that the use of mechanochemistry to activate chemical reactions often leads to a greener process with improved conversion and selectivity [4], [6], [141].

5.5.   CONCLUSIONS

Interest in mechanochemical processes has grown within the scientific community due to their environmentally friendly nature. However, a notable challenge lies in the batch nature inherent to mechanochemistry. Recent efforts aim to overcome this limitation by introducing continuous-flow approaches to mechanochemical processes, aligning with the twelve principles of GC.

One innovative strategy that integrates continuous-flow with beads-assisted processes is ICHeM technology, exemplified by the remarkable high-throughput reactor, IMPAºCT. This technology enables the production of various compounds, ranging from high-added value like vanillin [232] or biodiesel [269], to advanced catalysts, including diverse MOFs and CaDG for biodiesel production [140], [270], [271], [272].

Stainless steel, zirconia oxide, and agate are commonly used materials in the milling chamber and milling balls. Ball milling is frequently employed for synthesizing advanced materials such as MOF and nanomaterials. Moreover, it has found applications in waste recycling, biomaterials

production, and water and soil remediation. Emphasizing the need to monitor ball milling reaction conditions is crucial. Avoiding the presentation of processes as a "black box" enhances experiment repeatability and aids in comprehending the reaction kinetics. Ball milling processes offer a pathway to developing more sustainable procedures. This review shows how mechanochemical approaches align with all GC principles. Particularly, ball milling processes are often more environmentally friendly than conventional solvothermal processes, requiring less solvent and substituting thermal energy demand with electricity demand. Despite the benefits, there is a scarcity of LCA papers for ball milling processes. Utilizing this methodology to compare innovative syntheses with conventional processes could contribute significantly to understanding mechanochemistry and its potential to enhance widely used solvothermal processes.

This comprehensive exploration affirms mechanochemical strategies as pivotal in advancing sustainable and eco-friendly chemical synthesis, ultimately propelling the field towards a more efficient and environmentally conscious future.

6. LIFE CYCLE ASSESSMENT ON CALCIUM ZINCATE PRODUCTION METHODS FOR RECHARGEABLE BATTERIES

6.1. ABSTRACT

The world's energy transition from fossil to renewable energy is unthinkable without further research in energy storage. Decreasing the environmental impacts from the production of energy storage technologies is essential for achieving a green energy transition. Calcium Zincate (CAZN) is used as active material in rechargeable zinc-based batteries (and other products, such as heterogeneous catalysts for biodiesel or antifungal products). They present a low-cost, safer, alternative to Lithium based batteries and are targeted as replacement solutions for lead-acid batteries.

We propose a novelty in the synthesis of CAZN, the hydro-micro-mechanical synthesis (HMMS). The residence time of this new route is about 20 times lower than the traditional processes, so its production needs less infrastructure and can deliver quicker at an industrial scale. In addition, laboratory tests indicate that HMMS CAZN has more reaction surface area and the activation of the battery is 1.77 times faster.

Using the LCA method, we compare this new process with the current best option, hydro-thermal synthesis (HTS). The cradle-to-gate results per kg of CAZN already indicates that HMMS is an environmentally better alternative for all indicators; especially when considering the normalization of the results with the residence time and the surface area, HMMS delivers better results, with improvements of 97% in global warming, for instance. With this, we demonstrate that, outside of the cradle-to-gate, variables that make the final products better service units or give more function should be considered as valuable additional information when deciding among alternatives. This also highlights the importance of life cycle thinking when working with chemical processes and substances.

In the sensitivity analysis, we developed 7 scenarios related to the energy demand of the processes, and we incorporated the projection in the European electricity mix for 2030 and 2050.

Keywords: Life cycle assessment; Calcium Zincate; Mechanochemistry; Zinc-Batteries; Ball-milling

Highlights

- The raw materials shape the environmental results of CAZN production
- Particle size and reaction time are key factors affecting the results of the LCA
- The reaction time should be considered when calculating chemical LCAs
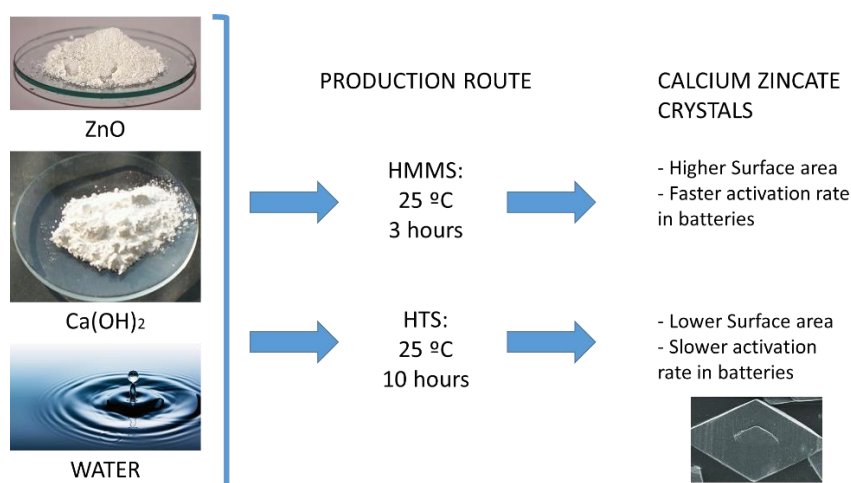
Figure 6-1 Graphical abstract of the LCA on different routes for calcium zincate production

6.2. INTRODUCTION

Energy storage is an important part of the transition to a carbon-free economy, and it meets several of the Clean Energy for All Europeans package's fundamental objectives. It provides a real technique of enhancing energy efficiency and integrating additional renewable energy sources into electrical networks by balancing power grids and conserving surplus energy [273]. Zinc-batteries present a low-cost, potentially safer alternative than other batteries produced from metals such as lithium or sodium, which typically use flammable organic electrolytes. Other properties, such as low potential (leading to a high cell potential), great reversibility (quick kinetics), low equivalent weight, and compatibility with aqueous electrolytes make it a popular battery material [274]. CAZN can be used in the production of: i) zinc anode of alkaline

electrochemical generators; ii) heterogeneous catalysts for the production of biodiesel; or iii) antifungal products. Zinc-batteries electrodes are the most common use of this product.

CAZN is traditionally produced through the following types of synthesis: hydro-chemical synthesis (HCS) [275], [276], HTS [277], and hydro-mechanical synthesis (HMS) [278], [279]. These syntheses require a long residence time and numerous production steps that make these processes both impracticable and environmentally unfriendly when developed at industrial scale [145], [210], [275], [276], [277], [278], [279], [280]. For example, HCS uses potassium hydroxide [275], [276], which is expensive and must be removed at the end of the process. HTS usually requires heating up and stirring a substantial amount of water to 75 ^{o}C to reach the acceptable conversion [277]. HMS is not continuous, cannot be scaled to an industrial scale, and it is energy-intensive [278], [279].

HMMS is an innovative way of synthesis [145], [280], patented in 2016 [210], which might be operated continuously and on an industrial scale. The proposed novelty opens the door to the industrialisation of this product, with a green, fast, and simple process.

In this paper, we are comparing HMMS with HTS. HTS is the most competitive of all the conventional methodologies because it only uses water as a solvent and it has a relatively low residence time, compared with the other processes. We validated the data from scientific and technical literature related to HMMS and HTS syntheses reactions with several experiments. The experiments for HMMS were developed by Deasyl in their laboratories in Switzerland and the experiments for HTS were performed at the University of Málaga (UMA) in Spain.

We compare these processes using the LCA methodology. LCA provides a comprehensive and holistic view of the environmental loads of the products or services understudy, covering a wide set of environmental impact categories [38], [39], [40], [41]. Operation within companies and production chains of environmental options follow the principles of Life Cycle Management [281]. This methodology is widely used to measure impacts throughout the lifespan of products in different sectors, also at industrial scale [2], [282]. In the present article, this is of relevance because, although both processes synthesise the same product (CAZN), its particle size (of the product) depends on the process used, and this will affect downstream processes. Comparing two production processes of the same product allows the LCA practitioner to focus mainly on those stages of the production chain that are different from each other, assuming that all other stages that are equivalent have the same environmental impact between the two processes [283]. As far as known by the authors, this is the first environmental study of the calcium zincate production process.

HYDRO-THERMAL SYNTHESIS (HTS)

According to the scientific literature [277], this process consists of heating the stoichiometric mixture of calcium hydroxide ($Ca(OH)_2$) and zinc oxide (ZnO) at 75 °C for 24 hours (12 hours of reaction and 12 hours of aging) with an excess of distilled water. CAZN crystals are retrieved by centrifugation, washed with demineralized water two times, and dried at 50 °C for 2 hours in vacuum. Unlike in the HCS, the HTS does not require a strong alkali medium or other solvent than water.

The reaction was replicated by DEASYL SA at the UMA for the purposes of our research. High conversion rates were achieved in only 10 hours. In addition, the crystals were obtained at ambient temperature with no need of heating the mixture to 75 °C. To be in the safe side, the HTS inventory data used for the comparison with HMMS are the best ones: the primary data that were tested in UMA. The flow diagram in Figure 6-2 presents the steps included in this process.
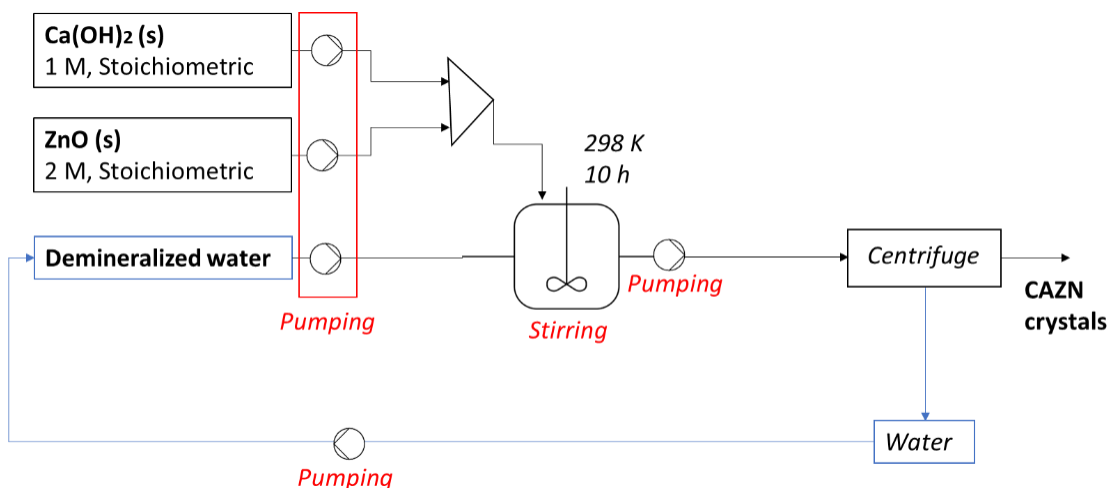
Figure 6-2 Boundaries for the hydro-thermal process [277]

HYDRO-MICRO-MECHANICAL SYNTHESIS (HMMS)

This method is an evolution of the conventional process of HMS. It consists of introducing a stoichiometric [$2 \cdot ZnO + Ca(OH)_2$] aqueous suspension through a high-efficiency continuous-flow mechanochemical reactor filled with an appropriate amount of zirconia oxide (ZrO_2) micro-milling balls. These micro-balls (0.5 to 1 mm in diameter) do not generate any appreciable pollution because of their wear and have a large lifespan of approximately 10,000 hours.

The milling step lasts only few minutes. It is used to activate and reduce the residence time of the reaction which takes place in a Continuous Stirred Tank Reactor (CSTR) in 30 minutes:

$$2ZnO(s) + Ca\,(OH)2(s) + 4H2O \rightarrow Ca\,(OH)2 \cdot 2Zn\,(OH)2 \cdot 2H2O(s) \qquad (eq.\ 6.1)$$
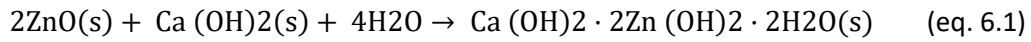
The best efficiency of the process is obtained for a water mass ratio between 3:1 and 5:1 at ambient temperature for 1-3 minutes, with a 30 to 90 L/h flow rate and a suspension of 300-600 g/L [145], [280]. This process is described by the flow diagram in Figure 6-3.
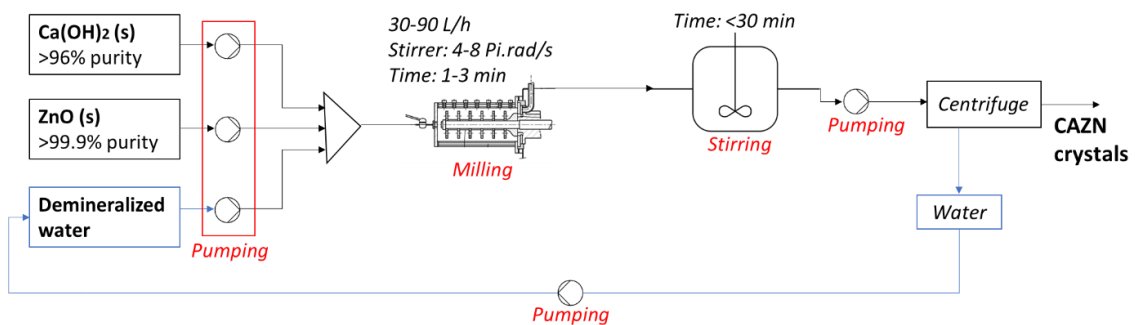
Figure 6-3 Boundaries for the hydro-micro-mechanical process [145], [280]

6.3.   MATERIALS AND METHODS

MATERIALS

Materials are key to understanding the overall impact of services or products, both per type and per quantity. Therefore, the design stage (such as laboratory conditions) must be given priority attention [284].

The materials utilized in the laboratory experiments and considered for the environmental evaluation comply with the criteria specified in the publications and patents of the HTS [277] and HMMS [145], [210], [280] processes:

1) $Ca(OH)_2$ with particle size from 0.01 to 1 μm, and purity of 96% or greater

2) ZnO with particle size from 0.01 to 1 μm, and purity of 99.9% or greater

3) Water, which has been purified with a demineralization process.

Most of the data that we use in the study are primary data tested at a laboratory scale. In addition, academic literature, scientific databases, or modelling complement these primary data. For instance, we use the publication of Piccinno et al., (2016) on advanced process calculations to scale up from the laboratory scale to the industrial scale [110]. This benchmark is widely used in the literature on LCA for chemical reactions [2].

All the secondary data were evaluated qualitatively using the Pedigree matrix [120], [121], all data being sufficiently reliable, complete, and without temporal, geographical, or technological differences. Even though, not having fully operational industrial scale data presents limitations, which are common in chemical LCAs.

LIFE CYCLE ASSESSMENT (LCA)

The environmental impact has been calculated with the LCA methodology, which is based on the ISO 14040 [35] and ISO 14044 [36] standards, and which is used to compare alternatives [283].

LCA is structured in four different iterative phases:

1) Definition of Goal and Scope

2) Development of LCI

3) LCIA

4) Interpretation of results.

The model for the LCA is developed using GaBi Professional Software (version 10.6.1.35), including its datasets [285] to characterize and quantify the impact of the raw and auxiliary materials. This is the world's leading LCA modelling and reporting software with the largest LCA databases for chemical products. In addition, AspenPlus (version 12.2) is used to simulate the processes, model the mass and energy balances for the LCI, and check the physical and chemical properties of the substances. This is the most widely used software for chemical process simulation and has extensive databases for this purpose.

The ReCiPe 2016 (version 1.1 midpoint, Hierarchist model) methodology is used for the calculation of LCIA [286]. According to a recent review on 47 different LCA of chemical reactions, this is the preferred method in this type of LCA [287], mainly because it brings together the main authors of the most previously used methodologies and because it perfectly summarises the

long list of LCI results in its different environmental indicators [288]. In addition, to maintain simplicity and have visual results, we cut off the emission sources with an environmental impact of less than 1%.

BOUNDARIES AND SCOPE

The present LCA consists of a cradle-to-gate approach, from the extraction of the raw material to the production of CAZN. The EoL of CAZN crystals after its use, typically in zinc batteries, is not included in the scope. Regardless of its production synthesis, the rate of Lead acid batteries and accumulators which are collected for recycling in the EU is 90% [289], we expect the Zinc based batteries to follow the same pattern. Water treatment, crystals washing, and drying requirements are equivalent in both syntheses, so they can be omitted for the comparison. The same happens with the distribution stage (batteries weight and volume are identical) and use stage (the efficiency of the battery is independent of the CAZN synthesis).

To calculate the environmental impact of the chemical processes, we have considered the following emission sources:
1) Input material flows
2) Flows of the energy used to heat or cool the reactants
3) Energy used in stirring, pumping, or milling the mixture.

FUNCTIONAL UNIT, ALLOCATION FACTORS AND NORMALIZATION

The FU serves as the reference basis of the calculation related with the environmental impacts of the system under study [35], [36]. In this case, the FU selected for the present study is 1 kg of CAZN for both processes.

The authors have identified that, in LCAs relating to the chemical industry sector, special care must be taken in the selection of the FU. Although outside of the cradle-to-gate LCA practice, there are variables such as the particle size of the final product or the residence time of the reaction which make the final product with more service units or more function. Therefore, this should be considered as valuable additional information when deciding among alternatives. The result of the LCA with an FU depending only on mass does not take this into account. There are several chemical LCA papers that already perform the study with a flowrate as FU [73], [78], [84], [94]. Another example is the consideration of module D within the EN 15804:2012+A2:2019 for

the consideration of information out of the cradle to gate scope in construction products LCAs [10], [11]. In the present paper, the results of the LCA per kg of intermediate product are changed in the sensitivity analyses with the application of the normalization factors described below.

The production routes present differences in the average particle size of the CAZN crystals. The particle size of the crystals directly affects the surface area, and it has an impact on the activation time of the battery. Deasyl, compared the standard CAZN crystals synthesized with HMMS (8-12 μm) [145], [210], [280] with the larger grain size synthesized with HCS (70-1000 μm) [275], [276], observing three times faster activation of the battery with the HMMS crystals. This phenomenon occurs due to a global feature in the field of interfacial electrochemistry: the more the contact surface area increases, the more the reaction velocity increases. The activation speed with HTS crystals (10-200 μm) [277] would be 1.77 times slower than with HMMS crystals, obtained with linear interpolation of the previously tested activation speeds of HMMS and HCS crystals. Furthermore, the difference in residence time of the processes means that the production rate of the HTS process is in the order of 20 times slower than HMMS.

According to the HTS experiments performed in the UMA laboratories, the HTS reactor volume must be about 3.33 times higher than the one for HMMS, as expected from the values of the kinetics of both reactions. For higher productions, several CSTR of equal size in series should be used to get reasonable reaction sizes. Figure 6-4 shows the conversion of $Ca(OH)_2$ as a function of the CSTR volume for a CAZN production with the HTS and the HMMS. This difference in reactor volume has been considered to account for the excess water used in each type of process when calculating the mass and energy balances.
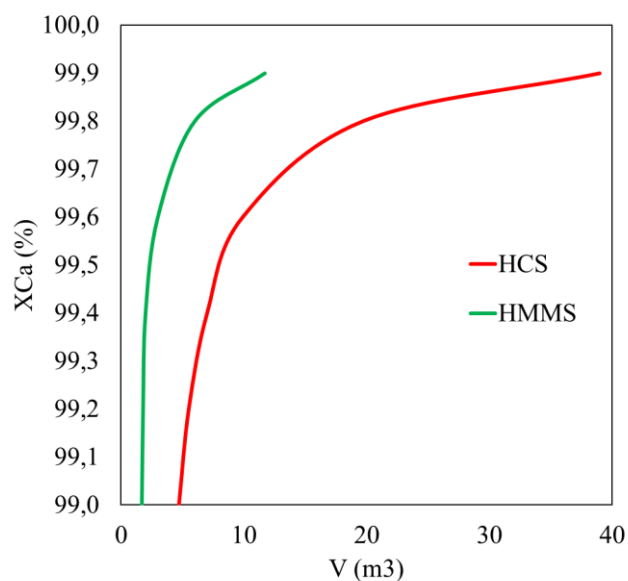
Figure 6-4 Conversion by HTS and HMMS as a function of the volume of the reactor

LIFE CYCLE INVENTORY

The LCI comprises the input and output mass and energy flows. Table 6-1 presents these inventories for each one of the reactions per 1 kg of synthesised CAZN.

Table 6-1. Bill of materials of HMMS and HTS

Mass Balance	HMMS	HTS
In		
$Ca(OH)_2$ (kg)	0.24	0.24
ZnO (kg)	0.53	0.53
Water (L)	3.07	10.13
Out		
Water (L)	2.76	9.117
Calcium zincate (kg)	1.00	1.00
Energy Balance	HMMS	HTS
Pumping (kwh)	$1.01 \cdot 10^{-5}$	$3.06 \cdot 10^{-3}$
Stirring (kwh)	$4.67 \cdot 10^{-4}$	$2.72 \cdot 10^{-2}$
Milling (kwh)	$8.00 \cdot 10^{-3}$	0.00
Centrifugation (kwh)	$2.11 \cdot 10^{-2}$	$5.99 \cdot 10^{-2}$
Total energy consumption (kwh)	$2.96 \cdot 10^{-2}$	$9.02 \cdot 10^{-2}$

As shown in the bill of materials, HMMS is a process with lower energy (electricity) and freshwater consumption. We have considered the European energy mix of 2017 from professional GaBi databases [285] for the study, as well as the projection (without consideration of the consequences of the war in Ukraine, yet) for years 2030 and 2050, according to the "EU Reference Scenario 2016 - Energy, Transport and GHG Emissions - Trends to 2050" published by the European Commission in 2016 [290]. These electricity projections are mainly used in LCA of the energy sector [291]. However, in LCA of chemical reactions, where they also provide important value, they are not so commonly used [2]. Years 2030 and 2050 are selected because of the European Commission's plans in the European Green Deal [49], as well as the availability of data on the projected energy mix in these years, both in the software used and in the literature. Inventories of input materials are described below.

LCI OF THE PRODUCTION OF THE MICRO-MILLING BALLS FOR HMMS

The micro-milling balls used in the HMMS are composed of 78-95% of ZrO_2 and other metals. They cover about 60% of the total volume of the reactor chamber [210]. The environmental impacts from the ball milling step in the production of HMMS crystals relate to the extraction of

zirconium. Also, the environmental impacts of the production of the micro-milling balls are comparable to the environmental impacts of the production of ZnO [292], one of the raw materials used in HMMS and HTS. In addition, the milling balls in HMMS can be reused for a lifespan of 10,000 hours.

Since one cycle in the ball milling step of HMMS lasts few minutes, the impact of the production of the milling balls allocated to one cycle is less than 0.01% and neglected for this study.

LCI OF THE CALCIUM HYDROXIDE PRODUCTION

According to GaBi professional database [285], calcium hydroxide is produced when water is slowly added to previously crushed or powdered quicklime (calcium oxide). The quicklime is made by burning different types of limestone.

LCI OF THE ZINC OXIDE PRODUCTION

ZnO is a multifunctional material with unique physical and chemical properties, due to its high chemical stability, high electrochemical coupling coefficient, a broad range of radiation absorption, and high photostability [293]. There are three main industrial large-scale production processes:

1) Pyrometallurgical synthesis
2) Hydrometallurgical synthesis
3) By-product of other chemical reactions.

The pyrometallurgical synthesis is the most utilized process.

Pyrometallurgical synthesis for ZnO production is based on the roasting of zinc ore according to the ISO 9298 standard [294]. It can be performed through the direct process (the American process) and classified as type A, or through the indirect process (the French process) and classified as type B. The indirect process is the most used in Europe. In this process, the raw material is zinc metal. Metallic zinc is melted in a furnace and vaporized at ca. 910°C. Then, ZnO is produced as an immediate reaction between the zinc vapor with the oxygen from the air [293]. We have simulated the French process to produce ZnO (Figure 6-5) to calculate its environmental impacts, because these are not directly available in the GaBi professional database [285]. We have considered the French process for both HMMS and HTS, and not the American one, as both routes have been studied in Europe.
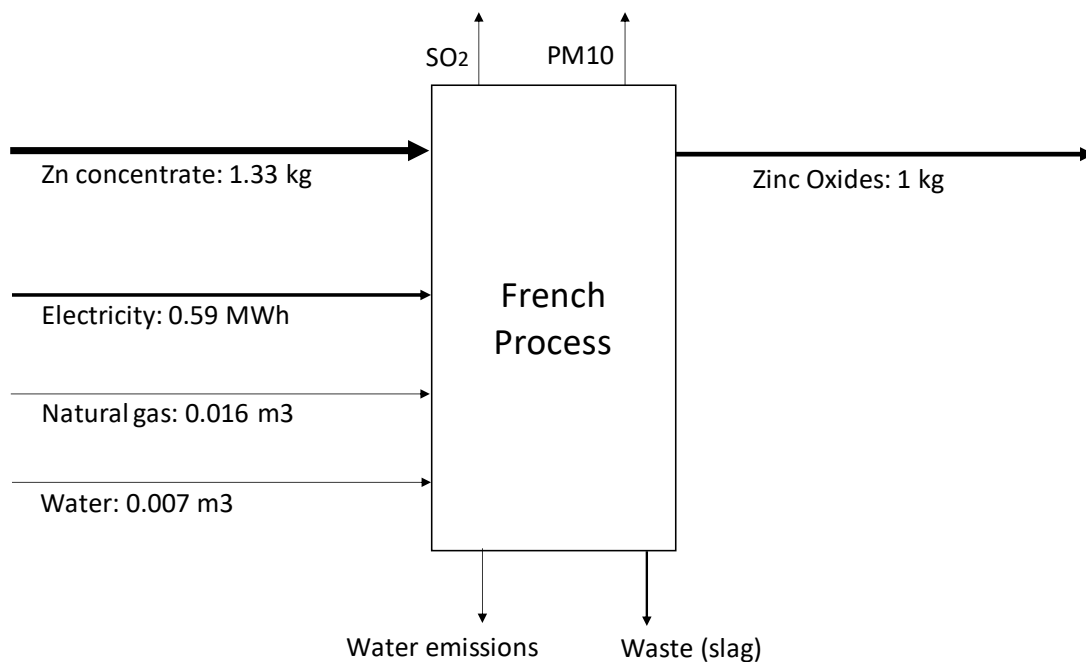
Figure 6-5 French Process input/output diagram for ZnO production [294]

For the transport stage of the raw materials, we have assumed a diesel-driven Euro V truck of 20-26 t gross weight and 17.3 t payload capacity. This capacity is the average value of the alternatives available in the GaBi professional databases [285] with 2020 as a reference year. Euro V is the vehicle emission standard for exhaust vehicles sold in the EU and European Economic Area (EEA) member states and the United Kingdom (UK) between 2008 and 2012 [295]. This period corresponds with the average age of trucks in Europe [296]. The Euro V standards are defined in a series of EU directives staging the progressive introduction of increasingly stringent standards.

Since batteries weight and volume are identical for both processes, only raw materials transport is included in the study, where a transportation distance of 100 km has been assumed.

ENERGY DEMAND

After selecting the most efficient processes (HTS and HMMS), we have compared their environmental impacts. Thus, we have considered each of the differences that may exist in each reaction (i.e., residence time and particle size) and have completed an exhaustive study with 7 different scenarios of energy demand in different stages of the overall process.

The scenarios have been selected to evaluate the uncertainty generated by some data discrepancies in the different literature sources used for each process or to evaluate different operational conditions that are being studied and optimised for each stage of the processes in the laboratory.

- 1_HEAT_MID, the temperature in CSTR in HTS is 50 °C. This is the average value between the experiments performed in UMA and the temperature reported in the literature [277].

- 2_HEAT_HIGH, the temperature in CSTR in HTS is 75 °C. This is the value reported in the literature [277].

For the two first scenarios, a theoretical value of 20% of energy savings is applied for heating and cooling [61], [71], [110], [297]. This is associated with optimization and process integration when it is upscaled from the laboratory to the industrial scale. According to the range reported in Piccinno et al. (2016), we add 5 more scenarios:

- 3_CF_LOW, with the lower energy demand value for centrifugation in both HTS and HMMS.

- 4_CF_HIGH, with the higher energy demand value for centrifugation in both HTS and HMMS.

- 5_DRY_YES, considering that the final product is being dried before the transport stage in both HTS and HMMS.

- 6_MILL_LOW, with the lower energy demand value for milling in HMMS.

- 7_MILLING_HIGH, with the higher energy demand value for milling in HMMS.

ELECTRICITY MIX

The European electricity mix is expected to change due to the more restrictive directives from the European Commission and the European Green Deal implementation [49]. This aspect

influences the impact categories. Therefore, to assess possible future environmental impacts, we developed a sensitivity analysis based on the future electricity grid mix in Europe for years 2030 and 2050 according to EU Energy trends data available in the Professional GaBi Databases [285]. The electricity mix sources are presented in Figure 6-6.
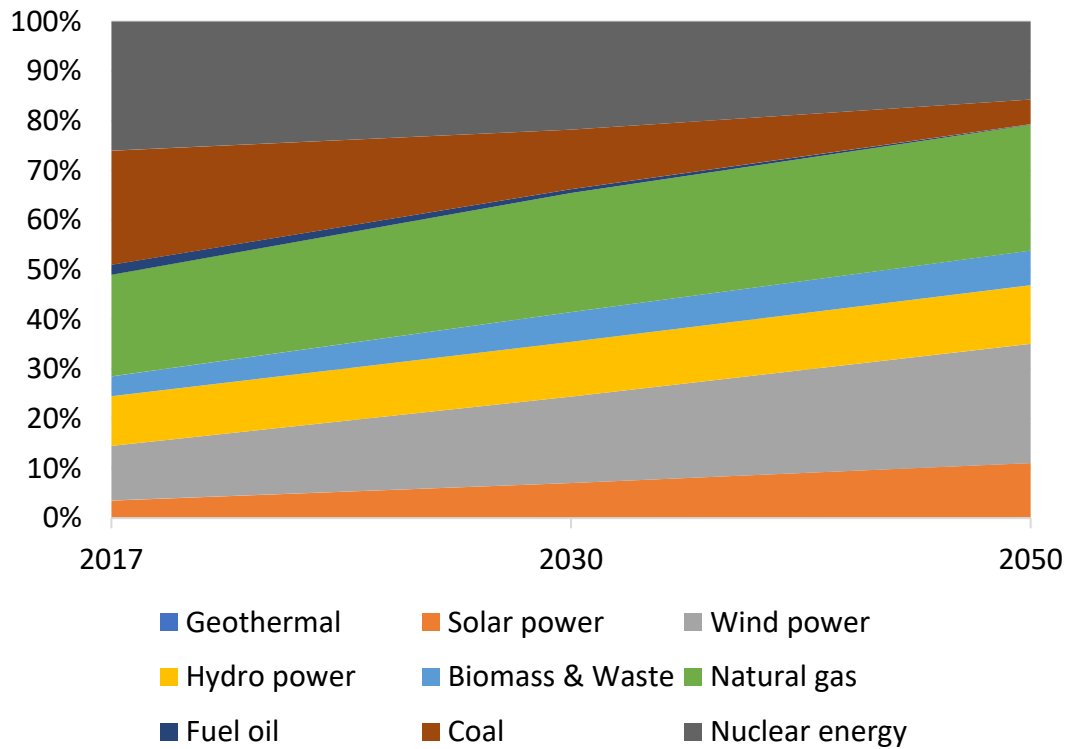
Figure 6-6 Projection electricity mix EU27 in 2030 and 2050

CAZN-TRANSPORT STAGE

CAZN crystals used as active material in zinc electrodes through a water-based process coating or paste, to be used in zinc batteries electrodes. It does not seem necessary to remove water after the centrifugation stage so we can reduce the electricity consumption for drying and the water consumption in the use phase. Even though, adding a drying stage also has benefits, taking up between 5 and 6 times less volume when transported from one place to another, as can be calculated from CAZN density and CAZN concentration in zinc-batteries electrodes [145], [280], [298].

Therefore, we have decided to include a study of the transport phase of the CAZN product to evaluate under which circumstances it is better to transport the product directly in suspension in water, and when it is better to pre-dry the final product to transport it in powder form.

Climate change is the principal environmental impact related to transport. We have used it to calculate the equilibrium distance of the environmental performance of two scenarios: transporting CAZN crystals mixed with water (without a drying stage) and transporting CAZN crystals in powder (with a drying stage).

6.4.   RESULTS AND DISCUSSION

GENERAL RESULTS

The results obtained for the whole LCA of CAZN production with HMMS and HTS show that most of the impacts are related to the extraction and refining of the ZnO because of its high energy consumption. This is presented in Figure 6-7.

HTS - ReCiPe 2016 v1.1 Midpoint (H)

HMMS - ReCiPe 2016 v1.1 Midpoint (H)

- Climate change, default, excl biogenic carbon [kg CO2 eq.]
- Climate change, incl biogenic carbon [kg CO2 eq.]
- Fine Particulate Matter Formation [kg PM2.5 eq.]
- Fossil depletion [kg oil eq.]
- Freshwater Consumption [m3]
- Freshwater ecotoxicity [kg 1,4 DB eq.]
- Freshwater Eutrophication [kg P eq.]
- Human toxicity, cancer [kg 1,4-DB eq.]
- Human toxicity, non-cancer [kg 1,4-DB eq.]
- Ionizing Radiation [kBq Co-60 eq. to air]
- Land use [Annual crop eq.·y]
- Marine ecotoxicity [kg 1,4-DB eq.]
- Marine Eutrophication [kg N eq.]
- Metal depletion [kg Cu eq.]
- Photochemical Ozone Formation, Ecosystems [kg NOx eq.]
- Photochemical Ozone Formation, Human Health [kg NOx eq.]
- Stratospheric Ozone Depletion [kg CFC-11 eq.]
- Terrestrial Acidification [kg SO2 eq.]
- Terrestrial ecotoxicity [kg 1,4-DB eq.]

Figure 6-7 LCA indicators of CAZN from the extraction of the raw material to transport stage of the final product

To compare HMMS and HTS, we have analysed the environmental impacts of only the CAZN production processes under the FU of 1 kg of CAZN. As expected, the results (Figure 6-8) are already favourable for HMMS at some midpoint indicators.

When normalizing the results of HTS by the particle size (multiplying by 1.77) and residence time (changing FU from kg to kg/h), the HMMS performs better in all the indicators of the ReCiPe 2016 methodology, as presented in Figure 6-9. Reaching about 44% of improvement in Climate Change indicator when normalizing only by the particle size, and improving by 97% in the same indicator when normalizing by both the particle size and the residence time.

Moreover, HMMS can perform even better in all the midpoint indicators if freshwater consumption is reduced. It is relevant to state that latest Deasyl experiments achieved a 3:1 ratio mass proportion of water-reactants without affecting the efficiency of the reaction.
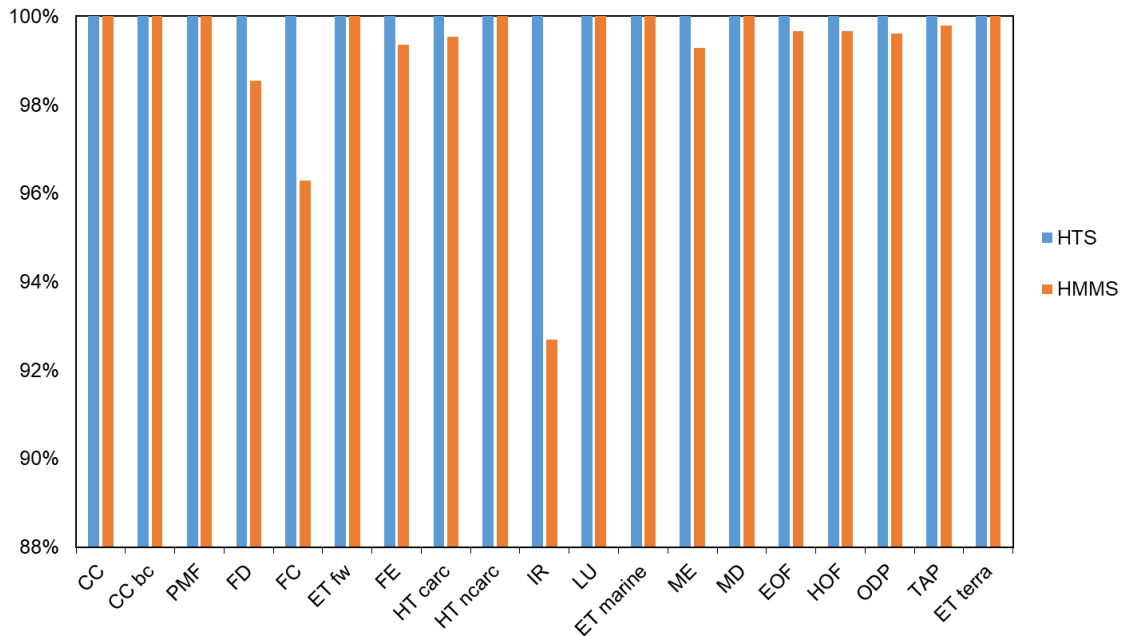
Figure 6-8 LCA indicators of CAZN production stage for HTS and HMMS (FU = 1 kg of CAZN)
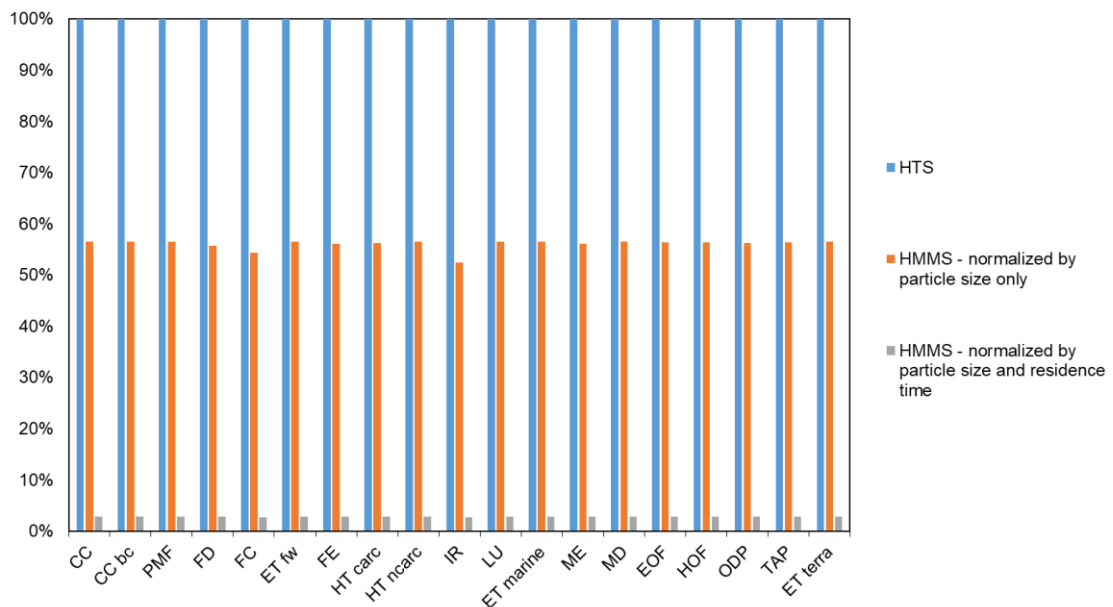
CC: Climate Change [kg CO2 eq.]; CC bc: Climate Change, incl biogenic carbon [kg CO2 eq.]; PMF: Fine Particulate Matter Formation [kg PM2.5 eq.]; FD: Fossil depletion [kg oil eq.]; FC: Freshwater consumption [m3]; ET fw: Freshwater ecotoxicity [kg 1,4 DB eq.]; FE: Freshwater Eutrophication [kg P eq.]; HT carc: Human toxicity, cancer [kg 1,4 DB eq.]; HT ncarc: Human toxicity, non-cancer [kg 1,4 DB eq.]; IR: Ionizing Radiation [kBq Co-60 eq. to air]; LU:

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Land use [Annual crop eq.·y]; ET marine: Marine ecotoxicity [kg 1,4 DB eq.]; ME: Marine eutrophication [kg N eq.];

MD: Metal depletion [kg Cu eq.]; EOF: Photochemical Ozone Formation, Ecosystems [kg Nox eq.]; HOF: Photochemical

Ozone Formation, Human health [kg Nox eq.]; ODP: Stratospheric Ozone Depletion [kg CFC-11 eq.]; TAP: Terrestrial

Acidification Potential [kg SO2 eq.]; ET terra: Terrestrial ecotoxicity [kg 1,4 DB eq.]

Figure 6-9 LCA indicators of CAZN production stage for HTS and HMMS (considering particle size and residence time)

SENSITIVITY ANALYSIS

ENERGY DEMAND

The comparison of the results for all the seven scenarios is presented in Figure 6-10. The process (HMMS or HTS) with less environmental impacts is highlighted in green and the process with more environmental impacts is highlighted in red.

	1		2		3		4		5		6		7	
	HTS	HMMS	HTS	HMMS	HTS	HMMS	HTS	HMMS	HTS	HMMS	HTS	HMMS	HTS	HMMS
Climate Change														
Climate Change, incl biogenic carbon														
Fine Particulate Matter Formation														
Fossil depletion														
Freshwater consumption														
Freshwater ecotoxicity														
Freshwater Eutrophication														
Human toxicity, cancer														
Human toxicity, non-cancer														
Ionizing Radiation														
Land use														
Marine ecotoxicity														
Marine eutrophication														
Metal depletion														
Photochemical Ozone Form, Ecosyst.														
Photochemical Ozone Form, H. health														
Stratospheric Ozone Depletion														
Terrestrial acidification														
Terrestrial ecotoxicity														

HMMS columns: i) dark green is for indicators that are environmentally friendlier for HMMS not even considering surface area or time, ii) medium green is for indicators that are environmentally friendlier for HMMS when considering surface area but not even time, iii) light green is for indicators which are environmentally friendlier for HMMS only when considering both surface area and reaction time, and iv) dark red is for indicators which are less environmentally friendly even considering both surface area and time.

HTS columns: i) dark green is for indicators that are environmentally friendlier even considering both surface area and time, ii) dark red is for indicators that are less environmentally friendly not even considering surface area or time, iii) medium red means less environmentally friendly for HTS when considering surface area but not even time and iv) light red means less environmentally friendly for HTS only when considering both surface area and reaction time.

Figure 6-10 Sensitivity analysis of the 7 scenarios for HMMS and HTS

According to Figure 6-10, when neither the particle size of the CAZN crystals nor the residence time of the reaction are considered, the HMMS is environmentally better for all the indicators in the scenarios which involve heating in the HTS (scenarios 1 and 2), but only for a few indicators in the other scenarios. For the remaining indicators in scenarios 3-7, the environmental impact is similar for both processes.

Even though, particle size has a direct relationship with activation rate in its use in batteries, as well as a direct relationship with its performance when used as antifungal product or heterogeneous catalyst. Residence time has also a high impact in the economic model of the system since all the infrastructure of the HTS must be upscaled 20 times to reach similar production rate of HMMS.

When considering both, particle size and residence time, the environmental impacts are lower in the HMMS case for all the indicators in all the scenarios.

We have projected, in Figure 6-11, the LCA results with the European electricity mix of 2030 and 2050 [290]. HMMS shows a better environmental performance than HTS for all the indicators in the next 30 years.
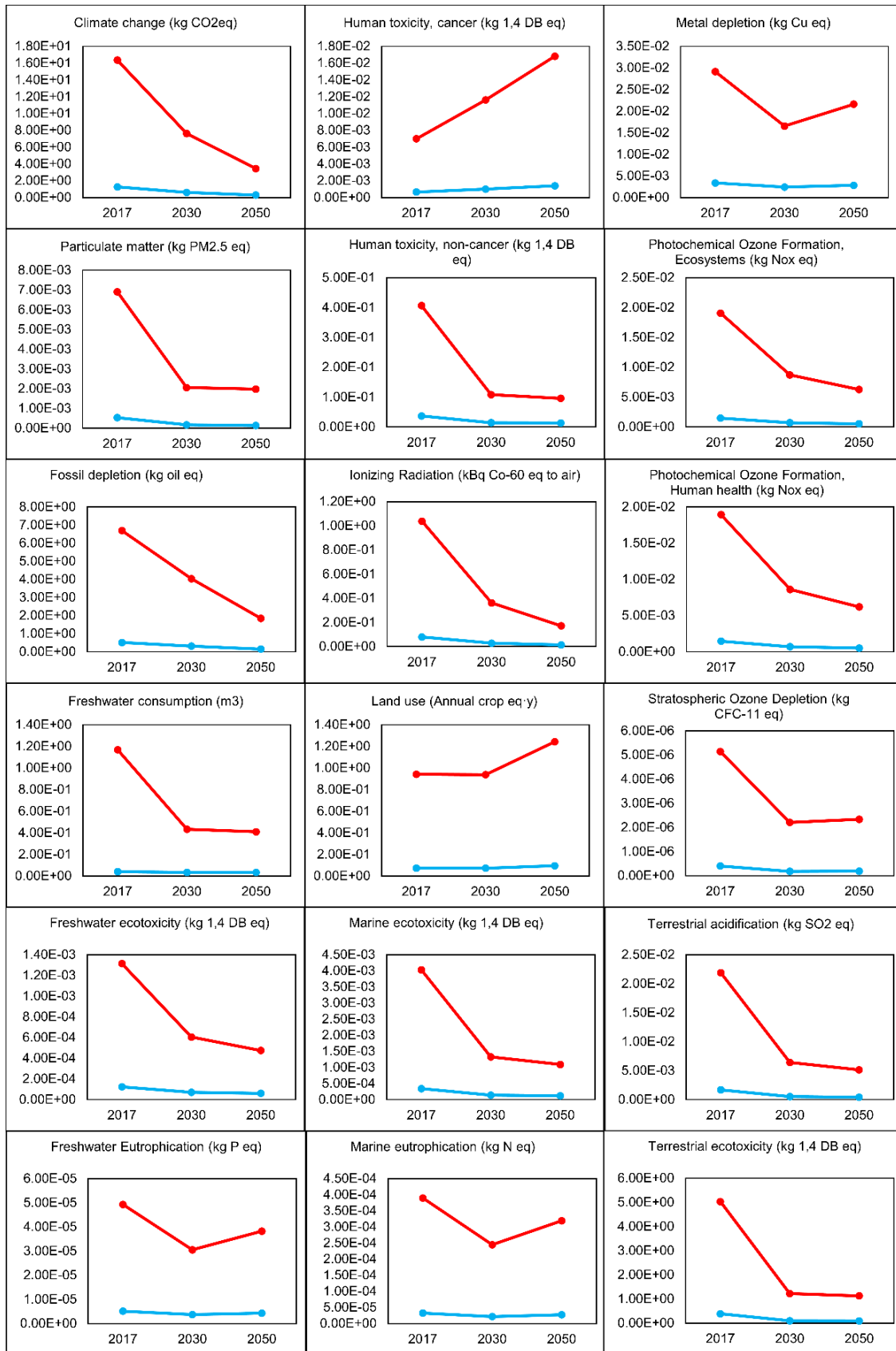
Figure 6-11 Projection of the LCA results in 2030 and 2050 where red line represents HTS and blue line represents HMMS

According to the results, only human toxicity and land use indicators are increasing in next years. This is due to the future energy mix foreseen for the years 2030 and 2050 according to the European Commission's green deal [49]. The increase in the share of energy produced from green and renewable sources leads to a reduction of the environmental impact on most midpoint indicators (i.e., climate change). However, these energy sources are not favourable in absolutely all midpoint indicators. The impact of some clean energy sources on land use (solar energy, wind energy, biodiesel....) is better known [299], [300]. Also, in the case of human toxicity potential, the electricity produced from wind energy (sharing about 30% of power generation in 2030 and 47% in 2050) has higher environmental impact than electricity produced from gas, for instance [301].

TRANSPORT STAGE

The equilibrium distance beyond which it is more advisable (from an environmental point of view) to dry the product and transport it in powder form than to transport it dissolved in liquid (in a liquid state) has been calculated to be about: 100 km if we assume drying stage powered with the European electricity mix of 2017; 56 km with the European electricity mix of 2030; and 36 km with the European electricity mix of 2050. For travel distances larger than those km, it is better to dry.

The study has been repeated for the endpoint indicators, which include all the midpoint indicators. The distances obtained are: 80.87 km for Damage to Human health and 85.88 km for Damage to Ecosystems with the European electricity mix of 2017; 45.28 km for Damage to Human health, and 48.09 km for Damage to Ecosystems with the European electricity mix of 2030; and 29.11 km for Damage to Human health and 30.91 km for Damage to Ecosystems with the European electricity mix of 2050.

The Resource availability endpoint indicator does not depend on the transport environmental impacts and, therefore, resulted better for the non-drying stage scenario at any distance.

6.5.   CONCLUSIONS

This study works out the life cycle environmental impacts of a new synthesis for CAZN crystals, the HMMS [145], [210], [280], and compares it with the most competitive alternative, the HTS [277].

The results show that extracting and processing the ZnO are the most relevant stages for both HMMS and HTS to shape the LCA results of CAZN productions.

HMMS presented better environmental performance for a cradle-to-gate study with a FU of 1 kg of CAZN only for some indicators (fossil depletion, freshwater consumption, freshwater eutrophication, carcinogenic human toxicity, ionizing radiation, marine eutrophication, ozone formation, ozone depletion, and terrestrial acidification) with similar results between HTS and HMMS in the rest of the indicators assessed. Even though, as reported throughout the paper, we have found that, with a FU depending only on the total mass produced in a cradle-to-gate study, we fail to consider relevant aspects of both processes, which have a direct impact on both the economic model of the system (residence time) and the performance of the final product (particle size). This is a very important point to bear in mind both in the case of this paper and in any LCA that seeks to compare different chemical processes delivering intermediate products. HMMS environmental impacts are clearly lower when these aspects are considered. This conclusion has been validated in the main scenario, after applying the normalization factors of the FU, as well as in the 7 alternative scenarios analysed.

Sensitivity analysis of the electricity mix help projecting the LCA results for the European electricity mix in 2030 and 2050, for which HMMS is performing better for all the environmental impacts.

Finally, the best transport strategy for both processes consists in not drying the final product if the CAZN crystals are to be used quite close to the production facility. For longer transport distances, it is advisable to dry the crystals to decrease the environmental emissions of the transport stage.

This paper has presented a simpler, greener, and faster route to obtain CAZN crystals. The fact that it is a continuous process, foresees a possible scale-up to pilot or industrial scale. In fact, the HMMS process is currently in the process of being scaled up and optimised by the company that provided the experiments for this paper. This could revolutionise their manufacture and their application in energy storage using zinc batteries.

Based on the 6th Assessment Report by IPCC published recently [302], the electrification in the world will increase, and it will be crucial to create a new and less environmentally harmful technology for energy storage capacities. This will improve the flexibility of the electricity grids, involve more renewable energy in the electricity production system, and create the possibility for involvement of electrical vehicles. Future research by the authors will be based on the development of ex-ante LCA for production of specific energy storage products that will use the proposed technological process.

7. WOOD CHIPS COMPONENTS SEPARATION WITH A NEW MECHANOCHEMICAL PROCESS COMPARED TO CHEMICAL DEPOLYMERIZATION: A TECHNICAL, ECONOMIC AND ENVIRONMENTAL COMPARISON

7.1. ABSTRACT

This article evaluates two processes – the wet milling and the chemical depolymerization for the end of life of wood waste – in terms of environmental performance (ex-ante life cycle assessment), energy balance, and economic analysis of the operating costs. Cellulose, hemicellulose, and lignin are essential components with numerous applications. The study provides valuable insights for industry stakeholders, policymakers, and researchers of the wet milling process, which is scarcely reported in literature.

The chemical depolymerization process is discontinuous and more energy-intensive, while the wet milling process is a continuous reaction demanding milder conditions and shorter times. However, the milling process requires a pre-treatment to reduce the wood chip size.

Economic analysis shows that the chemical depolymerization process has lower operational costs when considering the average European electricity price in 2019. This is a result of the price differences between steam and electricity. For lower electricity prices such as in France, or using utility-scale solar PV, the wet milling process has lower operational costs. The wet milling process also outperforms the chemical depolymerization process in most environmental indicators, such as global warming potential, particularly when using green electricity technologies.

Keywords: Cellulose; Economic analysis; Life cycle assessment; Wet milling; Lignin; Wood chips
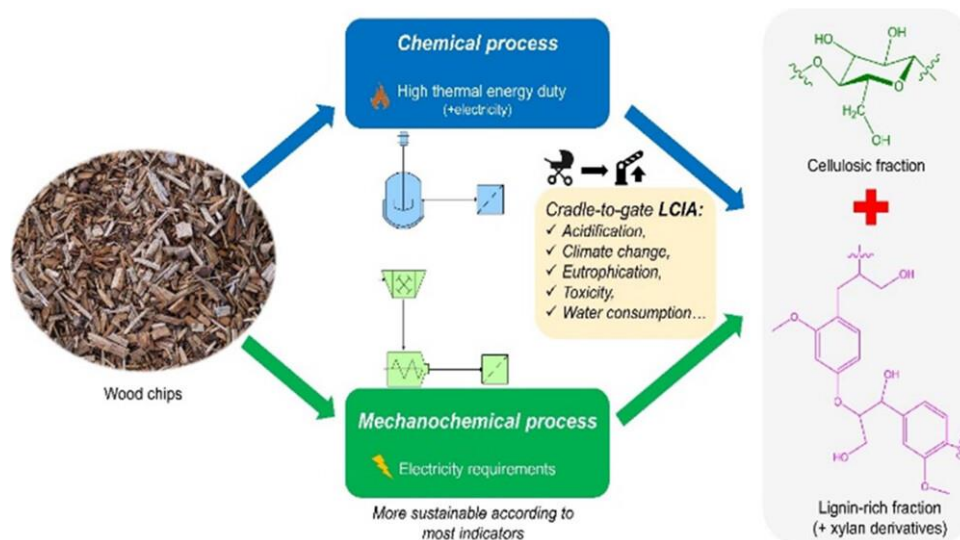
Figure 7-1 Graphical abstract of the LCA on different routes for cellulose extraction from wood chips

7.1. INTRODUCTION

Wood fibers are complex, hierarchically structured natural materials that are mainly constituted by cellulose, hemicellulose, and lignin [303], [304]. As each constituent has a chemical function, these are not homogeneously distributed in lignocellulosic fibers. Concretely, the outer cell wall layers, particularly the middle lamella, are mainly composed of lignin (60 – 70 wt%) and hemicellulose (20 wt%), while the cellulose content ranges from 10 to 20 wt%, on average [305]. The inner layers, namely the primary and the secondary walls, are much richer in hemicellulose and cellulose [305]. Amorphous constituents at the outer layers of fibers enable the binding between the different fibers in the lignocellulosic biomass, which leads to this hierarchically organized structure [306]. Today, several methods are used to decompose this naturally assembled structure, encompassing mechanical, thermomechanical, chemical, and combined approaches [307]. The choice of separation technique depends on the purpose.

For instance, cellulosic pulps are currently used in several sectors, papermaking being the most demanding, and their production usually implies the removal of lignin in several stages, such as cooking, fibrillation, and/or bleaching [308], [309]. On a smaller scale, cellulose is used for higher value-added products; such is the case of cellophane or rayon, or additives for different sectors, namely, cosmetics, paints, biomedicine, and the food industry [310], [311], [312]. Cellulose is also used in the textile sector, and besides the traditional usage of cotton, recent research keeps unveiling its potential for sustainable and functional fabrics [313]. Moreover, the potential of cellulose and hemicellulose for producing second- and third-generation biofuels (particularly bioethanol) should be highlighted [314]. The market for lignin-based products is still smaller than

that of cellulose, but they have been proven effective for fertilizing, sand-fixing, as bioactive compounds, and as adhesives, among other possibilities [315], [316], [317].

The need for increasing the sustainability of industrial operations for papermaking, lignin extraction, or any other purpose implies processing wood fibers, initiated development of greener processes, where the reduction of energy and decrease in consumption of chemicals is pursued. Wet milling is a process of chemical reactions induced by mechanochemical action which can usually be operated at room or moderate temperatures. These processes attracted attention because of its advantages compared with traditional processes such as chemical depolymerization process (CDP) in terms of energy savings, process intensification, and higher productivity [134], [137], [318]. However, there is limited understanding of the mechanochemical processes because they are usually conducted in closed devices, which are often regarded as black boxes [319]. Polymer mechanochemistry has been a topic of great interest over the last years, dealing with organic solvents reactions and operating with dissolved polymers [320]. On the other hand, the solid mechanochemistry of polymeric materials lacks generality, mainly because in the case of thermoplastic polymers, they absorb most of the mechanical energy for melting. In this sense, the mechanochemistry of wood-based biopolymers, such as the case of cellulose and hemicellulose/lignin, is of great industrial relevance [318].

The main advantage of applying mechanochemical or wet milling processes (WMP) to lignocellulosic materials is the increase of the available surface of fibers (due to size reduction effects) while providing the action of chemical reagents [4]. This operation can be conducted in several devices, such as ball mills (planetary, or vibrator), attritors, grinders, or high-pressure and ultrasonic homogenizers, but also in continuous flow millers and extruders [318]. Each equipment will impart specific forces over the lignocellulosic biomass, leading to different process efficiency and product characteristics.

In the present work, we propose a novel method for wood waste treatment and fiber separation. The WMP is evaluated by means of an ex-ante LCA and economic analysis of the operating costs, and compared to an extraction process, the CDP that was previously reported by Shuai et al. [317].

Ex-ante LCAs are used to inform decision-making during the early stages of product development or technology innovation, helping stakeholders understand potential environmental consequences and identify opportunities for improvement. In an ex-ante LCA, researchers estimate the environmental impacts based on available data, assumptions, and models related to the future implementation of the product or process under study. As it deals with future scenarios, results are estimative and uncertainties may be higher compared to retrospective LCAs, which assess existing products or processes. Nevertheless, ex-ante LCAs can

provide valuable insights for decision-makers, enabling them to make informed choices about the development and adoption of new technologies or processes with a focus on sustainability [321], [322].

Even though some articles regarding the use of mechanochemistry or wet milling as an example of avoiding other environmentally intensive processes have been recently published [139], [154], [323], [324], the scientific literature is scarce of LCAs of these processes. A comprehensive literature review of research articles performing LCA of fiber separation methods of wood chips by WMP or CDP was conducted using a rigorous search methodology by strings:

- (lca OR "life cycle assess*" OR "life cycle analy*" OR lci OR "Life cycle*") AND (cellulose OR lignin OR hemicellulose) AND (mechanochem* OR mechano-chem*)

- (lca OR "life cycle assess*" OR "life cycle analy*" OR lci OR "Life cycle*") AND (cellulose OR lignin OR hemicellulose) AND "chemical depolymeri*"

The search was conducted in Web of Science and Scopus, one of the most extensive scientific databases. This search yielded only 9 results for the first string and 13 for the second string. Filtering for only research articles resulted in zero findings for both strings. This emphasizes the novelty and significance of the present paper.

7.2. PROCESS DESCRIPTION

CHEMICAL DEPOLYMERIZATION

The extraction stage of the process reported by Shuai et al. [317] operates in a batch reactor at a liquid:solid ratio of 4:1, using 6 mm diameter wood chips as a source of biomass. This operation takes place at 80 °C for 3 h under agitation, in an acidic medium, and in the presence of formaldehyde. At an industrial scale, the heating of the reactor is typically provided with low-pressure (LP) water steam, according to the operating conditions of the process. The last step consists of cake filtration that separates the solid from the liquid fraction. According to the authors, the liquid fraction mainly contains lignin and derivatives of xylan (often, the main constituent of hemicellulose), while the solid fraction is mainly composed of glucans (attributed to cellulose) and a small fraction of lignin [317]. Figure 7-2 provides a flow diagram of the CDP used as a base scenario for the present study.
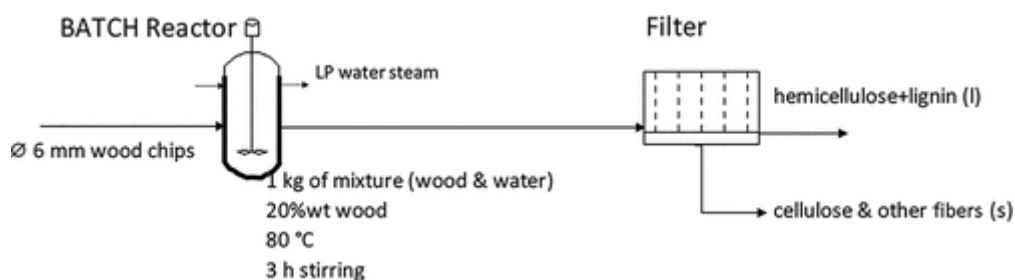
Figure 7-2 Flowchart of the chemical depolymerization for fiber extraction [317]

WET MILLING PROCESS

The WMP consists of a high-efficiency bead mill filled with ZrO_2 (stabilized with 20% CeO) micromilling beads, DYNO-MILL MULTI LAB, which is dedicated to continuous flow wet-milling application. It uses the collision of zirconia microbeads with the reactants as the main principle to activate the reaction. This mechanical energy only requires indirect use of electricity, which is supplied to the motor to motion the rotor and discs of the machine. The microbeads housed in the milling chamber represent, by volume relative to the total volume of the stationary chamber, from 55 to 70%. They are substantially spherical, with a mean diameter ranging from 0.5 to 1 mm and a Vickers hardness measured according to standard EN ISO 6507-1 typically ranging from 1000 to 1400 HV1 [210].

This process is still in its design phase, and the preliminary tests are performed at a laboratory scale provided the most optimal conditions presented in the paper. The WMP works at liquid:solid ratios between 50:1 and 10:1, operating at temperatures ranging from 25 to 80 °C for 5 to 60 min.

The consumption of reagents for a certain yield and the filtration step are considered equivalent to the CDP, even though it is believed that the lower concentration of wood might allow for an easier separation depending on the filtration technology and the properties of the cake [210].

The WMP (Figure 7-3), in the laboratory, requires a pretreatment with a hammer mill to reduce the size of the wood chips from 6 to 1 mm in diameter. The size reduction before the DYNO-MILL MULTI LAB helps to avoid accumulation and therefore gives a narrower residence time which can be assimilated to the liquid flow rate presented.
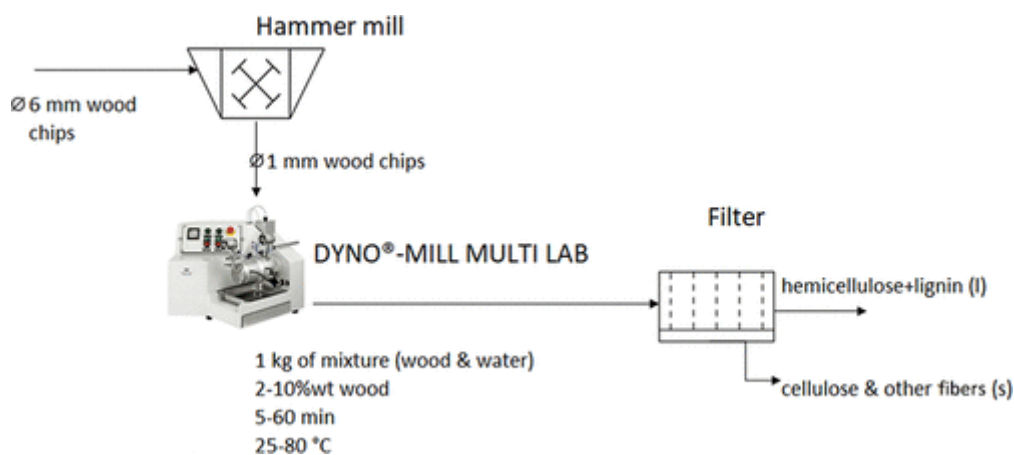
Figure 7-3 Flowchart of the WMP for fiber extraction

When scaling up the process to pilot or industrial scale, using a bigger mechanochemical reactor, possibly makes this pretreatment no longer necessary. However, as this hypothesis has not yet been fully validated and remains with a conservative approach, the energy demand in the hammer mill step is considered in the following sections. In addition, specific surface changes could also have an impact on the process efficiency.

The main issue to be addressed is whether the energy input of the pregrinding step and the lower wood concentration inside the reactor are outweighed by the advantages of the continuous WMP. These advantages include savings achieved by reducing the operating temperature and the residence time.

7.3. METHODOLOGY

LIFE CYCLE ASSESSMENT

LCA is a widely used systematic tool that estimates the environmental impacts of products or production processes considering every stage in their life cycle [38], [40], [41]. According to the framework presented in the ISO 14040 (2006) and ISO 14044 (2006), an LCA is regulated in four phases: goal and scope, LCI, LCIA, and interpretation.

The product sustainability solutions software Sphera LCA for experts (version 10.7.1.28) is being used to quantify the environmental impacts of WMP and CDP by making use of its extensive databases. The PEF has been selected to perform a multicriteria measurement of the environmental performance of the processes. This method has been developed by the European Commission (2018) as one of the building blocks of the flagship initiative of the Europe 2020 Strategy–"A Resource-Efficient Europe" [325]. The midpoint indicators were weighted following

the same methodology from the European Commission to evaluate their relevance for the study and which categories are more important in the evaluated system. Weighting in the LCA is a step in the interpretation phase that involves assigning relative importance or significance to different impact categories based on value choices or preferences. It helps to consolidate and simplify the results of an LCA, making it easier to compare alternatives and providing informed decision-making [326], [327].

The FU of the study is used as the basis of the calculation. In this article, the scope of the study is treating wood waste by breaking down wood chips into cellulose, hemicellulose, and lignin. Therefore, the FU is the quantity of wood waste introduced into the reactor. The fact that we are comparing a batch process (CDP) with a continuous process (WMP) makes selecting a consistent FU a challenge. Taking the direct CDP as a basis, its flow rate has been calculated at 0.0667 kg/h (0.2 kg of wood fed to a 3 h batch). In the case of the WMP, the technology operates with a different wood fraction and residence time than the CDP; in other words, with different flow rates. To ensure that the study was conducted under the same baseline, with the same wood input and output for both the WMP and CDP, an allocation factor was used. The allocation factor was based on the ratio between the flow rate of the CDP and the flow rate of each scenario of the WMP. This method of defining the flow rate has been discussed and implemented in various publications [2], [4], [73], [78], [84], [94]. Another example of a similar approach is the consideration of module D within the EN 15804:2012 + A2:2019 for the inclusion of information beyond the cradle-to-gate scope in construction product LCAs [10], [11]. These allocation factors are presented in Table 7-1 for 11 different scenarios defined from the operating ranges presented in the WMP section.

Table 7-1. Allocation factors applied to the wet milling process scenarios

Process	Scenario	Wood fraction flowrate, kg/h	Allocation factor*
CDP	Average values	0.067	1.0
WMP	1: Average values	0.10	0.67
WMP	2: Minimum wood fraction	0.040	1.7
WMP	3: Maximum wood fraction	0.20	0.33
WMP	4: Minimum reaction time	0.50	0.13
WMP	5: Maximum reaction time	0.050	1.3
WMP	6: Highest temperature	0.10	0.67
WMP	7: Room temperature	0.10	0.67
WMP	8: Maximum milling energy consumption	0.10	0.67
WMP	9: Minimum milling energy consumption	0.10	0.67
WMP	10: 0.77 mm final particle size	0.24	0.28
WMP	11: 3 mm final particle size	0.040	1.7

*Allocation factor = Chemical depolymerization process flowrate / Wet milling process flowrate (for each scenario)

The study's stages included in the LCA correspond to the production of the raw material, the thermal energy needed to heat the reaction mixture, and the mechanical energy needed to move, mix, mill, or stir the wood waste. This is a cradle-to-gate study. The boundaries of both processes are represented in Figure 7-4.
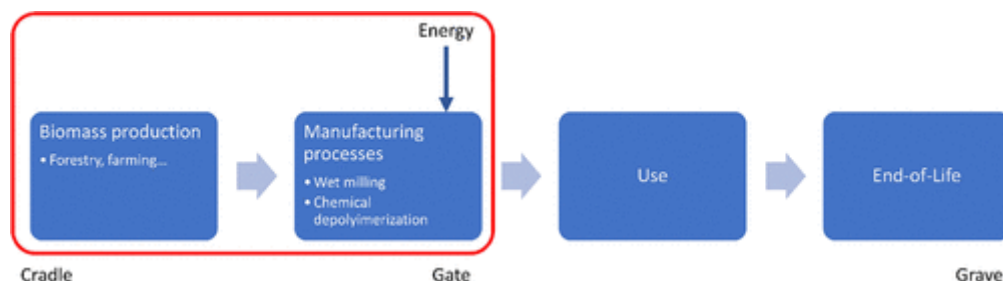
Figure 7-4 Boundaries of the LCA

The LCI is then utilized to gather data on raw materials, energy, and emissions and determine environmental impacts. We have presented the material flows and operating conditions for each scenario in Table 7-2, while Table 7-3 displays the energy flows.

Table 7-2. Material flows and operating conditions (1 kg mixture inside the reactor)

Process	Scenario	Water fraction (wt%)	Wood fraction (wt%)	Cp_{mix} (J/g ºC)	Time (h)	Tmax (ºC)
CDP	Average values	80.	20.	3.7	3.0	80.
WMP	1: Average values	95	5.0	4.1	0.50	52
WMP	2: Minimum wood fraction	98	2.0	4.2	0.50	52
WMP	3: Maximum wood fraction	90.	10.	4.0	0.50	52
WMP	4: Minimum reaction time	95	5.0	4.1	0.10	52
WMP	5: Maximum reaction time	95	5.0	4.1	1.0	52
WMP	6: Highest temperature	95	5.0	4.1	0.50	80.
WMP	7: Room temperature	95	5.0	4.1	0.50	25
WMP	8: Maximum milling energy consumption	95	5.0	4.1	0.50	52
WMP	9: Minimum milling energy consumption	95	5.0	4.1	0.50	52
WMP	10: 0.77 mm final particle size	88	12	3.9	0.50	52
WMP	11: 3 mm final particle size	98	20.	4.2	0.50	52

Scenarios 10 and 11 have been tested with higher wood fraction, which presented difficulties in operating the reactor and worse quality in the final product. Therefore, as presented in Figure 2, best operating conditions have been defined as a wood fraction between 2-10 wt%.

Table 7-3. Energy balance of the different scenarios under study

Process	Scenario	Energy used heating (kJ)	Energy used stirring/ milling (kJ)	Energy used in pre-treatment (kJ)	Energy consumption (kJ)
CDP	Average values	290.	1.76	-	292
WMP	1: Average values	99.0	24.0	52.5	184
WMP	2: Minimum wood fraction	250.	60.0	52.5	372
WMP	3: Maximum wood fraction	48.0	12.0	52.5	121
WMP	4: Minimum reaction time	20.0	4.80	52.5	85.2
WMP	5: Maximum reaction time	200.	48.0	52.5	308
WMP	6: Highest temperature	202	24.0	52.5	287
WMP	7: Room temperature	-	24.0	52.5	84.8
WMP	8: Maximum milling energy consumption	99.0	38.4	52.5	198
WMP	9: Minimum milling energy consumption	99.0	19.2	52.5	177
WMP	10: 0.77 mm final particle size	41.0	8.00	78.5	128
WMP	11: 3 mm final particle size	247	60.0	14.5	322

The results are projected with the present electricity mix in Europe (Figure 7-6), the projected electricity mix in 2030 (Figure 7-7), and the projected electricity mix in 2050 (Figure 7-8). These projections are derived from the "EU Reference Scenario 2016–Energy, Transport and GHG Emissions–Trends to 2050" published by the European Commission [132]. The environmental factors used for the different electricity mix are available in the Sphera professional databases [285].

MATERIAL

6-mm diameter lodgepole pine wood chips were previously dried in an oven at 50 °C to a moisture content of 11.7 wt % and stored in hermetic plastic bags at room temperature. This is the raw material used by Naimi et al. [328]. Naimi et al. [328] reported the energy consumption equations that are used in this study to estimate the energy balance of the pretreatment step of the WMP. For the sake of comparison, similar wood chips are assumed as raw materials in both WMP and CDP.

The WMP needs to reduce the size of the wood chips from 6 to 1 mm in diameter to be able to process the wood in the DYNO-MILL MULTI LAB. According to the material and required size, this may be performed using a hammer mill equipped with swing hammers and powered by a three-phase induction motor at a speed of 3490 rpm [328], [329].

Naimi et al. [328] designed a series of experiments for different screen sizes with different initial and final particle sizes [328]. Energy consumption during this operation was measured and reported as summarized in Table 7-4. For the present work, solely the values for the initial size of wood chips, 6 mm in diameter, and their final particle size, 1 mm, have been utilized. Specific energy was linearly interpolated from the values reported in Table 7-4 according to eq 7.1.

$$\text{Linear Interpolation (y)} = y_1 + \frac{(x-x_1)\times(y_2-y_1)}{(x_2-x_1)} \qquad \text{(eq. 7.1)}$$

where x_1 and y_1 are the first coordinates; x_2 and y_2 are the second coordinates; x is the point to perform the interpolation; y is the interpolated value.

Table 7-4. Specific energy of the grinding pre-treatment for the wet milling process. Data extracted from the paper published by Naimi et al. [328]

ID	d_{fp}[1] (mm)	d_{op}[2] (mm)	Specific energy (kWh/t)
1	9.7	1.1	16
2	9.7	0.77	25
3	3.6	1.1	8.2
4	3.6	0.77	19

[1]dfp: Diameter of the feed particles; [2]dop: Diameter of the output particles

The linear interpolation formula is the simplest method that is used for estimating the value of a function between any two known values. We calculated y = specific energy by interpolating rows 1 and 2 of Table 7-4, for x = diameter of the output particles = 1 mm. Then, we repeated the interpolation with rows 3 and 4 of Table 7-4. Finally, we interpolated both results for x = diameter of the fed particles = 6 mm.

Based on eq. 7.1 and the interpolated data from Table 7-4, we assume 14.57 kW h/t (52,454 J/kg) as the average energy consumption of the pretreatment in the hammer mill.

ENERGY BALANCE

The energy consumption of the rest of the equipment was estimated with the advanced process calculations published by Piccinno et al. [110]. The energy input in the CDP is therefore the sum of the thermodynamic equations for stirring and heating energy, which includes the energy needed to reach the reaction temperature and the energy needed to compensate for the heat loss. The energy input for the WMP is the energy associated with the specifications of a hydro-micromilling reactor, which is 8–16 kW h/t. The energy input is consistent with the range provided by Piccinno et al. [110] for a ball miller. As mentioned in Grinding Set-Up, the filtration step has been considered equivalent for both processes, and thus, it is excluded from the comparative analysis.

ECONOMIC ANALYSIS OF THE OPERATING COSTS

Regarding the economic comparison, raw material costs for treating 0.0667 kg/h of wood waste are the same for both processes, and therefore, they have been excluded from the comparative analysis. Therefore, the point is to evaluate if the pretreatment will reduce the particle size before the mechanochemical reactor is viable despite increasing the operational costs. This might be the case because of the expected savings in the reaction step compared to those of the CDP.

Most recent data at the time of performing the study was used in the analysis. Low-pressure steam price of 4.44€/100 kW h according to Turton et al. [330] without credit for power has been assumed for the supply of heating energy in both processes. To compare the importance of electricity prices on process costs and the variability of current energy markets, three different scenarios have been considered in a sensitivity analysis. The electricity prices which have been used are:

- 21.59€/100 kW h, the average electricity price in Europe in 2019 according to Eurostat [331]
- 17.65€/100 kW h, the average electricity price in France in 2019 [332]
- 5.98€/100 kW h, corresponding to the electricity costs from utility-scale solar photovoltaics (PV) in 2019, according to the International Renewable Energy Agency (IRENA) report from the year 2020 [333]

ENERGY BALANCE

The overall energy demand, along with the energy demand for heating, stirring, or milling, and the pretreatment (if any) of the CDP and the different scenarios of the WMPs are presented in Table 7-3.

Therefore, CDP is more energy-intensive in 8 of the 11 scenarios studied. This is due to the high energy demand for heating the mixture to 80 °C and keeping this temperature for 3 h. According to the operating conditions (80 °C), this heat is typically supplied with LP water steam (on an industrial scale). On the other hand, the WMP has a higher electricity demand for grinding and milling the wood. The main challenge of the WMP relies on the optimization of the wood fraction introduced in the reactor, as inferred from the results of scenario 2. The key to this process is to take advantage of its lower operating temperature and residence time, as we can learn from the results of scenarios 4 and 7. Finally, results from scenarios 10 and 11 indicate that it is advisable to spend more energy reducing size in the pretreatment than in the reaction itself. The energy requirements for the pretreatment step of the WMP have been plotted in Figure 7-5 to evaluate its tendency. As can be seen, the increase in the energy demand is exponentially correlated to the reduction of the particle size.
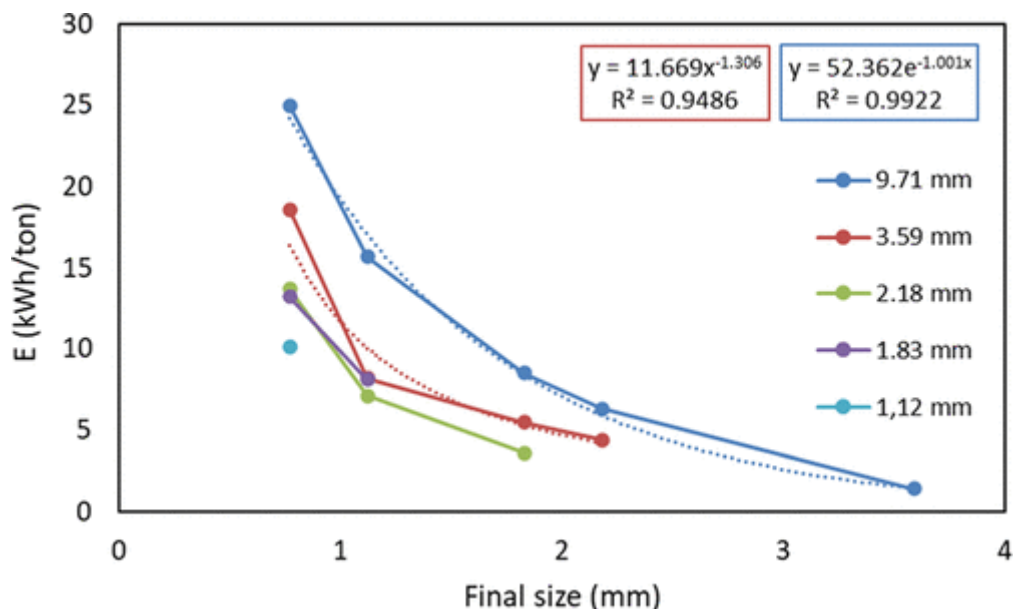
Figure 7-5 Energy demand depending on final particle size [328]

The energy consumption is used to determine the operational cost of the processes. This was calculated for three different alternatives. Table 7-5 presents the operational costs for a European average electricity price in 2019, Table 7-6 presents the operational costs for a French average electricity price in 2019, and Table 7-7 uses the electricity costs from utility-scale solar PV.

Table 7-5. Economic balance for European average electricity price, 2019

Process	Scenario	LP water steam cost (€/3000h)	European electricity price (€/3000h)	Total cost (€/3000h)
CDP	Average values	10.7	0.320	11.0
WMP	1: Average values	3.62	15.3	18.9
WMP	2: Minimum wood fraction	9.22	21.7	30.9
WMP	3: Maximum wood fraction	1.76	13.1	14.9
WMP	4: Minimum reaction time	0.720	11.8	12.5
WMP	5: Maximum reaction time	7.32	19.6	26.9
WMP	6: Highest temperature	7.40	15.3	22.7
WMP	7: Room temperature	-	15.3	15.3
WMP	8: Maximum milling energy consumption	3.62	17.8	21.5
WMP	9: Minimum milling energy consumption	3.62	14.4	18.0
WMP	10: 0.77 mm final particle size	1.51	15.6	17.1
WMP	2: Minimum wood fraction	9.06	13.4	22.5

Table 7-6. Economic balance for French average electricity price, 2019

Process	Scenario	French electricity price (€/3000h)	Total cost (€/3000h)
CDP	Average values	0.260	10.9
WMP	1: Average values	12.5	16.1
WMP	2: Minimum wood fraction	17.8	27.0
WMP	3: Maximum wood fraction	10.7	12.5
WMP	4: Minimum reaction time	9.64	10.4
WMP	5: Maximum reaction time	16.0	23.3
WMP	6: Highest temperature	12.5	19.9
WMP	7: Room temperature	12.5	12.5
WMP	8: Maximum milling energy	14.6	18.2
WMP	9: Minimum milling energy	11.8	15.4
WMP	10: 0.77 mm final particle size	12.7	14.3
WMP	11: 3 mm final particle size	11.0	20.0

Table 7-7. Economic balance for utility-scale solar PV average electricity price, 2019

Process	Scenario	Utility-scale solar PV electricity price (€/3000h)	Total cost (€/3000h)
CDP	Average values	0.09000	10.7
WMP	1: Average values	4.23	7.85
WMP	2: Minimum wood fraction	6.02	15.2
WMP	3: Maximum wood fraction	3.63	5.39
WMP	4: Minimum reaction time	3.27	3.99
WMP	5: Maximum reaction time	5.42	12.7
WMP	6: Highest temperature	4.23	11.6
WMP	7: Room temperature	4.23	4.23
WMP	8: Maximum milling energy	4.94	8.57
WMP	9: Minimum milling energy	3.99	7.61
WMP	10: 0.77 mm final particle size	4.31	5.82
WMP	11: 3 mm final particle size	3.72	12.8

The CDP requires thermal energy, besides reagents such as formaldehyde and HCl, whose consumption is assumed not to impart a difference in the scope of the study. However, it can be relevant to study energy usage associated with distillation to purify the final product if required [334]. This is expected to be supplied with LP water steam, which is significantly more inexpensive than the electricity required by the WMP. Assuming as electricity price the average electricity price in Europe in 2019 (Table 7-5), even though the CDP is more energy-intensive, its operational costs are lower than those of the WMP. When considering the electricity price in France in 2019 (Table 7-6), which is 18% lower, we already observe one scenario (4: minimum reaction time) that is favourable for the WMP. Finally, regarding the electricity costs from utility-scale solar PV, 7 of the 11 scenarios are already favourable for the WMP. Those are 1: average values, 3: maximum wood fraction, 4: minimum reaction time, 7: room temperature reaction, 8: maximum milling energy consumption, 9: minimum milling energy consumption, and 10:0.77 mm final particle size.

It is important to consider the direction in which the electricity mix is moving in the different countries of the European Union [49], [132] and the increasingly strict restrictions on the use of fossil fuels and polluting processes. This could make the WMP even more interesting in the coming years.

Moreover, after comparing the deviation of the operational cost for each scenario, we can determine which variables have a greater effect on the final cost to prioritize them in the optimization stage. Table 7-8 presents the variability of the operational cost, depending on the configuration of different operating conditions. The maximum, minimum, and average value of the result in each operating condition has been categorized as worst, average, or best,

depending on the operational costs generated in each case. Those operating conditions with higher variability are those that should be prioritized as it means that they have a greater influence on operating costs. In addition, the "best" column indicates the costs associated with the best economic scenario for each variable, with the minimum reaction time (scenario 4) being the most inexpensive process setup.

Table 7-8. Variability of operational costs depending on each factor

Operating conditions	WORSE (€/3000h)	BEST (€/3000h)	Variability (%)
Wood fraction	30.9	14.9	85%
Reaction time	26.9	12.5	76%
Temperature	22.6	15.3	39%
Particle size	22.5	17.1	29%
Milling energy	21.5	18.0	18%

ENVIRONMENTAL ANALYSIS

Figure 7-6 to Figure 7-8 gather the environmental midpoint impacts according to the PEF methodology. The calculation has been made for the 11 scenarios using the results of the CDP as a basis for a percentage. Those impacts higher than 100% mean that they are categories in which the CDP has better environmental performance (color-coded in red). On the other hand, those midpoint indicators with less than 100% indicate that they are categories in which the WMP is environmentally better (color-coded in green). In the case of an environmental impact equal in both processes, this has been identified in yellow.

Considering that most of the indicators are colored green, this anticipates that the WMP is environmentally better in most cases. Both processes demand similar amounts of raw material. So on, the advantage of WMP is mainly due to the use of electricity instead of steam.

Scenarios	1 (%)	2 (%)	3 (%)	4 (%)	5 (%)	6 (%)	7 (%)	8 (%)	9 (%)	10 (%)	11 (%)
Acidification	44	44	62	38	53	48	41	47	44	73	35
Climate Change	57	92	53	36	84	77	38	61	56	60	77
Ecotoxicity, freshwater	82	90	95	71	95	83	81	90	79	111	65
Eutrophication, freshwater	125	140	123	117	136	126	125	131	123	130	120
Eutrophication, marine	38	37	56	33	46	43	34	40	38	66	31
Eutrophication, terrestrial	38	36	55	32	45	42	33	39	37	65	30
Human toxicity, cancer	57	75	63	42	75	68	46	61	55	72	61
Human toxicity, non-cancer	60	79	64	45	78	72	48	63	58	72	66
Ionizing radiation	196	252	194	158	242	196	195	223	186	229	163
Land Use	27	13	52	27	28	27	27	28	27	62	12
Ozone depletion	190	243	188	154	234	190	189	216	181	221	160
Particulate matter	30	19	53	28	32	31	29	31	30	63	17
Photochemical ozone formation	37	35	55	31	44	42	33	39	36	64	30
Resource use, fossils	61	99	55	38	90	82	40	65	59	61	83
Resource use, mineral & metals	120	166	116	91	156	132	108	134	115	134	119
Water use	120	125	114	119	121	120	120	121	120	113	123

Figure 7-6 LCIA of the WMP over the Impacts of the Chemical Process (Present Time)

Scenarios	1 (%)	2 (%)	3 (%)	4 (%)	5 (%)	6 (%)	7 (%)	8 (%)	9 (%)	10 (%)	11 (%)
Acidification	42	41	60	36	50	46	38	45	41	70	33
Climate Change	52	84	49	32	77	72	32	55	51	55	73
Ecotoxicity, freshwater	75	80	89	65	86	76	74	81	72	103	59
Eutrophication, freshwater	140	161	136	128	156	141	140	149	137	144	133
Eutrophication, marine	36	34	54	31	43	41	32	38	36	64	29
Eutrophication, terrestrial	36	33	53	30	42	40	31	37	35	63	28
Human toxicity, cancer	61	80	66	45	80	72	50	65	59	76	65
Human toxicity, non-cancer	58	77	63	44	76	71	47	62	57	71	65
Ionizing radiation	117	140	127	97	141	117	116	131	112	149	94
Land Use	29	15	53	28	30	29	29	29	28	64	13
Ozone depletion	226	296	219	183	280	226	226	258	215	258	192
Particulate matter	30	19	53	28	32	31	29	30	30	63	17
Photochemical ozone formation	35	32	53	30	42	40	31	36	35	62	28
Resource use, fossils	56	93	51	34	84	78	35	60	55	57	80
Resource use, mineral & metals	144	201	137	110	187	156	133	163	138	159	140
Water use	120	124	114	119	121	120	120	120	119	112	123

Figure 7-7 LCIA of the WMP over the Impacts of the Chemical Process (2030)

Scenarios	1 (%)	2 (%)	3 (%)	4 (%)	5 (%)	6 (%)	7 (%)	8 (%)	9 (%)	10 (%)	11 (%)
Acidification	40	38	58	34	47	44	36	42	39	68	31
Climate Change	46	75	44	27	69	66	26	48	45	48	67
Ecotoxicity, freshwater	70	73	85	62	80	71	69	75	68	99	55
Eutrophication, freshwater	151	177	144	136	168	151	150	161	147	155	143
Eutrophication, marine	35	32	53	30	41	39	31	36	35	62	28
Eutrophication, terrestrial	34	31	52	29	40	39	30	35	34	61	27
Human toxicity, cancer	65	87	70	49	86	77	54	71	63	81	69
Human toxicity, non-cancer	57	76	62	44	75	69	46	61	56	70	64
Ionizing radiation	104	122	116	88	125	105	104	116	100	136	83
Land Use	29	16	54	28	31	29	29	30	29	64	14
Ozone depletion	332	447	309	264	417	332	332	383	315	365	285
Particulate matter	29	18	52	28	31	30	28	30	29	62	16
Photochemical ozone formation	34	30	52	29	40	38	29	35	33	61	27
Resource use, fossils	51	86	47	31	78	73	31	55	50	52	75
Resource use, mineral & metals	196	274	181	150	253	208	185	224	187	212	185
Water use	119	124	113	118	120	119	119	120	119	112	122

Figure 7-8 LCIA of the WMP over the Impacts of the Chemical Process (2030)

Most of the midpoint indicators of the WMP get better results with the implementation of green electricity technologies. This is due to the higher use of electricity compared to the CDP. Nevertheless, some indicators such as water use, use of minerals (zirconia), and ozone depletion remain better in the CDP.

To evaluate the significance of the midpoint indicators that perform worse in the WMP, these indicators have been weighted using the European Commission's Environmental Footprint 3.0 methodology [335]. Among these indicators, water use, mineral use, and ozone depletion have relatively low weights, while land use and fossil resource use are more significant. This is probably due to the intensive use of energy for heating or milling the mixture and due to the use of wood as a raw material. In this case, while the carbon emissions of the wood chips are primarily biogenic, land use takes a significant role. The calculated weights for all the midpoint indicators can be found in Table 7-9.

Table 7-9. Midpoint indicators weighting

Midpoint indicator	Weights *	
	CDP	WMP
Acidification	0.0030%	0.0040%
Climate Change	3.1%	4.1%
Ecotoxicity, freshwater	1.3%	2.2%
Eutrophication, freshwater	ca. 0%	ca. 0%
Eutrophication, marine	0.0010%	0.0010%
Eutrophication, terrestrial	0.011%	0.010%
Human toxicity, cancer	ca. 0%	ca. 0%
Human toxicity, non-cancer	ca. 0%	ca. 0%
Ionizing radiation	0.058%	0.15%
Land Use	75%	61%
Ozone depletion	ca. 0%	ca. 0%
Particulate matter	ca. 0%	ca. 0%
Photochemical ozone formation	0.0030%	0.0030%
Resource use, fossils	20.%	29%
Resource use, mineral & metals	ca. 0%	ca. 0%
Water use	1.1%	3.9%

*It should be emphasized that the weights assigned to the midpoint indicators are independent within each process. These weights serve to evaluate the relative importance of the different indicators within each process, rather than comparing the weight of a single indicator between the two processes [35], [36].

7.5. CONCLUSIONS

An ex-ante LCA has validated that the WMP exhibits superior environmental performance for most of the studied midpoint indicators compared to the CDP. Furthermore, its prospects

appear more promising, largely due to its reliance on mechanical energy rather than thermal energy. However, some midpoint indicators demonstrate better results for the CDP process, although these indicators are less important in the weighting assessment. By maximizing the wood fraction introduced into the reactor and recycling the water used in the process, even better results for the water use indicator can be achieved.

Regarding the economic analysis and, considering the possibility that, in a scaling up of the process, the requirements of the pretreatment with the hammer mill would not be so demanding, it can be anticipated that the results obtained correspond to a lower limit of the energy costs of the WMP, which still needs further validation at industrial scale. Consequently, the WMP is a promising innovative alternative that, depending on the electricity price, may be performed at lower operational costs than direct chemical extraction.

As presented in the article, shifting to mechanochemical systems can provide numerous benefits, such as improving efficiency and selectivity, reducing the need for solvents and thermal energy, or enhancing scalability. The fact that the WMP requires electricity, and the CDP requires thermal energy highlights the environmental potential of the WMP. With the greenification of electricity, as forecasted in the European Green Deal, this assessment might increase.

However, further experimentation is required to determine how promising the mechanochemical approach is compared to an acidic formaldehyde-assisted CDP with no mechanical fractionation. In future research, we aim to optimize the scenarios that demonstrate superior performance in terms of energy consumption, economic evaluation, and LCA. In addition, by scaling these scenarios up to pilot or industrial levels, we can obtain more realistic data, thereby enabling more comprehensive assessments and insights.

8. SUSTAINABILITY OF CELLULOSE MICRO-/NANOFIBERS: A COMPARATIVE LIFE CYCLE ASSESSMENT OF PATHWAY TECHNOLOGIES

8.1. ABSTRACT

Cellulose micro- and nanofibers (CMNFs) are commonly regarded as "greener" than petro-based materials. The high energy input that their production still demands, along with the use of chemicals or heat in some pretreatments, asks for a critical view. This paper attempts a life cycle assessment of CMNFs produced from bleached hardwood kraft pulp via three different pre-treatments before mechanical homogenization. First, a fully mechanical route, based on a Valley beating pre-treatment. Second, an enzymatic route, based on endoglucanases and requiring certain temperature (~50°C). Third, a TEMPO-mediated oxidation route, considering not only the impact of the chemical treatment itself but also the production of TEMPO from ammonia and acetone. The main output of the study is that both, mechanical and TEMPO-mediated oxidation routes, present lower impacts than the enzymatic pre-treatment. Although the mechanical route presents slightly milder contributions to climate change, acidification, eutrophication, and other indicators, saying that TEMPO-mediated oxidation is environmentally unfeasible should be put under question. After all, and despite being disregarded in most assessment publications up to date, it is the only well-known way to selectively oxidize primary hydroxyl groups and thus producing kinds of CMNFs that are unthinkable by other ways.

Keywords: Enzymatic hydrolysis; Life cycle assessment; Mechanical treatment; Nanocellulose; Pulp and paper; TEMPO-oxidized Cellulose Nanofibrils

Highlights

- Following three different pre-treatments defines environmental priorities
- It is proposed that functional unit should be normalized for each process
- TEMPO-mediated oxidation is greener than the enzymatic process for CNF production

- A fully mechanical process showed the least environmental impact for CNF production
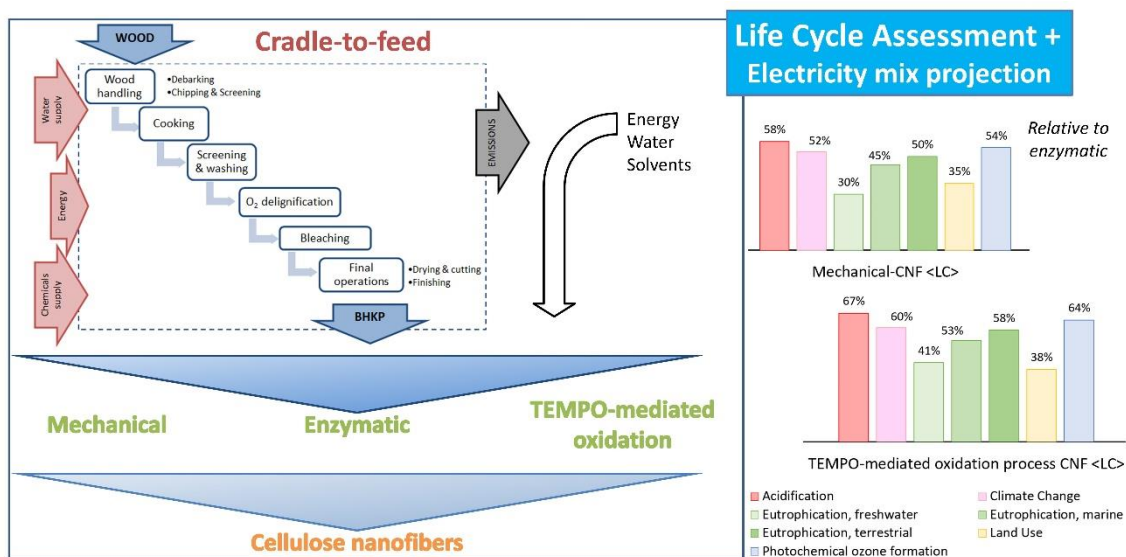
Figure 8-1 Graphical abstract of the LCA on different routes for cellulose nanofibers production

8.2. INTRODUCTION

The concept nanocellulose is generally found as an umbrella term encompassing, besides cellulose nanocrystals and bacterial cellulose, both micro- and nanofibrillated cellulose. These cellulose micro- and nanofibers (CMNFs) are increasing their presence in different application fields:

- Paper and packaging products, where nanocellulose is used as filler, coating component, barrier properties enhancer or plastic films replacement [336], [337], [338], [339], [340]

- High-end technological applications, such as adhesives, hierarchical materials, electroacoustic devices, sensors and electronics [339], [341], [342], [343]

- Low-weight engineering applications, such as green composites, interior automotive applications, foams, ultra-filtrating membranes, and insulation materials [341], [344]

- Biomedical applications, as a carrier for drug delivery or as a scaffold for tissue engineering [341], [344], [345], [346]

It is worth to mention that mineral fillers, in addition to organic ones, are also used to improve properties of materials in different applications [347].

The nanocellulose market value worldwide in 2020 was estimated in 297 million US dollars and it is forecasted to grow up to 783 million US dollars by 2025 [348]. CMNFs will compete in the

future with cement as reinforcement material, with plastic in packaging markets, with synthetic binders in coating processes, with cotton in hygiene and absorbent products, with carbon fiber in reinforced composites used in automotive and aerospace components, with fiberglass in insulation applications, with silica aerogels in the oil and gas industry, and with other future novel applications [349]. The environmental performance of CMNFs may be an issue when deciding to use them in all these possible markets and with massive productions.

Several production methods to transform the individual cellulosic fibers into microfibrils or nanofibrils have been introduced, although they are mainly optimized at the laboratory level [350]. Generally speaking, a nanofibrillation stage, often by means of a high-pressure homogenizer (HPH), follows a certain pre-treatment, which is key to avoid clogging and excessive energy consumption. The most popular pre-treatments are mechanical beating [344], [351], [352], acid hydrolysis [344], [352], [353], enzymatic hydrolysis [344], [353], carboxymethylation [250], [354], and oxidation of hydroxyl groups. The latter is usually mediated by sodium periodate or by 2,2,6,6-tetramethyl-1-piperidinyloxy radical (TEMPO) [355], [356], [357], [358].

However, there are few publications on the environmental assessment of these production processes. Previous LCA studies on CMNFs comprise:

- Comparison of carboxymethylation and enzymatic hydrolysiss before nanofibrillation [354], [359]
- Comparison of carboxymethylation and TEMPO-mediated oxidation [360]
- Energy consumption assessment of a nanocellulose production method that combined mechanical shear stress with hot-compressed water treatment [361]
- Cellulose nanowhiskers based on mechanical and chemical acid treatments [362]
- Lignocellulosic nanofibers to increase the number of times that paper can be recycled in a circular economy [363]

Tangentially to the topic, an attributional LCA of woodchip production [364], the influence of time in life cycle assessments [365], a sustainability study (techno-economic and environmental analysis) of paper pulp reinforced with CMNF [366], a cradle-to-gate LCA of the Eucalyptus globulus short-rotation plantations and chips extraction in Chile [367], the assessment of delignification as a pre-treatment for a nanolignin synthesis process [368], and a case study of peracetic acid bleaching of wood pulp [369] are worthy of mention.

In most of these publications, chemical pre-treatment routes presented higher environmental impacts. Nonetheless, due to lack of data, numerous assumptions were considered. Comparing

chemical modifications (substitution, oxidation) to mechanical treatments or depolymerizations is not a straightforward task, as the very nature of the material produced is different. Furthermore, TEMPO-mediated oxidation is often disregarded for its unfeasibility, despite being actually carried out by major companies like Nippon Paper, at least for high value-added products [370]. By generating carboxylate groups, which are easily hydrated and carry negatively charge, chemical pre-treatments promote steric and electrostatic repulsion between like-charged cellulose chains. This allows for higher yields during the second stage of the process (nanofibrillation), being able to attain samples consisting entirely of cellulose nanofibers (CNFs). For the sake of simplicity and comparison, and in a possible inaccurate but common decision, we will henceforth refer to all fibrillated products in this work as "CNFs", even if they contain microfibers.

This paper deals with an LCA of CNFs produced via three different pre-treatments before the nanofibrils are separated by mechanical homogenization:

1) Fully mechanical route based on a refining pre-treatment

2) Enzymatic route

3) TEMPO-mediated oxidation route

The FU serves as the reference basis of the calculation related with the environmental impacts of the system under study. However, when a cradle to gate LCA is being performed for chemical processes, there might be variables which affect to the function of the final product. Although this takes place outside of the cradle to gate boundaries, these issues should be accounted as valuable additional information. Specially when we are comparing among different alternatives. The preliminary FU was 1 kg of nanocellulose on dry basis. Nonetheless, since the different pre-treatments end up resulting in products of different properties, the FU is then corrected (normalized) on basis of the final properties promoted by these nanofibrillated cellulose products. In the case of this work, it is assumed that the intended use is the reinforcement of paper. For instance, similar methodology is applied in module D within the EN 15804:2012+A2:2019 for construction products LCA [10], [11].

8.3. METHODOLOGY AND MATERIALS

PRIMARY AND SECONDARY DATA

Primary data consist of the independent variables chosen along the experimentation, plus measurements of certain dependent variables. The former include the amounts of reagents and water spent in each case, the temperature, the extent of mechanical refining, the stirrers' settings, and the pressure and number of cycles. Their values chosen for modelling are not arbitrary, but resulting from the experience of the group and optimization studies [371], [372], [373].

The source of cellulose was a bleached hardwood kraft pulp (BHKP), taken as a commercial product from a pulp mill. The materials and procedures to treat this cellulosic pulp by mechanical beating, enzymatic hydrolysis and TEMPO-mediated oxidation can be found in detail in the above-cited works. Briefly, reagents for the enzymatic process included Novozym 476 from Novozymes A/S (Denmark) and a buffer consisting of acetic acid and sodium acetate, both from Sigma-Aldrich (Barcelona, Spain). The oxidation, on the other hand, required TEMPO, NaBr, NaClO, and NaOH, which were likewise obtained from Sigma-Aldrich. Needless to say, the fully mechanical process is chemical-free. Distilled water was consistently used in all cases. The fibrillation process was carried out in a HPH, NS1001L PANDA 2 K-GEA, following all the pre-treatments. It run at 2% consistency, 3 times at 300 bar and 7 times at 600 bar.

The main dependent variable to be measured was energy consumption. It was determined using a device from Circutor (Barcelona, Spain), CVM-C10, which gives values of the power and current intensity required from the electrical grid. Considering previous works performed within the research group [363], [374], [375], CNFs from BHKP were used for paper reinforcement. Handsheets obtained with a dosage of 3 wt.% of CNFs in bulk and 97 wt.% BHKP were mechanically characterized for tensile strength, as ISO 1924-2 describes [376].

Scanning Electron Microscopy (SEM) was conducted to qualitatively assess the morphology of the obtained CNFs. The sample preparation consisted on the formation of a nanopaper by means of solvent casting, pouring a suspension of CNFs at 0.2 wt% consistency in a petri dish and drying it at low temperature. The resulting nanopapers were released from the petri dish and observed in a Hitachi S-3000 microscope, working at 7 kV; samples were previously covered with carbon via sputtering.

All the secondary data consulted has been checked under the criteria defined in the pedigree matrix (reliability, completeness, temporal correlation, geographical correlation and

technological correlation) [120], [121]. Further references can be found below, depending on the specific process to be modelled.

LCA is a holistic and comprehensive methodology for assessing the environmental loads and potential impacts of a product, process, or service in each stage of its life cycle, from the extraction of the materials to the management of the disposed product after its use (cradle-to-grave). Following the ISO standards 14040:2006 [35] and 14044:2006 [36], its results were structured within the following stepwise procedure: goal and scope, LCI, LCIA, and interpretation of results. Out of the possible environmental performance indicators [38], [39], [41], we decided to evaluate Global Warming Potential, Acidification Potential, Nutrient Enrichment, Photochemical Ozone Formation, Primary Energy Consumption and Use of Agricultural Land.

The LCA was developed also following the product environmental footprint (PEF) methodology, which has been fostered by the European Commission [377], [378]. Environmental impacts were calculated using the GaBi Professional Software (version 10.6.1.35) for LCA. This was performed by:

1) Considering the impacts of the input material flows
2) Adding the impacts of the output material flows post-treatments
3) Adding the thermal energy demand
4) Adding the mechanical energy demand

8.4. MODELLING

GENERALITIES

Each of the pre-treatments considered (mechanical, enzymatic, and oxidative) may include more than one unit operation. Unit operations may be inexcusable, as in the case of washing to remove the excessive amounts of salts generated along TEMPO-mediated oxidation, or seemingly optional but experimentally proven necessary to reach the desired outcome, as in the refining step to ease enzymatic hydrolysis.

In all these possible routes, the pulp and the micro- and nanofibers from it are computed on a dry basis, even though they are moist at all times. The impact of electricity consumption corresponds to the European average electricity mix from the year 2018 according to GaBi

databases [285]. Energy balances considered these electricity inputs. Mass balances were performed choosing 1 kg BHKP as the calculation basis and neglecting the loss of cellulosic materials by filtration.

PULP PRODUCTION

The overall impact of the CNF production depends both on the feedstock (cellulose fiber) and on what technology we apply to this feedstock. Various publications deal with CNFs produced from different feedstocks, including in the spectrum of wood, cane, straw, leaf, bast, fruit and seed [379]. Because of this wide range of raw materials and previous experience by the authors, we have decided to use one specific stock: eucalyptus wood treated using kraft pulping and bleaching. Kraft pulp production is the dominant pulp-making process due to the high quality of the resulting printing paper, liner, fluting, and other products whose strength is of utmost importance. A pulp mill comprises highly energy-intensive procedures such as debarking, chip refining, cooking, washing, screening, bleaching, further washing, and drying. A simplified diagram of the production process of BHKP is shown in Figure 8-2.
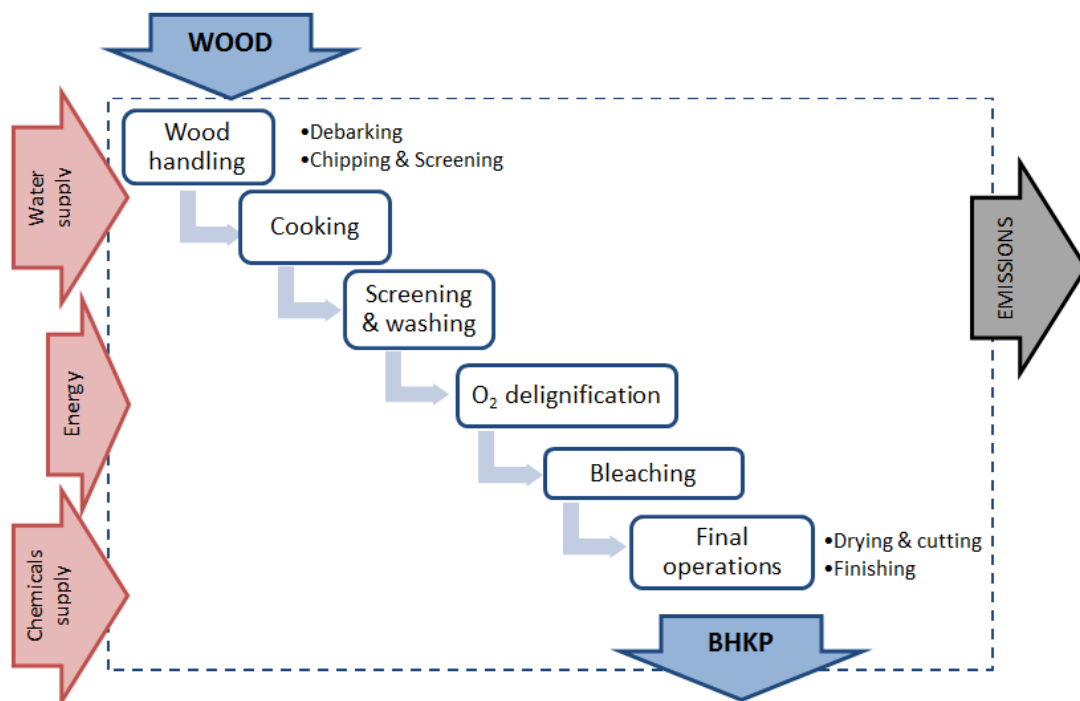
Figure 8-2 Flowchart of an industrial process to obtain bleached hardwood kraft pulp (BHKP)

The best available techniques to produce pulp, paper and board were established under the EU Commission Implementing Decision of 26 September 2014. The first paper analyzing the environmental life cycle effects of the European pulp and paper industry was published in 1996 [380]. Probably, the most relevant reference using the feedstock selected in this study is the one on environmental impact assessment of total chlorine-free pulp from Eucalyptus globulus in Spain [381]. It concludes that inherent activities related to BHKP such as cooking, bleaching and wastewater treatment are not always the main contributors to the environmental impact of the process. Upstream chemical and fuel productions, besides on-site energy production systems, seem to be important contributors to different impact categories [382], [383], [384].

The LCA for the BHKP production feedstock has been calculated with the available GaBi databases [285]. It includes activities such as forest management, sawmilling, logs storing, debarking, and milling. Given that this pulping process is common to all CNFs considered, the uncertainty associated to this process affects the three pre-treatments.

MECHANICAL PRE-TREATMENT

The mechanical production process of cellulose nanofibers involved a refining process in a Valley pile as the main step. 1 kg dry BHKP was diluted to 1.57 % consistency, following TAPPI standard T200 [385], to proceed with refining for 3 hours. When the refining process stopped, the sample was filtrated to a consistency of 20%, not requiring washing. An amount of this sample was taken, diluted with tap water at 2% consistency, and homogenized to obtain a dilute suspension of micro- and nanofibers. Figure 8-3 shows the different steps followed in the mechanical production process of CNFs. In the absence of chemicals, the most relevant environmental impacts lie in water consumption, although much of it is recycled, and electricity inputs.

Functional unit: 1 kg of CNF

Electricity   **Water**

67.71 L   3.204 kW·h   0.039 kW·h   45.9 L

| Dry BHKP | 1.0 kg | Suspension in water at 1.57% consistency | | Refining process in Valley pile | | Vacuum filtration (20%) | | Dilution (2%) |

63.39 L

19.448 kW·h

Homogenization
3 runs at 300 bars
7 runs at 600 bars

	1 kg CNF-mec
Energy (kW·h)	22.69
Water (L)	50.22

CNF-mec
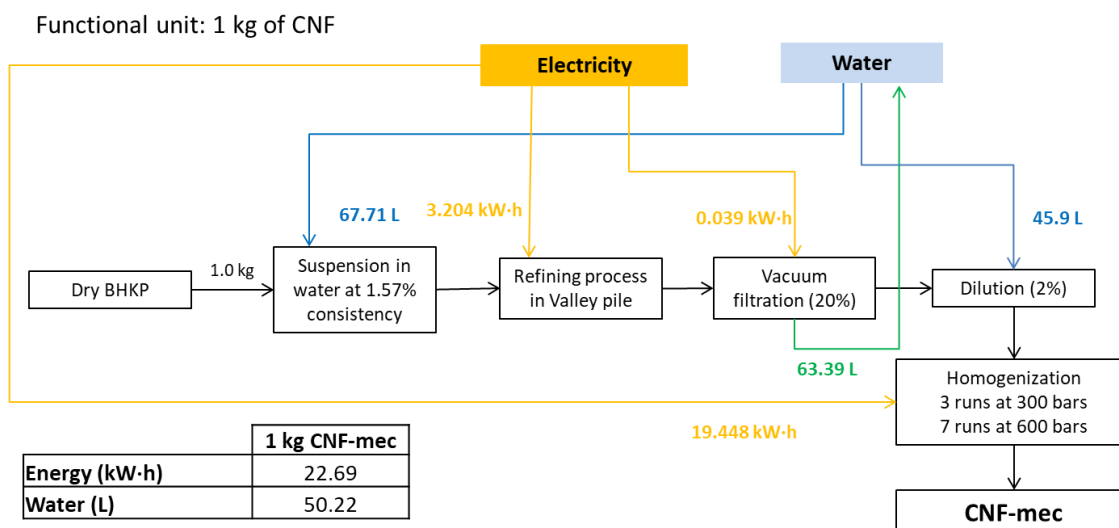
Figure 8-3 Process diagram of the production of CNFs by a mechanical pre-treatment

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ENZYMATIC HYDROLYSIS

Owing to the high specificity of enzymes, generally speaking, their main objectives are to increase the quality of product, yield, while reducing energy and chemicals consumption, hopefully converting traditional processes into "green" ones [386]. Nonetheless, the extent to which the crystallinity of cellulose prevents the access of glucanases to the acetal bonds, the failure to hydrolyze them at room temperature, the need for pH control, and the slow rate of reaction compel us to adopt a critical attitude in this case. Moreover, the enzymatic process to obtain CNFs involves some additional steps in comparison with the mechanical one. The schematic process of the enzymatic experiments is presented in Figure 8-4.
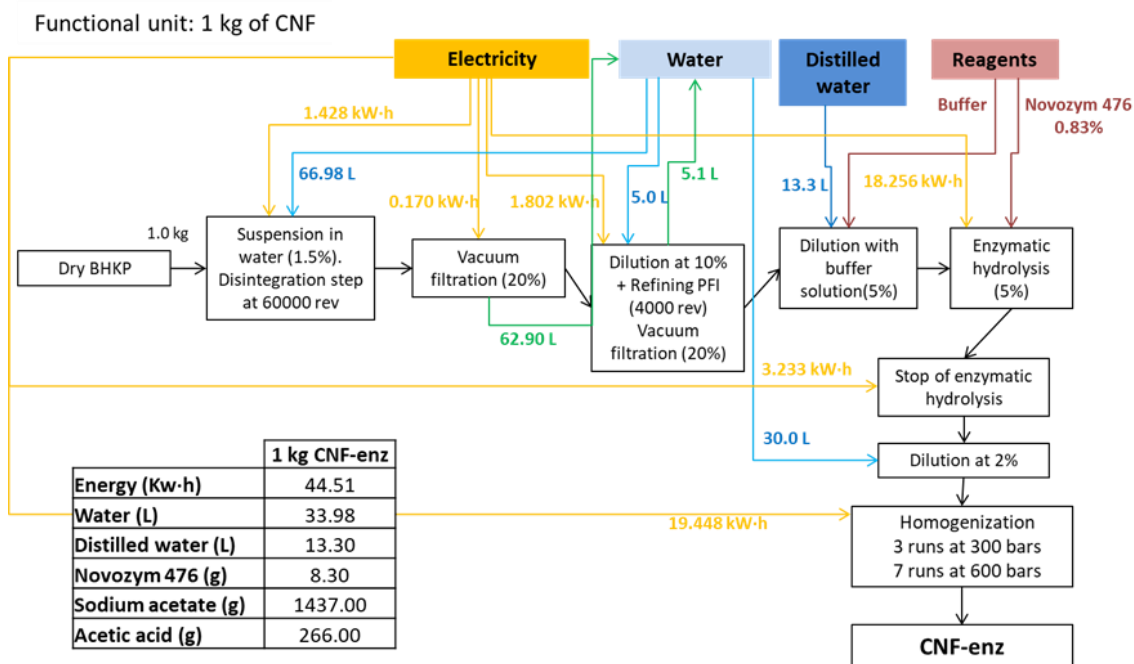
Figure 8-4 Process diagram of the production of CNFs by enzymatic pre-treatment

1 kg dry BHKP was diluted to 1.5% consistency and disintegrated for 20 minutes at 3000 rpm (60000 revs.), following the ISO 5263-1 standard [387]. When the disintegration process stopped, the sample was filtrated to 20% consistency and, after that, an additional dilution at 10% consistency was done on the pulp sample, which was next refined in a PFI mill to 4000 revs. The enzymatic hydrolysis needs to maintain a pH of around 5. To comply with this, the next dilution step to 5% consistency was done with a buffer solution, where 95.8 g of sodium acetate and 16.92 mL of acetic acid per liter of solution were added. After the buffer dilution, the enzymatic hydrolysis was performed by supplying Novozym at a concentration of 0.83%. During the enzymatic treatment, the temperature was maintained at 50 °C, and the contact time was 180 minutes.

Novozym 476 is a mono-component endoglucanase with a cellulose-binding domain which preferably degrades cellulose in the unordered regions. This glucanase is produced from a genetically modified strain of Aspergillus fungus. The cellulolytic activity is 5000 endocellulose units per gram of material, i.e., 5000 ECU/g [388]. The product was delivered in aqueous suspension. After the reaction, an increase in bath temperature to 80 °C deactivated the enzyme. The product was diluted to 2% consistency and homogenized to obtain micro- and nanofibers.

From the literature [386], [389], [390], [391], we extracted valuable information about environmental impacts of Novozym 476. An exhaustive study used five types of enzymes in a cradle-to-gate impact assessment [386], covering primary energy consumption (88 MJ/kg of the

120

final product), global warming (7.53 kg CO_2 eq/kg of the final product), acidification (23.77 g SO_2 eq/kg of the final product), nutrient enrichment (21.6 g PO_4 eq/kg of the final product), photochemical ozone formation (2.71 g ethylene eq/kg of the final product) and use of agricultural land (3.46 m^2·year/kg of the final product).

The acetic acid is assumed to be produced from methanol by low-pressure carbonylation. This is the most commonly used process in the industry [392]. In turn, sodium acetate is a sodium salt produced by the neutralization of acetic acid with sodium hydroxide. The environmental factors of such neutralization were obtained with a proxy from GaBi Professional databases [285], assumed to be like the neutralization of citric acid with sodium hydroxide to produce trisodium citrate (similar pKa, similar enthalpy of neutralization). Using proxies is a common way of LCA simplification, whenever actual data is not found [393].

TEMPO-MEDIATED OXIDATION

This chemical process to obtain CNF is based on the use of the stable radical TEMPO, as a catalytic reagent in combination with other oxidative reagents such as sodium hypochlorite, as Figure 8-5 shows. The oxidizing agent directly (and selectively) acting on primary hydroxyl groups is TEMPO itself, but it is regenerated in the process thanks to the parallel oxidation of Br– (co-catalyst), together with the reduction of ClO– (spent oxidizer). The process diagram is presented in Figure 8-6.
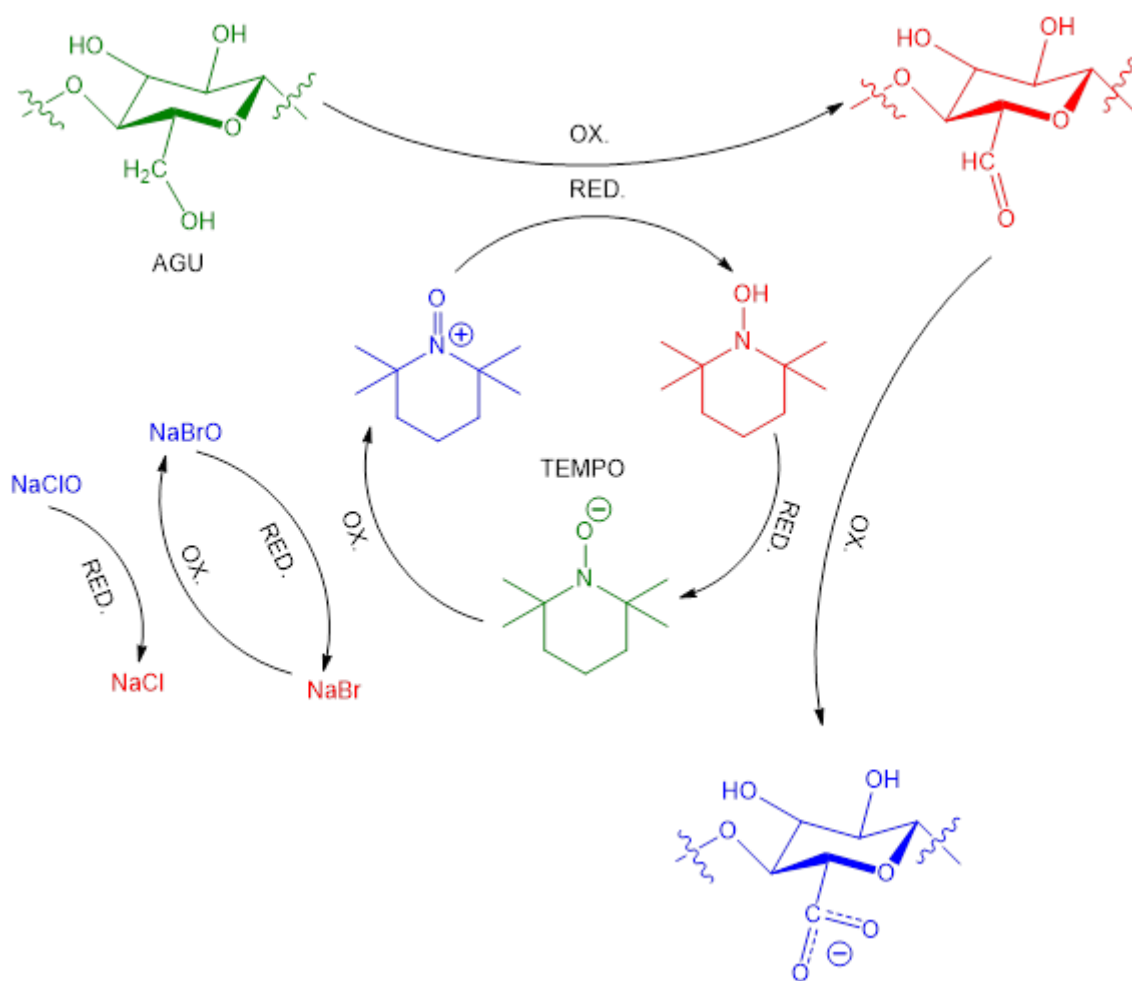
Figure 8-5 Oxidation of the primary hydroxyl groups of cellulose, at pH 10, considering a TEMPO/NaBr/NaClO system [394]

	1 kg CNF-TEMPO
Energy (Kw·h)	33.99
Water (L)	183.31
Distilled water (L)	94.88
NaBr (g)	100.00
TEMPO (g)	16.00
NaClO (g)	745.00
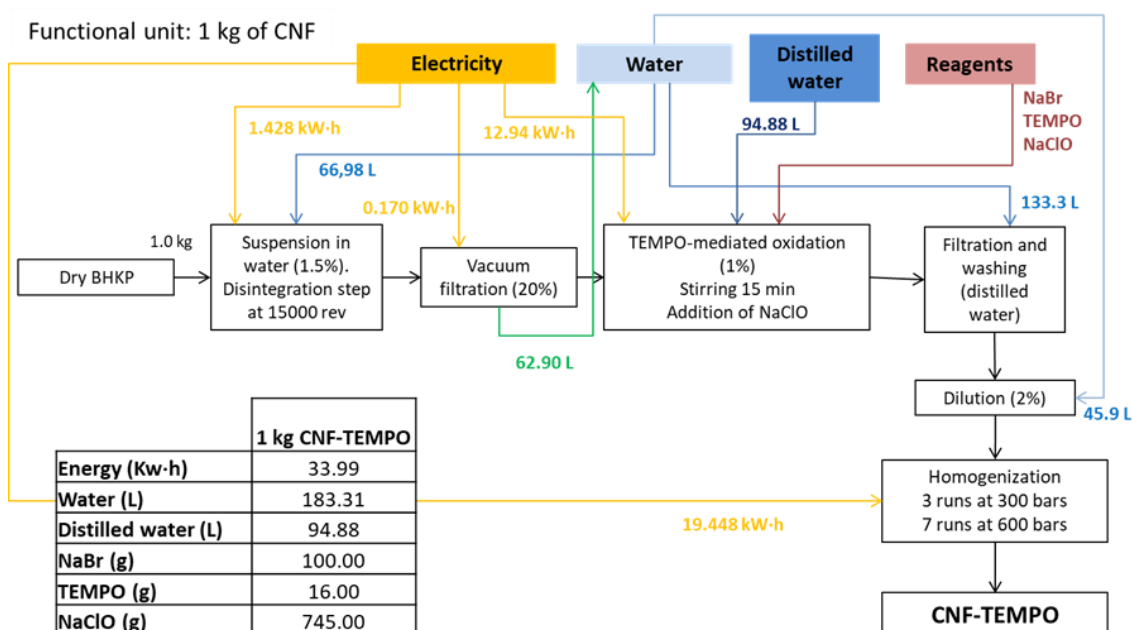
Figure 8-6 Process diagram of the TEMPO-mediated oxidation for the production of CNFs

The catalytic oxidation process also started with 1 kg BHKP and was suspended in tap water at a consistency of 1.5%, before disintegrating to 15000 revs. The subsequent reaction was performed at 1% consistency and under alkaline conditions [395]. In a typical oxidation experiment, cellulose fibers were dispersed in distilled water containing TEMPO (0.016 g per g of pulp) and NaBr (0.1 g per g of pulp). The mixture was stirred for 15 min to assure good dispersion of all the substances. After this, a 15% NaClO solution was added dropwise to the slurry. The volume of NaClO is calculated so as to add 10 mmol per gram of cellulose. The pH was kept at 10 by the addition of 0.5 M NaOH. The increase of volume by effect of this addition was neglected. The oxidation finishes when the pH remained stable at 10. This is not included in the mass balance nor in Figure 8-6 because due to its low mass fraction compared to the other reagents, it is not significant to the LCA results. The oxidized pulp was then filtered and washed with distilled water five times. Finally, the fiber suspension was cooled at room temperature before going through mechanical treatment. Fibrillation of oxidized fibers was performed by pumping the fiber suspension at 2% consistency through the high-pressure homogenizer 3 times at 300 bars and 7 times at 600 bars of pressure.

There is only one reference in the literature that takes into account the TEMPO-mediated oxidation route in an LCA study [360], but they do not include the TEMPO reagent due to the limited information in the inventory databases. In the present paper, the impact of TEMPO production is considered.

Sodium hypochlorite is produced after reacting chlorine with a sodium hydroxide solution. Those are assumed to be produced from salt (NaCl) dissolved in water, purified, and fed to an electrolysis unit. For sodium bromide, we assumed a proxy by assimilating its environmental factors to those of sodium chloride.

MODELLING OF TEMPO PRODUCTION

TEMPO was discovered in 1960 [396] and is usually prepared by oxidation of 2,2,6,6-tetramethylpiperidine (TEMP) with hydrogen peroxide. The environmental data on the TEMPO production process is scarce, and the model we offer to consider its impact as part of the LCA relies on secondary data. Energy balances are estimated with an advanced calculation benchmark for industry equipment [110].

The modelled process starts from simple products that can be easily registered in databases (ammonia, acetone, zeolite catalysts, etc.). Direct condensation of acetone and ammonia

catalyzed by zeolites produces triacetonamine (TAA) or 4-oxo-TEMP, the precursor of TEMPO [397], as Figure 8-7 shows. The maximum yield of this reaction is 22.6% [398]. Better yields of TAA production (28.4%) may be obtained from fast pyrolysis of sewage sludge using acetone as an absorption solvent but this is still not implemented at the industrial level [399].
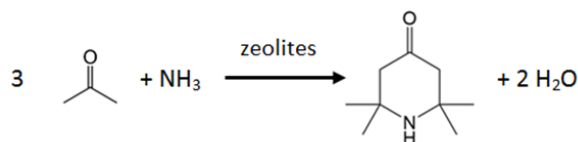
Figure 8-7 Condensation of acetone and ammonia catalysed by zeolites to produce triacetonamine (TAA)

The reaction runs as follows (see Figure 8-8): mixing 34.8 g of acetone with 4 g of ammonium nitrate, adding 0.5 g of zeolite (CaY), adding 3.1 mL of 28-30% aqueous ammonia. The mixture is stirred for 20 minutes. The temperature is kept between 20-25 °C. The best selectivity is obtained by combining a highly hydrophilic zeolite with a high acetone-ammonia feed ratio [397]. Reaction time is set at around 17 hours to reach a yield of 22.6% at room temperature. In the end, the relationship acetone-ammonia is 6:1. Once the reaction is finished, residual acetone is evaporated using a vacuum pump at room temperature, zeolite is filtered, and the product is washed 5 times with 60 mL of diethyl ether. The ether phase is dried with magnesium sulphate and filtered. Residual ether is evaporated, and the dry final product (TAA) is obtained.

The next step is to convert TAA using reduction with hydrazine hydrate towards an instable hydrazone, which is then cleaved in the presence of alkali into TEMPO and nitrogen [400]. For this purpose, molten TAA is mixed into a stirred vessel with hydrazine hydrate in a molar ratio of 1.5. The mixture is heated to 80-90 °C. The resulting hydrazone solution is transported to distillation bottoms at the base of a distillation column held at a temperature of 175 to 195 °C. These distillation bottoms comprise a high-boiling solvent (250 cm^3 or 279 g of triethylene glycol), paraffin oil (56.3 g) and an alkali metal hydroxide (42.1 g of KOH). The hydrazine is spontaneously cleaved under these conditions. In addition to the nitrogen released, a reaction mixture comprising TEMPO, water and hydrazine is distilled off. The condensation product formed two phases, which are separated. The organic phase contains 91% of TEMPO having >99% purity.

Different works have described techniques for the last step of oxidation of TEMP, using hydrogen peroxide-sodium tungstate systems [401], hydrogen peroxide in absence of tungstate [402], or electrochemical techniques [403]. Hydrogen peroxide is used as an oxidizing agent to synthesize TEMPO using a multi-necked flask, equipped with a propeller agitator, reflux condenser, dropping funnel and pH electrode. 28.25 g of TEMP are mixed with 46 mL of

methanol and 4.07 mg of MgCl$_2$·6H$_2$O, previously dissolved in 1 mL of water. TEMP, methanol, and the magnesium chloride solution are heated to 65 °C. Then, over 45 minutes, 45.3 g of a 30% aqueous H$_2$O$_2$ solution are added dropwise and stirred for 7 hours at 65° C. The evolution of the reaction can be monitored via gas chromatography analysis. To purify the TEMPO, 5 mL of 10% sulfuric acid is added, and the reaction mixture is extracted four times with 50 mL of cyclohexane. The cyclohexane is removed by distillation, and the final yield of this synthesis route is 85.5%.
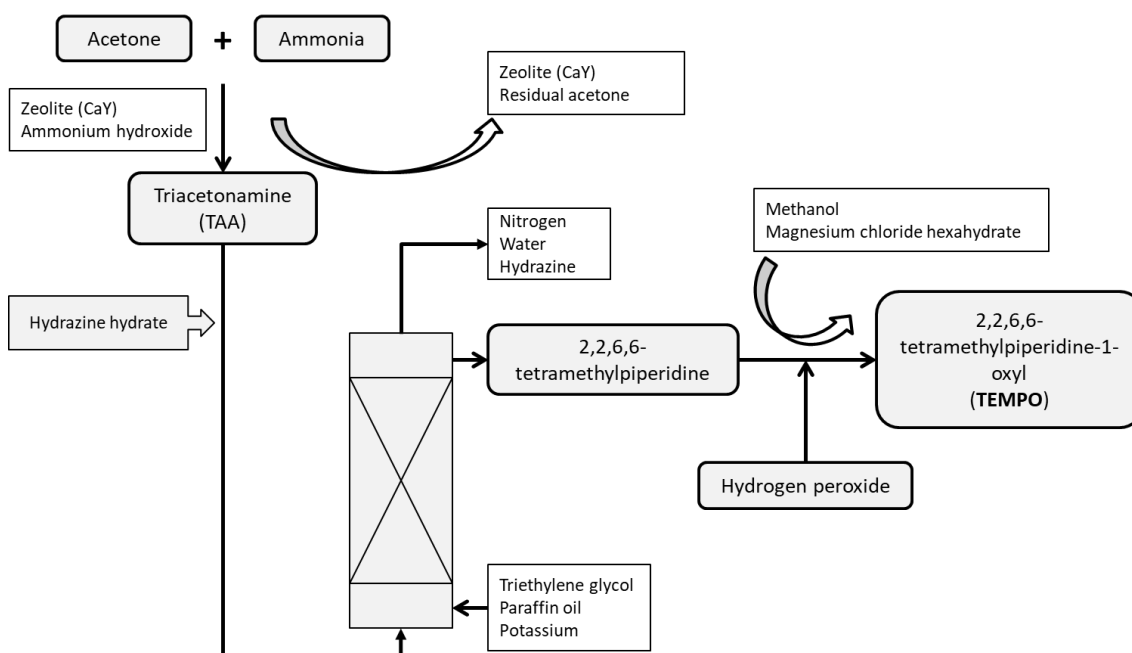
Figure 8-8 Process diagram of the TEMPO production route [397], [398], [399], [400], [401], [402], [403]

8.5. LIFE CYCLE ASSESSMENT

FUNCTIONAL UNIT AND SYSTEM BOUNDARIES

Since the three CNFs have different morphologies, their LCA values should not be compared directly. The energy consumptions might vary depending on their degrees of nano-fibrillation or conditions of mechanical treatment in water. However, there is no suitable standard method at present to accurately determine the degrees of nano-fibrillation of CNFs, and thus it is not possible to prepare CNFs with the same degrees of nano-fibrillation or the same CNF morphologies for comparison of their LCA values.

Therefore, the yield of fibrillation – that provides the mass fraction of nanosized objects in the CNF suspension – of each type of CNF (TEMPO-oxidized, enzymatic, and mechanical), and SEM images showing the morphological differences between them are presented in Figure 8-9.

Yield of fibrillation was determined by centrifuging a diluted CNF suspension (0.2 wt%). The nanofibrillated fraction, contained in the supernatant, was isolated from the non-nanofibrillated, which was assumed to get retained in the sediment. The recovered sediment was oven-dried until constant weight and referred to the initial dry mass, obtaining the non-nanofibrillated fraction. The nanofibrillated fraction was calculated by difference.
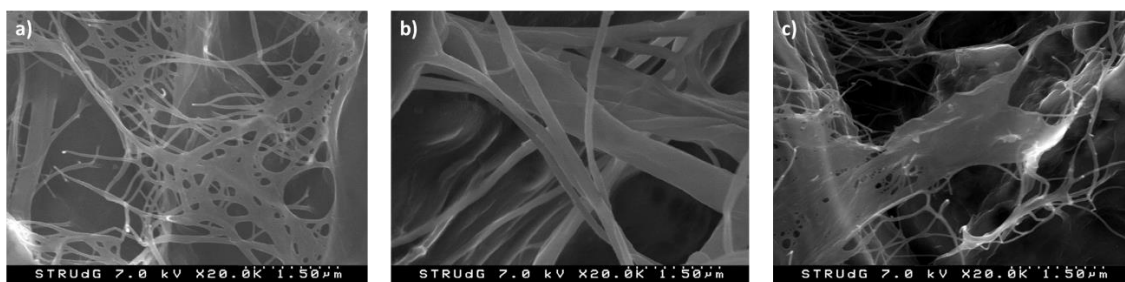
Figure 8-9 Morphological differences between: a) TEMPO-oxidized CNF (yield of fibrillation = >95%); b) Enzymatic CNF (yield of fibrillation = 39%); and c) Mechanical CNF (yield of fibrillation = 21%)

TEMPO-oxidized CNFs exhibited an entangled 3D-structured network of nano-sized fibrils. In addition, the surface of the obtained CNFs appeared to be smooth and without excessive surface fibrillation, which is attributed to the effect of carboxyl groups during fibrillation, which contributed to fiber disruption. In the case of enzymatically hydrolyzed CNFs, the surface also was found to be smooth and with no significant surface fibrillation, but diameters were considerably bigger than in the case of TEMPO-oxidized CNFs. Finally, in the case of mechanically obtained CNFs, the surface fibrillation of the CNFs became apparent, as well as their bigger size, with some fibers in the microscale, rather than in the nanoscale. The absence of functional groups that may contribute to fibrillation (as in the case of carboxyl groups) or the use of enzymes for shortening the cellulose chain, the effect of the high-pressure homogenizer was found to be much more aggressive, leading to a higher heterogeneity on the size distribution and, in addition, to a higher branching of the obtained CNFs.

The FU chosen is not centered solely on the amount of CNFs produced, given that the three pre-treatments considered result in products of different nature. To our judgment, it is sensible to define the FU with regards to their purpose. In the context of paper strengthening, by means of

bulk addition as described above, the following improvements in comparison with the no-CNFs-addition case:

- **TEMPO-oxidized CNFs**: 101% of tensile strength increase

- **Enzymatic CNFs**: 103% of tensile strength increase

- **Mechanical CNFs**: 71% of tensile strength increase

Taking into account that the range of tensile strength variations is linear up to additions of 6% CNFs [374], to achieve the same increases as the enzymatic route, in weight percentage, TEMPO-oxidized CNFs should be added at 3.06% and mechanical CNFs at 4.35%.

Therefore, the FU will be corrected to 1.02 kg of TEMPO-CNFs, 1.00 kg of enzymatic CNFs and 1.45 kg of mechanical CNFs. Consistently with this approach, these numbers would vary should the purpose of the nanocellulosic materials differ from paper strengthening.

The analysis includes the extraction of the raw materials, chemicals, and energy as well as the processing of CNFs following the three different routes, but it does not take into consideration the final use or disposal phase of the CNFs obtained (therefore, a cradle-to-gate scope is taken). Industrially, the requirement of high-pressure homogenization is usually avoided since it consumes a high amount of energy. However, we compare the processes in the laboratory conditions where this stage is used. Since we are considering the same conditions in the homogenization stage of all the pretreatments, this does not affect the LCA conclusions.

The end-of-life stage is not considered to be relevant for the study because CNF waste management would not depend on the technology used to produce it (Figure 8-10).
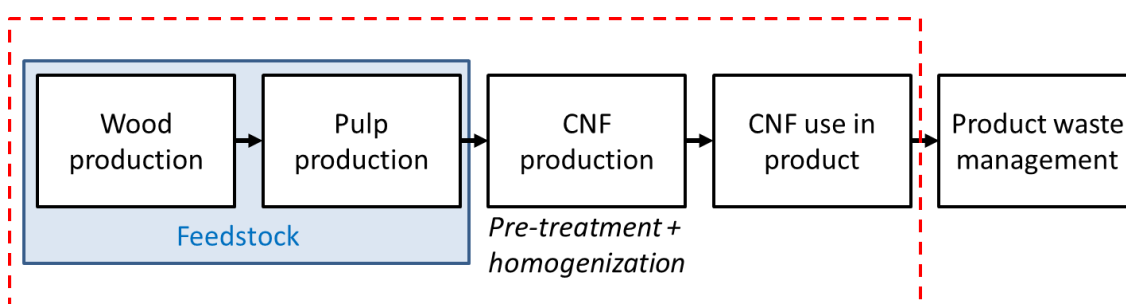
Figure 8-10 System boundaries of the study

LIFE CYCLE IMPACT ASSESSMENT OF THE THREE TECHNOLOGIES

Like most nanomaterials, the production of CNFs is, albeit rapidly evolving, still in an early stage of technological development, in which lab-scale processes with high consumption of energy

and materials are employed. When scaling to an industrial level, recycling, energy integration and further optimization stages are implemented. This material and energy reduction is estimated at 20% approximately, according to multiple publications [101], [110].

The LCIA is calculated from the LCIs of the processes depicted in Figure 8-3, Figure 8-4, Figure 8-6. The results show that the environmental impacts associated to the mechanical pre-treatment are slightly lower than the environmental impacts of the TEMPO-mediated oxidation pre-treatment. In turn, both the mechanical and the TEMPO-mediated oxidation pre-treatments have much lower impacts than the enzymatic pre-treatment for most of the PEF midpoint indicators. It can be pointed out that alternative enzymatic processes with high consistency are expected to exert a lower environmental impact that the one estimated in this work [404]. Nonetheless, the same can be said of other pre-treatments for nanofibrillation, including high-consistency oxidation, kneading or extrusion [405].

Figure 8-11 shows the results for some of the indicators assessed (acidification, climate change, eutrophication, land use and photochemical ozone formation), corresponding to the same environmental indicators evaluated in the above-cited Novozym 476 LCA [392]. This has been calculated as a percentage of the environmental impact of each process normalized to the highest impact value, corresponding in all cases to the enzymatic pre-treatment.
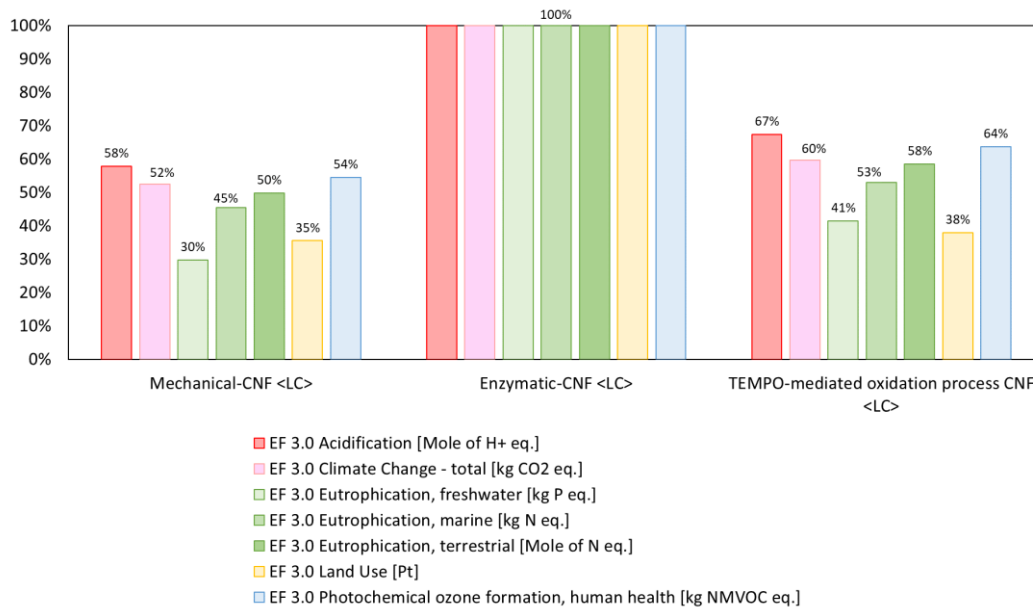
Figure 8-11 LCIA midpoint indicators (PEF) of the mechanical, enzymatic and TEMPO processes

The projection of the European electricity mix in the next decades (2030 and 2050) [290] does not present any change in the tendency presented in the results of the LCA. Figure 8-12 presents this projection, quantifying the environmental impact of each midpoint indicator as a percentage with respect to the highest impact value. Even though the state of affairs in the European Union at the time of finishing this study invites to disbelief, we could expect the same qualitative trend when comparing mechanical and oxidative pre-treatments to the enzymatic one. Considering that the three processes are fed with electricity as main energy source, they would be similarly affected by modifications in the electricity mix. Assuming an evolution of the electricity mix towards a greener mix, the impact associated with reagents and solvents will become more important. Which, in this sense, will be beneficial for the mechanical process.

a) mechanical-CNF process b) TEMPO-mediated oxidation; fw: freshwater; m: marine; t: terrestrial
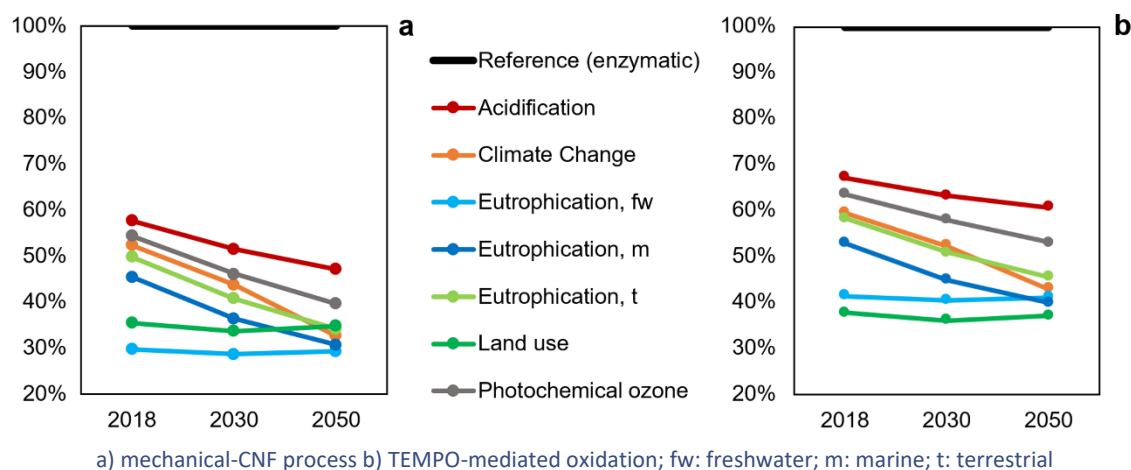
Figure 8-12 Environmental indicators projection according to the European electricity mix evolution (2018-2030-2050)

8.6.   CONCLUSIONS

The main finding of this life cycle assessment is that both mechanical and TEMPO-mediated oxidation routes, present lower impacts than the enzymatic pre-treatment. This confronts the truism or generalization that enzymatic processes are 'greener' alternatives to their chemical counterparts. Reasons for that are the need of a buffer solution for pH control, the temperature, and the time required (roughly, enzymatic > oxidative > mechanical). The conclusion stays the same when considering 1 kg CNFs as the FU and when correcting said FU on the basis of the required amount for a paper strengthening function. It is worth noting, however, that well-

established conditions at laboratory level were assumed in all cases, and that these conventional conditions may differ significantly from the optimal ones.

Mechanical processes require fewer resources, nominally water and electricity. However, the physical properties of the product are worse (e.g., tensile strength), which means that a larger amount of CNFs must be produced to achieve similar properties to the CNFs obtained with the other pre-treatments. For this specific purpose, the TEMPO-mediated oxidation route achieves a product that, in terms of the required addition in papermaking to obtain sheets of similar tensile strength, matches the one produced via the enzymatic route.

Therefore, these factors should be considered when deciding which production route is the most appropriate, and this decision will depend on the quality required for the intended application of the final product.

9. COMPARED LIFE CYCLE ASSESSMENT FOR NICOTINE EXTRACTION FROM TOBACCO LEAVES ACCORDING TO PROCESSES AND EXPERIMENTAL CONDITIONS AT LAB SCALE

9.1. ABSTRACT

Tobacco plants are grown worldwide by thousands of families who are financially dependent on the crop for cigarette production. The stricter tobacco laws force these producers to find alternatives to sell this product. In addition, in this regard, the European Union must look to develop its own greener processes giving at the same time independence from eastern countries. Nearly 50% of the current overall market for nicotine, which is being used, as a bioactive compound, comes from China. The present study compares the environmental life cycle impacts of different methods to extract nicotine from tobacco leaves (the maceration and the mechanochemical process). These have been compared with an ecoefficiency analysis in terms of environmental performance (with life cycle assessment methodology), financial performance (with an economic analysis of the operational costs) and assessing energy consumption as a transversal indicator. The maceration process would be more advisable in the case that energy supply is considered a limiting resource. Even though, this might be compensated using solar panels or other renewable energy sources.

In addition, the mechanochemical process achieves higher nicotine extraction rate (1.91wt%) than the maceration process (1.78wt%). After the complete evaluation, it has been concluded that the highest nicotine extraction rate of the mechanochemical process compensates for its higher energy consumption. Therefore, when considering the whole life-cycle, the mechanochemical process presents about 7% lower environmental impacts and slightly better (2%) economic balance than the maceration process.

Keywords: Economic analysis, Life cycle assessment (LCA), Mechanochemistry, Nicotine, Tobacco leaves

Highlights

- Mechanochemical process has a higher nicotine extraction rate (1.91wt%)

- The mechanochemical process is about 7% better in environmental performance

- Mechanochemical process consumes 2.21 times more electricity at lab scale

- The economic results are slightly better (2%) for the mechanochemical process

- Using forecasted electricity mixes has higher impact on the mechanochemical process
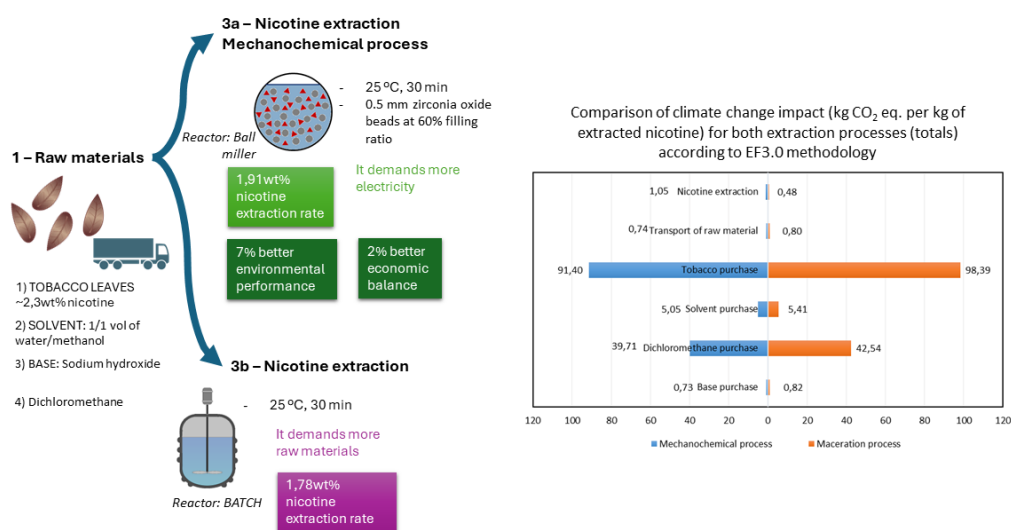
Figure 9-1 Graphical abstract of the LCA on different routes for nicotine extraction from tobacco leaves

9.2. INTRODUCTION

Tobacco plants grow in more than 124 countries, using about 3.8 million hectares of agricultural land [406]. The economy of thousands of families depends on this crop for cigarette production, but smoking bans and every time stricter restrictions create the need to find other purposes for tobacco crops [407]. Tobacco plants may be processed as a source of second-generation bio-fuel, chemical feedstock, or many valuable bioactive compounds, such as nicotine [408].

Nicotine, firstly isolated from the tobacco plant in 1828 by two German chemists, Posselt & Reimann, is the principal alkaloid (95% of the total alkaloids) in tobacco. It is a carcinogen compound responsible for the addictive nature of tobacco use [409]. In addition, it is a powerful neurotoxin that has been employed either in several medical uses [410], [411] or as an insecticide [412].

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Nicotine is mostly used in the mixture that is fed to electronic cigarettes, for recreational use, or for people trying to quit smoking with medical help. Electronic cigarettes, still containing harmful substances, generally contain fewer toxic and carcinogen chemicals than regular cigarettes [413], [414], [415].

Nearly 50% of the worldwide market for nicotine comes from China [416], where it is usually produced with energy-consuming and non-sustainable processes [417], [418]. Process intensification of nicotine extraction is needed. In addition, the European Union must look to develop its own greener processes giving at the same time independence from Eastern countries.

Nicotine constitutes about 2.5% of the tobacco plant by dry weight [419]. Once it has been extracted, the tobacco leaves still contain a high quantity of cellulose, hemicelluloses, and lignins, which can be extracted to increase the valorisation of this vegetal waste [420], [421], [422].

The main objective of this article is to perform a LCA to validate the environmental competitivity of an innovative process for the mechanochemical extraction of nicotine from tobacco leaves against the conventional process of maceration in a discontinuous tank. The maceration process has been selected as reference, since it can be considered as more environmentally competitive than the other conventional processes.

Details concerning the selection of the two processes compared in this research are presented in the supplementary material. The disadvantages of the not selected processes include: i) large consumption of solvents (25-200L) [423]; ii) raw material:extractant between 1:10 and 1:100 w:w [423]; iii) use of solvents which may damage the industrial equipment [423]; iv) need of special installation for distillation [417]; v) use of expensive and not specific solvents [423]; or vi) use of hardly available gases [417], [418], [419], [420], [421], [422], [423], [424].

In essence, the study contributes to the existing literature by addressing the pressing need for sustainable nicotine extraction processes within the European context. By exploring alternatives to conventional extraction methods and highlighting their environmental and economic implications, we aim to provide valuable insights for policymakers, researchers, and stakeholders involved in the tobacco industry. The novelty of this work lies in its interdisciplinary approach, bridging the gap between environmental sustainability, economic viability, and technological innovation in nicotine extraction from tobacco leaves. As far as known by the authors there is not any LCA for nicotine production in the scientific repositories. By elucidating the competitivity of mechanochemical extraction against the conventional maceration method – both in environmental and economic terms due to its continuity and scalability, utilizing

electricity as the main energy source – we aim to offer practical solutions towards greener and more sustainable nicotine production practices.

MECHANOCHEMISTRY

As defined by International Union of Pure and Applied Chemistry (IUPAC), mechanochemistry are chemical reactions activated by the absorption of mechanical energy. This mechanical energy is supplied through various means such as by shearing, stretching, grinding, or milling [425]. Recent advancements have shed light on the mechanochemistry's potential [426], [427], [428], [429], [430], especially in chemistry and material synthesis [431], [432]. Specifically, the mechanochemical processing of cellulose and related substances has been extensively classified by reaction type and discussed the potential of mechanical equipment [267], [433], [434], [435]. Finally, there are several studies investigating not only the mechanochemical reaction but also its implications in terms of sustainability [429]. Noteworthy examples include patents such as WO2016156749A1 "Method for manufacturing calcium zincate crystals, and the uses thereof" for the so-called IMPAºCT reactor, which has been utilized in diverse applications and products development [268], [436], [437], a smaller version of this reactor, has been used in the present study: a high-efficiency bead mill filled with ZrO2 (stabilized with 20% CeO) micro-milling beads, DYNO®-MILL MULTI LAB, operating in continuous flow wet-milling. This reactor uses the collision of zirconia microbeads with the reactants to activate the reaction. This mechanical energy only requires indirect use of electricity fed to the engine to motion the rotor and discs of the machine. The microbeads in the milling chamber represent, by volume relative to the total volume of the stationary chamber, about 60%. They are spherical, with a mean diameter ranging from 0.6 to 0.9 mm and a Vickers hardness measured according to standard EN ISO 6507-1 typically ranging from 1000 to 1400 HV1 [437].

9.3.   PROCESS DESCRIPTION

Both processes involve the same raw materials: dried tobacco leaves (10-20 wt%) introduced into an agitated tank, mixed with methanol, water, and sodium hydroxide.
In the case of the mechanochemical process (Figure 9-2), nicotine is extracted in a high efficient agitator bead mill reactor from WAB-Group® (DYNO®-MILL RESEARCH LAB), filled with 0.5 mm zirconia oxide micro-balls at a 60% filling ratio. The zirconia balls use mechanical energy to

enhance the kinetics and thermodynamics of the reaction [209], [438], [439], [440]. It operates at 25 ºC for 30 min, with a cooling unit working at 15 ºC to ensure temperature regulation. A mixture 1/1 vol of water/methanol is used as a solvent, and sodium hydroxide, as a base.

In the case of the maceration process (Figure 9-3), nicotine is extracted in a batch glass reactor operating at 25 ºC for 30 min and implementing the same cooling unit and quantities of solvent and base as the mechanochemical process. The main drawback of this route is that this is a discontinuous process with a lower nicotine extraction rate.

After nicotine extraction, in both processes, tobacco leaves are recovered by filtration and may be reintroduced to the agitator tank to optimize the nicotine extraction rate.

The nicotine, water, methanol, and sodium hydroxide mixture are introduced into a 3-stages extraction column in a 50 vol%. The other 50 vol% is dichloromethane, which is fed to extract the nicotine from the solution. While the mixture of water, methanol, and sodium hydroxide may be recycled to the agitator tank, the nicotine and dichloromethane pass through an evaporation

column which separates both compounds at 40 ºC. Dichloromethane may be recycled to the first 3-stages extraction column.

The experiments were performed for both processes (mechanochemical and maceration) with i) experiment 1: 20 wt% NaOH, and ii) experiment 2: 5 wt% NaOH. Figure 9-2 and Figure 9-3 depict mechanochemical and maceration of the process flow diagram, respectively, for both experiments 1 and 2.
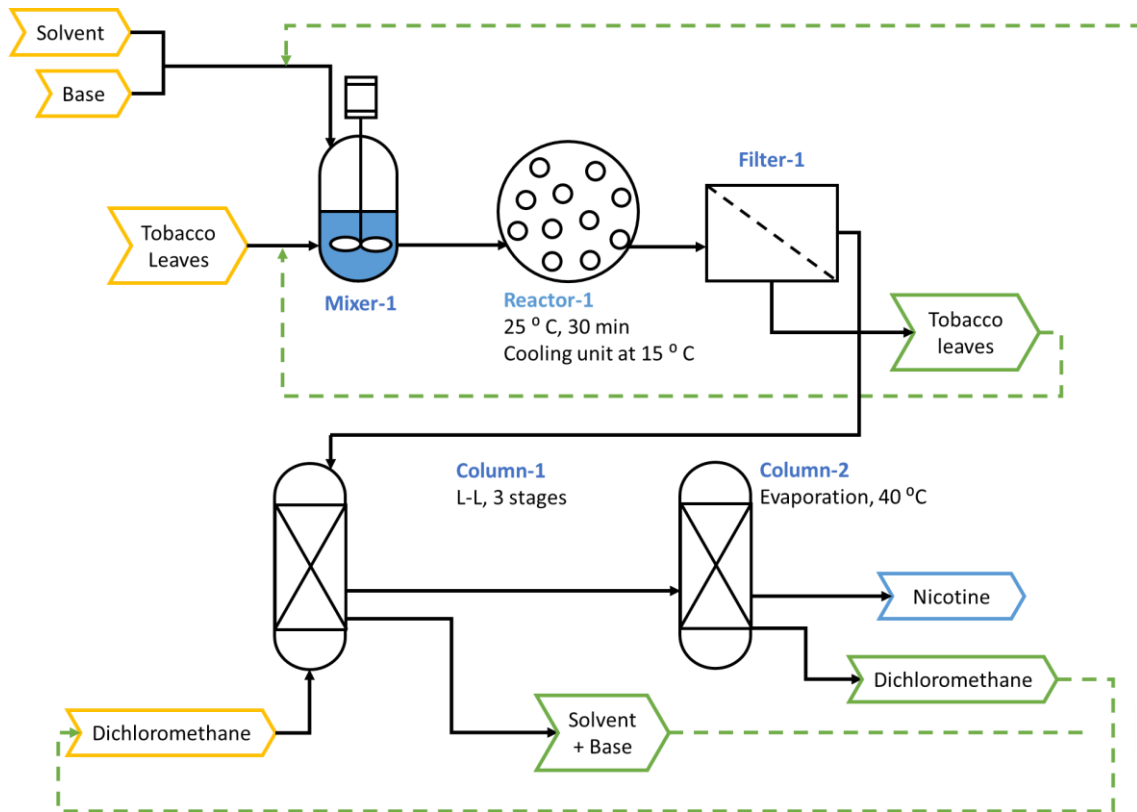
The 1) yellow tags correspond to raw material fed to the process, the 2) green tags are the sub products, the discontinuous lines are reusability potential streams, and the 3) blue tag is the product of the process (nicotine). The operating conditions of each unit is provided next to it.

Figure 9-2 Process flow diagram of nicotine extraction from tobacco leaves with the mechanochemical process (experiment 1 & 2). L-L: liquid-liquid extraction
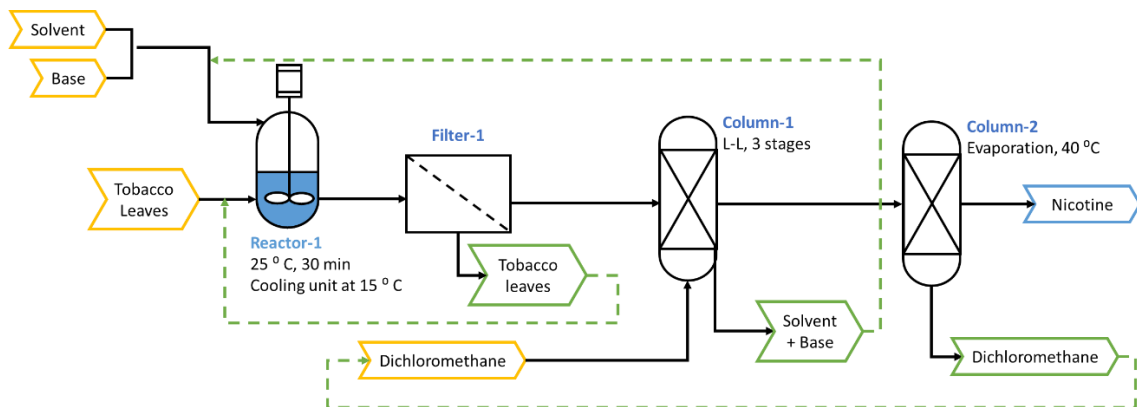
The 1) yellow tags correspond to raw material fed to the process, the 2) green tags are the sub products, the discontinuous lines are reusability potential streams, and the 3) blue tag is the product of the process (nicotine). The operating conditions of each unit is provided next to it.

Figure 9-3 Process flow diagram of nicotine extraction from tobacco leaves with the maceration process (experiment 1 & 2). L-L: liquid-liquid extraction

In addition, a third experiment was performed to assess how the performance increased with the tobacco leaves drying and blending pre-treatment. This was carried out with 20 wt% NaOH and a 10% mass of tobacco leaf ground in the pre-treatment. For this 3rd experimental conditions, Figure 9-4 present the pre-treatment applied to the tobacco leaves in both the mechanochemical and the maceration process flow diagrams.
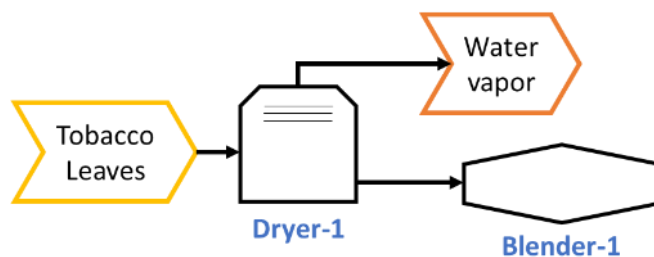
Figure 9-4 Pre-treatment flow diagram of the tobacco leaves for experiment 3 in both mechanochemical and maceration processes

9.4. MATERIALS AND METHODS

Next section outlines the tools, techniques, and procedures used in the study, ensuring transparency and reproducibility.

TOBACCO LEAVES

Tobacco leaves are purchased directly from a small farm from the north of France (approximately 700 km far from the nicotine extraction plant in Geneva, Switzerland) which is dedicated to agriculture businesses. No further treatments have been applied to the raw material. Tobacco leaves are harvested and dried to a moisture content ranging from 6.5 and 15 wt%. The nicotine contained in these leaves represents 1.9-2.3 wt% according to the Kapalina company which has analyzed this raw material.

QUALITY OF DATA

The consulted data is extracted preferably from primary sources, such as experiments performed by the Swiss company Deasyl SA. Secondary sources have been required for

assumptions and scaling up. We assessed the data with the Pedigree matrix, designed by Weidema & Wesnæs (1996) [441] and modified by Ciroth (2009) [442], using only reliable and complete data without temporal, geographical, or technological differences.

The estimation of the energy consumption at the industrial level has been performed with the Piccinno et al. (2016) [443] benchmark, which presents advanced process calculations, hypotheses, and assumptions for the scaling up of laboratory data to the industrial environment. In the case of the agitator bead mill reactor energy consumption, it has been calculated by multiplying the reaction time by the nominal power of the equipment.

Finally, the operational cost of both processes has been calculated with the guidelines and recommendations reported by Peters et al. (2003) in their book: Plant Design and Economics for Chemical Engineers (McGraw-Hill Chemical Engineering) 5th edition [444].

TRANSPORT STAGE

The raw materials have been assumed to be transported with a diesel-driven Euro V truck of 20-26 t gross weight and 17.3 t payload capacity. This capacity is the average value of the alternatives available in the Sphera databases using 2020 as reference year [445]. Euro V is the vehicle emission standard for exhaust vehicles sold in the European Union and EEA member states and the United Kingdom between 2008 and 2012 [446]. This period corresponds with the average age of trucks in Europe [447]. The Euro V standards are defined in a series of European Union directives staging the progressive introduction of increasingly stringent standards.

LIFE CYCLE ASSESSMENT (LCA)

The LCA is a systematic tool that measures the environmental impacts of products considering every single stage in its life cycle. It covers several environmental indicators such as total climate change potential, among others [448], [449], [450], [451]. According to the framework presented in the ISO 14001 [452], [453], an LCA is structured in phases: goal and scope, life cycle inventory (LCI), life cycle impact assessment (LCIA), and the interpretation stage.

The expert decision support LCA software, GaBi (version 10.6.1.35), was used to quantify the environmental impacts of the processes thanks to its extensive databases. The product environmental footprint (PEF) has been selected to measure the environmental performance of the two processes. The LCA boundaries are cradle-to-gate for the following assets: i) Input

material flows, ii) flows of the energy used to heat and cool the reactants, and iii) energy used to stir, pump, and mill the mixture. The end-of-life stages are equivalent in both processes. Figure 9-5 below shows the boundaries of the processes studied, as it has been simulated in the GaBi software.
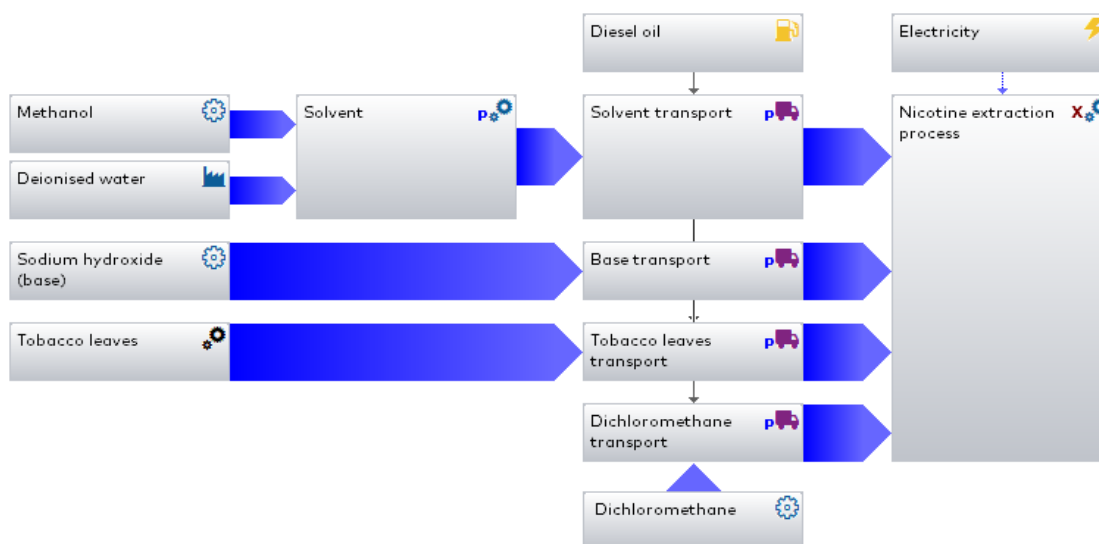
Figure 9-5 Process boundaries of the environmental impacts (GaBi, Sphera). The thickness of the blue arrow provide a qualitative insight of the material flow of each compound

One kilogramme of extracted nicotine was set as functional unit for inventory calculation and impact assessment. In addition, the three indicators selected to present a visual and understandable comparison between the two routes to extract 1 kg of nicotine from tobacco leaves are: i) Climate Change, total (kg CO2 eq.), ii) Energy consumption (kJ), and iii) the operational costs of each process, considering the raw material and required energy.

The main difference between both processes is that while the mechanochemical process works with mechanical energy induced by zirconia micro balls, the maceration process does not have this stage. Even though, the environmental impact of the zirconia balls fabrication can be neglected for the study since their lifespan is around 10,000 hours (and 1 cycle of the process lasts only 0.5 hours) [436].

LIFE CYCLE INVENTORY (LCI)

The LCI includes the input and output flows (materials and energy) of the product system [452], [453]. According to Deasyl SA experiments, the best nicotine extraction rate with the mechanochemical process is 1.91wt%, and it has been obtained in the third experiment (20 wt% NaOH and a 10% mass of tobacco leaf ground in the pre-treatment), after 30 min. This corresponds to 83.04% of the ideal theoretical value of 2.30 wt% nicotine present in the tobacco leaves purchased for the experiments. The best nicotine extraction rate with the maceration process is 1.78 wt%, obtained also in the third experiment after 30 min. Corresponding to 77.39% of the ideal theoretical value.

According to our experience with these micro-ball-milling technology, it turns important to avoid different ball sizes added to the ball mill jar. You want to achieve a very fine distribution of your milling elements. If you do not, you do a grinding of the balls between the balls themselves (leading to leaching and increasing the operating costs).

The main differences between the processes are in the extra energy necessary in the agitator bead mill reactor since the extraction time was set at 30 minutes with a gross power between 2.2 and 4.0 kW [436]. Then, to extract the same amount of nicotine, it is necessary to feed more raw material in the case of maceration process than in mechanochemical one. But the mechanochemical process will consume more energy than the maceration process. These results are presented in Table 9-1:

The environmental factors taken for electricity for both systems are those for the European average in the year 2018.

Table 9-1. Raw materials and energy required for extracting 1 kg of nicotine

	Mechanochemical process	Maceration process
Tobacco leaves (kg)	52	56
Solvent (kg)	277	299
Base (kg)	17	19
Dichloromethane (kg)	418	448
Energy consumption (kJ)*	10,178	4,598

*This is gross energy used in a conservative approach to deal with uncertainty in the real energy consumption of the machine. The calculated value corresponds to the maximum value, but it could be optimized to 50% in a lab scale or to less than 10% in a production machine.

LIFE CYCLE IMPACTS ASSESSMENT

A total of 16 midpoint indicators have been calculated with the PEF methodology [454], [455]. Table 9-2 presents the results obtained for both processes in percentage, being the 100% the maximum value obtained at each midpoint between the mechanochemical and maceration processes. Most midpoint indicators suggest that the best process from an environmental perspective is the mechanochemical process, which, despite requiring a higher energy consumption, has a higher nicotine extraction rate and a lower raw materials demand than the maceration process to extract the same weight of nicotine.

Table 9-2. LCIA with PEF methodology results

	Mechanochemical process	Maceration process
Acidification (mol of H^+eq.)	93.0%	100.0%
Total Climate change (kg CO_2 eq.)	93.9%	100.0%
Total freshwater ecotoxicity (CTUe)	93.1%	100.0%
Freshwater eutrophication (kg of P eq.)	92.8%	100.0%
Marine eutrophication (kg of N eq.)	93.0%	100.0%
Terrestrial eutrophication (mol of N eq.)	92.9%	100.0%
Total cancer human toxicity (CTUh)	93.3%	100.0%
Total non-cancer human toxicity (CTUh)	93.3%	100.0%
Ionizing radiation (kBq U235 eq.)	100.0%	97.9%
Land use (Pt)	92.9%	100.0%
Ozone depletion (kg CFC-11 eq.)	95.2%	100.0%
Particulate matter (Disease incidences)	92.6%	100.0%
Photochemical ozone formation (kg NMVOC eq.)	93.2%	100.0%
Resource use of fossils (MJ)	93.6%	100.0%
Resource use of minerals and metals (kg Sb eq.)	93.2%	100.0%
Water use (m³ world eq.)	93.0%	100.0%

INTERPRETATION OF RESULTS

CLIMATE CHANGE

Climate Change (total kg CO2 eq.) indicator, follows a similar trend to the other midpoint indicators. Sometimes, it is advisable, for the sake of readability, to simplify the results

assessment [456] and even to reduce the number of environmental indicators [451], [457] for a better life cycle management [458].

Looking stage by stage, the only point where the mechanochemical process has a greater environmental impact is in the nicotine extraction step, due to its higher electricity consumption. This point can be corrected with cleaner energy mixes such as the use of renewable energy or nuclear energy, which is less advisable.

However, it does not compensate the higher raw material demand of the maceration process. The greatest environmental impact is seen in the purchase of tobacco leaves and is associated with their cultivation, curing, production, drying, transport, and distribution. It would be interesting to study sustainable agriculture applications to reduce this carbon footprint [459], [460] as well as reusing the tobacco leaf after nicotine extraction. In addition, the impact associated with the solvent (dichloromethane) also has a significant weight, which could be reduced after developing a study to assess the feasibility of replacing dichloromethane with a greener solvent.

Figure 9-6 shows the distribution of Climate Change (total kg CO_2 eq. indicator) among the different steps of the process.
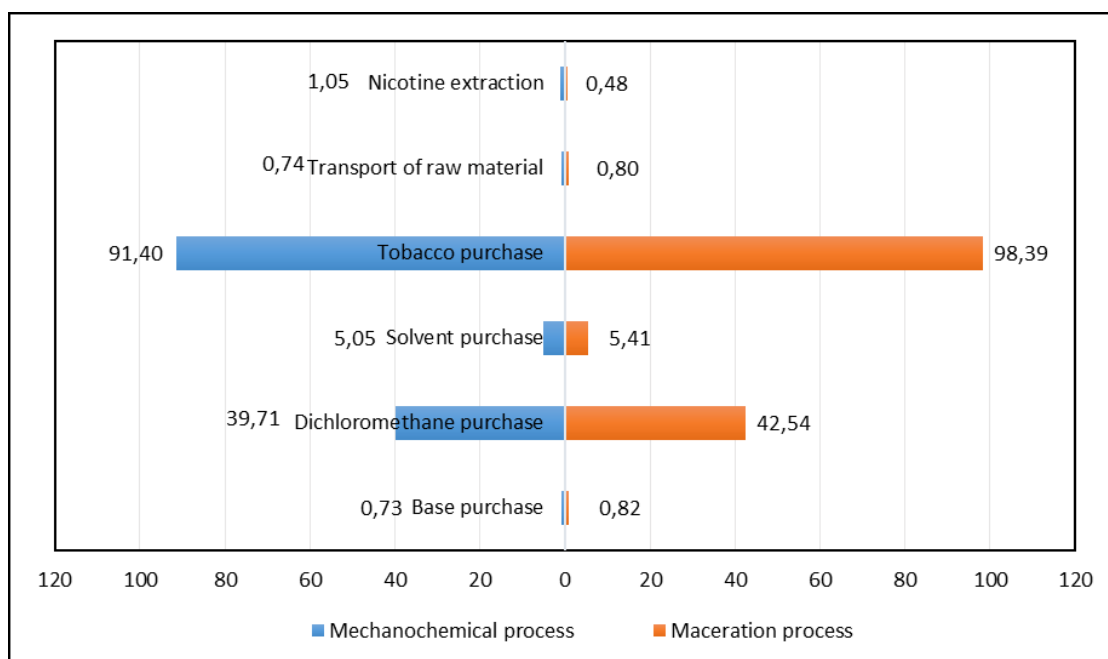
Figure 9-6 Comparison of climate change impact (kg CO_2 eq. per kg of extracted nicotine) for both extraction processes (totals) according to EF3.0 methodology

ENERGY CONSUMPTION

The only drawback of the mechanochemical process, when compared to the maceration process in terms of energy consumption, is that it consumes more electricity during the process stage. It is therefore advisable to apply strategies such as the use of renewable energy use or nuclear energy use (less recommended) to power the mechanochemical process for nicotine extraction and decrease its carbon footprint. Considering the new European Energy Directives and the European Green Deal [461], we foresee that the mechanochemical process has a larger potential for environmental improvement in the coming years. Finally, as it is stated in Table 9-2, it should not be forgotten that the results of the energy consumption are gross energy used in a conservative approach to deal with uncertainty in the real energy consumption of the machine. The calculated value corresponds to the maximum value, but it could be optimized to 50% in a lab scale or to less than 10% in a production machine.

ECONOMIC ANALYSIS

The economic balance includes only the operational costs since there is no available reliable data on the prices of the industrial equipment necessary for each process. We assume that the possible differences between this equipment for each process will be compensated by the operational balances due to their long-life cycle. We have calculated the economic operational balance as the difference between the price of 1 kg of nicotine and the costs of the raw material and electricity used to extract 1 kg of nicotine for both processes.

The average electricity price in the European Union is 0.2322 EUR/kwh [462], for household consumers in the first half of 2021. The average prices of the raw materials and the product are presented in table 3 [463].

Table 9-3. The average price of the raw material [463]

Product	Average price (EUR/kg)
Mixture of 1/1 vol of water/methanol	0.27
Sodium hydroxide	10.59
Tobacco leaves	0.40
Dichloromethane	0.63
Nicotine	200.00

The economic balance results are slightly better for the mechanochemical process (+152.32 EUR/kg of extracted nicotine) than in the maceration process (+149.02 EUR/kg of extracted nicotine). The fact that it requires less kg of raw material offsets its higher electricity demand. Despite the recent volatility of electricity prices, this does not have a relevant impact on this economic study: although the amount of energy required in the mechanochemical process is higher than in the maceration process, its economic impact is clearly lower than that of the other raw materials involved in the processes. A variability analysis was carried out to quantify the price at which the mechanochemical process becomes less profitable than the maceration process (considering only variable costs). It has been determined that this does not happen until electricity costs are multiplied by an order of magnitude of 10.

ECO-EFFICIENCY ANALYSIS

Eco-efficiency indicators measure the relationship between environmental and financial performances of an economic activity for certain global environmental problems. In addition, it also deals with social and technical performance indicators [464]. The present research considers the climate change impact category for the environmental performance and the economic analysis of the operational costs for the financial one. Regarding the social and technical performances, same final product quality has been assumed in the mechanochemical and the maceration processes. Even though, the Energy consumption has been used as transversal indicator considering that the more energy consumption requires a process, the less eco-efficiency results it will achieve.

Figure 9-7 summarizes the calculation of the Eco-efficiency analysis as well as its results for mechanochemical and maceration processes. Following the methodology from Balaguera, the indicators we wish to enhance are placed in the numerator and the indicators we wish to avoid will be placed in the denominator of the fraction [464]. In the formula used, the factor of the carbon footprint and energy consumption are dividing the financial performance of the process. Indicators are considered as a tool for decision making and evaluation of the performance of each process [465]. The decision must be made for each specific scenario, as the optimal solution may vary from one to another. The higher the eco-efficiency indicator is, the better the performance and therefore the more preference in the decision process will be.
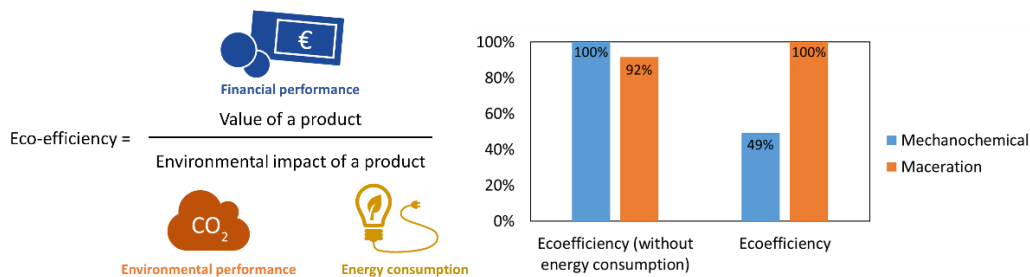
Figure 9-7 Eco-efficiency analysis calculation graphical scheme

The results of the eco-efficiency analysis show that energy consumption is an indicator with a high impact on the bottom line, mainly because of the difference in energy requirements between the two processes. On one hand, it can be argued that energy consumption is already included in both economic balance of operational costs and Climate change impact category. In that case, and if we do not consider energy consumption to measure eco-efficiency, the mechanochemical process performs slightly better than the maceration process. However, in scenarios where the energy supply is considered as a limiting resource, the eco-efficiency of the maceration process is clearly favourable compared to that of the mechanochemical process. This highlights the need of optimizing and scaling up the mechanochemical process when it is used instead of maceration. While the maceration seems to perform better at lab scale where we operate without process integration or energy optimization, the mechanochemical process will offer better performance at higher level of production.

9.6. CONCLUSIONS

The comparison between the mechanochemical and the maceration process for the extraction of nicotine from tobacco leaves presents positive and negative points for both studied processes. Choosing one process or the other must be made based on the information related to each specific scenario. This article provides a reference to support this decision making from an economic and environmental point of view.

The mechanochemical process achieves the highest efficiency in nicotine extraction, but however consumes more energy at laboratory scale. After performing the LCA and the economic analysis of the operational costs, we can conclude that the higher nicotine extraction rate of the mechanochemical process balances its higher energy requirements when calculating the overall impacts. The mechanochemical process presents better environmental and economic performance. In addition, the power consumption calculated corresponds to the gross energy consumption, and it is the maximum theoretical value that would be consumed. This value might

be optimized to 50% at laboratory scale or to less than 10% in a production machine. According to this estimation, the mechanochemical process would be surpassing maceration also in energy consumption if it is scaled up and optimized.

The step with the highest environmental impact in both processes corresponds to the use of tobacco leaves as raw material and the use of dichloromethane as extraction solvent. The impact of tobacco leaves can be reduced by applying sustainable agricultural techniques or up-cycling post extraction tobacco leaves (more than 98% in weight) as biomass or as source of other compounds such as lignin, cellulose, or hemicellulose. In addition, the use of other extraction solvents with lower life-cycle environmental impact should be investigated. The use of tobacco crops also has an impact on the use of land for both processes. While they are contributing to biogenic carbon absorption, they are also occupying an area of land that otherwise, could be use for food crops, photovoltaics, or other purposes. Regarding this indicator, mechanochemical process slightly outperforms the maceration process, reducing the impact by 7%.

The eco-efficiency analysis presents different results depending on the consideration of energy consumption as a transversal indicator. If we assume that energy consumption is already accounted in the climate change impact category and in the economic analysis, the eco-efficiency performance of the mechanochemical process will be slightly better than the maceration process. Even though, there will be scenarios where the energy supply will be a limiting resource. In that case, the less energy-intensive process (maceration) would be more suitable than the mechanochemical process. So on, it is essential to work towards the energy optimization as a priority if switching from maceration to mechanochemical processing. In addition, regarding the energy consumption of nicotine extraction step from the mechanochemical process, its environmental impact will depend on the energetic mix. Considering the direction of the European Union towards a greener energy mix, the results of the mechanochemical process LCA would be even better in the next years.

In summary, both processes operate at atmospheric conditions of temperature and pressure, with a cooling unit at 15 ºC to ensure temperature regulation. Both processes use equivalent post-treatment processes. So on, the main difference between each configuration lies on the use of the mechanochemical reactor to activate the reaction. This, enhances the reaction achieving higher extraction rate of nicotine in the mechanochemical process (1.91 wt%) than in the maceration (1.78 wt%). Both processes achieve the maximum performance after the third experiment, with 20 wt% NaOH used as a base for pH regulation and a 10% mass of tobacco leaf ground in the pre-treatment. The highest efficiency of nicotine extraction rates with mechanochemical process leads to an average of 7% reduction in the environmental impacts of

all midpoint indicators. This also leads to slightly better (2%) economic balance in the mechanochemical balance.

10. POTENTIAL ADVANTAGES OF THE IMPLEMENTATION OF ASPENPLUS V12 AND COSMORS IN LCA FOR CHEMICAL PROCESSES

As introduced in the preface of this thesis, the application of process simulation software such as AspenPlus v12 or CosmoRS was mainly explored during a stay at the Pontificia Universidad Católica de Chile. These were basically used to study the production of biodiesel from used cooking oils (UCO), and the valorisation of waste glycerol into CaDG, catalyst to produce biodiesel from UCO, and solketal, additive to improve the properties of biodiesel.

Using AspenPlus v12 allows you to simulate chemical processes with rigorous models so that it is easy to recalculate mass and energy balances for different scenarios and operating conditions. This allows the calculation of the optimal point of a process from an energy, economic, or environmental point of view when combined with other tools. Moreover, having more comprehensive databases for chemical products makes it a very valuable ally for conducting retrosynthetic studies of your process when calculating the LCA. The main limitation of the software lies in the need to have significant knowledge of the thermodynamic behavior of your mixture, as well as of the reaction or equilibrium. Therefore, the use of the software should be complemented with experimental research in the laboratory.

CosmoRS allows the prediction of physical and chemical properties of chemical compounds based on their charge distribution. The software is particularly limited to the use of incompressible liquids and short-chain molecules. However, it is especially useful for understanding the behavior of a compound or mixture, and it can be used as a proxy in LCA calculations.

11. GENERAL CONCLUSIONS OF THE THESIS

The present thesis, titled "Life cycle assessment as a tool for the industrialisation of chemical and mechanochemical processes" aims to compare the environmental impact of innovative mechanochemical processes with conventional processes used in the manufacturing of the same product while addressing key challenges in the field of LCA for chemical reactions, such as data gap management, laboratory data scaling, and reducing or eliminating uncertainty.

As a general conclusion, this thesis has demonstrated that LCA methodology can be used in the context of chemical industry by using a multilevel procedure, providing comprehensive solutions to deal with the common data uncertainty due to confidentiality issues, scaling up requirements, or others, that we encounter in this field, thus contributing to the advancement of LCA methodology. From a practical point of view, the workflows defined throughout this thesis can be used to develop LCA studies for chemical processes and use the results to scale up laboratory processes by selecting the best operating conditions in terms of environmental and economic impact.

The objectives 1 and 2 have been addressed throughout this thesis with a review paper that has been presented analysing the state of the art of the application of the LCA methodology for chemical and industrial processes (chapter 4). As a result of this review, a modus operandi has been designed as a guide to calculate the environmental impact of the processes presented between chapter 6 and chapter 9. This modus operandi is the methodological approach and workflow presented in chapter 3.

This first review has identified the importance of mass and energy balances for the calculation of LCA in chemical processes, the need to include the reaction time in the FU, and the different techniques to scale up from laboratory data to pilot plant or industrial data.

To introduce the topic of mechanochemistry, as well as the reactor and the main technology used by Deasyl, a framework of the most recent publications of mechanochemical processes used for green chemistry applications is presented in chapter 5.

The outcome of this review is the identification of the existing gap in the literature of LCA measurements for these types of chemical processes, as well as the importance to provide primary data instead of treating the mechanochemical reactor as a black box, what increases uncertainty, and lack of repeatability.

The objective 3, regarding social and economic perspective, is briefly investigated in chapters 7 to 9.

Energy as a critical resource will play a very important role in the coming years. Considering that mechanochemical processes use electricity instead of steam, conventionally produced by burning natural gas, propane, or naphtha, they could benefit from the electricity mix predicted in the European green deal.

Finally, and according to the objective 4, several frameworks based on basic equations of thermodynamics and reactor kinetics have been used to scale up laboratory mass and energy balances to the industrial level.

The Pinch analysis has been identified as a good tool to consider the energy savings produced when scaling and optimizing a process from the laboratory. When the data allowed it, process simulation software such as AspenPlus v12 or CosmoRS have been successfully used in combination with conventional LCA software, in which the most realistic and rigurous thermodynamic models for the processes in question have been simulated.

Finally, some conclusions on the working framework. Having an industrial doctorate has fostered collaboration between academia and industry, which for me enhances the practical application of concepts that often remain within the academic realm and are difficult to implement in real-world industrial settings. On a more personal note, this thesis has supported my development in both the academic and industrial sectors, while also allowing me to begin my research career by participating in various conferences, publishing in top international journals, and collaborating with a wide range of research groups.

All in all, this work may have contributed to the development of strong strategy for the calculation of LCAs of chemical processes in the design stage, enhancing the importance of decision making in this early step of the chemicals production.

11.1. LIMITATIONS AND RECOMMENDATIONS

The main limitations of the study are in many cases related to the uncertainty generated by the laboratory data, which in some cases are not definitive, or are to be optimised with the scaling of the process. This limitation has been addressed through the application of thermodynamic frameworks and the use of process simulation software.

On the other hand, the fact of working with chemicals means that in many cases environmental information in databases is limited for confidentiality reasons. The more extensive Sphera and Ecoinvent databases have been used in this thesis. However, for those chemical compounds not available, the system expansion methodology has been used, or the use of (retro)synthetic analyses or proxies when the available information was not sufficient.

As a recommendation for future studies of the application of LCA in the chemical sector, work could be done on the application of CosmoRS for the prediction of environmental impacts. CosmoRS allows the prediction of physical and chemical properties of compounds from their charge distribution. The use of CosmoRS should therefore be treated only as a proxy. However, it would help to deal with the uncertainty and the lack of data we currently have in this field.

Finally, working on the creation of thermodynamic frameworks in spreadsheets to automate the scaling of mass and energy balances of chemical processes is also an interesting direction to explore, which would allow the LCA practitioners to save a lot of time in their studies.

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