



UNIVERSIDADE D
COIMBRA

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**LIFE CYCLE ASSESSMENT OF A BIOPOLYMER
FILM PRODUCED FROM MANGO WASTES
PERFORMED AT AN EARLY DEVELOPMENT
STAGE**

M.Sc. Dissertation

December 2020

Life cycle assessment of a biopolymer film produced from mango wastes performed at an early development stage

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Dissertation in the context of the Master in Energy for Sustainability presented to the Department of Mechanical Engineering of the University of Coimbra

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Coimbra
December 2020

Acknowledgements

I would like to express my gratitude to all those who in some way helped me in this dissertation. Special thanks to my supervisor, Professor Fausto Freire for his valuable guidance that helped me raise the standards of my research work, and for welcoming me in the Centre for Industrial Ecology, giving me a workplace for the development of this research. I thank my co-supervisor, Dr. Maria Cléa Figuerêdo, for her careful revisions and advice in the past few years, and for involving me in the SET-LCA project, which helped me get here.

I would also like to thank Dr. Carla Rodrigues for her contributions to this research, as well as my colleagues at the CIE, who provided a friendly and intellectually-rich environment for the development of this work.

Thanks to my colleagues at Embrapa, especially Eligenes, Ed, Anne, for the data provided for this study, Dr. Henriette Azeredo, Priscila Silva and Vitória Oliveira, for answering my many questions about the films they produced, and to Adriano Mattos, for sharing his experience and giving me useful reading material on film manufacturing technology.

Many thanks to my friend and colleague Edilene Andrade, who helped me clarifying some ideas in the text, and who years ago, helped me start my research career in LCA.

I thank my family for encouraging me to always do and be more, especially my mother and sisters, three powerful women that inspire me every day.

To my dear friends in Brazil and Portugal, especially Irvylle, Jônatas, Joel, Eduardo, and Patrícia for making this time much more pleasant and fun.

And to Gabriel for all the love and support.

The research presented in this thesis was partly supported by the Portuguese Science and Technology Foundation (FCT) under the projects SET-LCA (CENTRO-01-0145-FEDER-030570) and SABIOS (POCI-01-0145- FEDER-016765).

Abstract

The development of bio-based plastics is a key element for the transition to a bioeconomy, especially value-added materials produced from agro-wastes. Life cycle assessment (LCA) can be used to evaluate the environmental performance of such materials from a holistic perspective. However, assessing novel products at low technology readiness levels requires an innovative way to conduct LCA, involving process scale-up and future manufacturing scenarios. The goal of this thesis is to perform an LCA of a biopolymer film, produced from mango processing wastes, at an early research stage. Specific aims are: 1- obtain a scale-up model for the production of the biopolymer in two formulations, and to identify environmental hotspots and improvement opportunities in their production; 2- to compare the biopolymer to low-density polyethylene (LDPE); 3- to identify which aspects influence the environmental performance of the biopolymer and its comparison to LDPE; and 4- to identify critical aspects and provide recommendations for future research on early-stage LCA of biopolymers.

Two film formulations based on mango kernel starch from previous laboratory-scale work were scaled-up and modelled at industrial-scale: Film 1 had a starch nanocrystals (SNC) reinforcement; Film 2 was filled with SNC and cellulose nanocrystals (CNC). The scaled-up model for CNC, SNC, and film production was performed by applying an engineering-based tool for batch chemical processes focused on the estimation of energy requirements. The LCA included the following processes: collection of waste, separation of seed components, production of starch, starch nanocrystals, cellulose and cellulose nanocrystals, and film manufacturing. A cradle-to-gate boundary and a functional unit of 1 kilogram of biopolymer film were adopted. In a reference scenario, mango seeds were considered wastes of the mango pulping process, whereas, in an alternative scenario, were modelled as by-products, with the inclusion of crop production and pulping. Mass allocation was applied as reference, but economic allocation was considered in sensitivity analysis.

The results for industrial-scale show a large reduction in energy use in relation to the lab-scale, mainly due to higher energy efficiency and heat integration at industrial-scale. Consumption of chemicals was also reduced at industrial-scale e.g., by solvent recovery in distillation.

The impact assessment was performed for non-renewable energy use, climate change, terrestrial acidification, and freshwater eutrophication. Most impacts for Film 1 are from starch and SNC production. For Film 2, CNC had a considerable share of the impacts and is the main contributor to non-renewable energy use and acidification impacts. Improvement scenarios were assessed, namely changing hydrolysis acid and assuming higher yields for starch, SNC, and CNC, showing that a large reduction of impacts can be attained for both formulations. Film 1 performed better than Film 2 in all impact categories analysed. Scenario analysis for feedstock considerations and film manufacturing techniques of Film 1 showed large variations in the impacts. The inclusion of agricultural and pulping phases increased the impacts of the film; these additions were higher considering mass than economic allocation. Two film manufacturing techniques were analysed: casting (reference) and extrusion. Film extrusion had lower impacts than casting.

The comparison of Film 1 and LDPE on a 1-kg basis shows that the biopolymer performed better than LDPE for non-renewable energy; however, LDPE film had lower climate change,

acidification, and eutrophication impacts. A combination of improvements was analysed for the biopolymer Film 1, as well as replacement ratios based on a 1 m² functional unit, to achieve equivalent climate change impacts as LDPE. In two situations, this was attained: 1-Maximising starch and SNC extraction yields while producing the film by extrusion and 2- If a sufficiently thinner biopolymer film was achieved for the same application. The unfavourable results of the biopolymer in relation to LDPE can be related to the higher technological maturity of the fossil polymer, and the biopolymer has more room for improvement. Recommendations were proposed for analysing biopolymers at early stage, concerning functionality, scale-up, data completeness, and performance.

Keywords: prospective, ex-ante, scale-up, bio-based plastic, nanocrystals, agro-waste

Resumo

O desenvolvimento de plásticos de base biológica é essencial para a transição para uma bioeconomia, especialmente materiais produzidos a partir de resíduos agrícolas. A avaliação do ciclo de vida (ACV) pode ser usada para avaliar o desempenho ambiental destes materiais. No entanto, analisar novos produtos, em baixos Níveis de Prontidão Tecnológica, requer uma abordagem inovadora na ACV, que envolve escalonamento de processos e cenários de produção futuros. O objetivo desta tese é realizar a ACV de um filme biopolimérico produzido a partir de resíduos de processamento de manga em um estágio inicial de desenvolvimento. Os objetivos específicos são: 1- obter um modelo escalonado para a produção do biopolímero em duas formulações, e identificar pontos críticos e oportunidades de melhoria em sua produção; 2- comparar o biopolímero ao polietileno de baixa densidade (PEBD); 3- identificar que aspectos influenciam o desempenho ambiental do biopolímero e sua comparação com o PEBD; e 4- identificar aspectos críticos e fornecer recomendações para pesquisas futuras de ACV de biopolímeros em estágios iniciais de desenvolvimento.

Duas formulações de filme baseadas em amido de caroço de manga obtidas de trabalhos anteriores em escala laboratorial foram escalonadas e modeladas em escala industrial: Filme 1, com um reforço de nanocristais de amido (NCA), e Filme 2, com reforço de NCA e nanocristais de celulose (NCC). O modelo escalonado para NCC, NCA e produção de filme foi realizado aplicando uma ferramenta baseada em engenharia para processos químicos em batelada focada na estimativa de requerimentos energéticos. A ACV incluiu os seguintes processos: coleta de resíduos, separação dos componentes da semente, produção de amido, nanocristais de amido, celulose e nanocristais de celulose e a produção do filme. Uma fronteira do berço ao portão e uma unidade funcional de 1 quilograma de filme de biopolímero foram adotados. Em um cenário de referência, as sementes de manga foram consideradas resíduos do processo de polpação da manga, enquanto, em um cenário alternativo, foram modeladas como subprodutos, com a inclusão da produção agrícola e da polpação. A alocação mássica foi aplicada como referência, mas a alocação econômica foi considerada em uma análise de sensibilidade.

Os resultados para a escala industrial mostram grande redução no uso de energia em relação à escala de laboratório, principalmente devido à maior eficiência energética e integração térmica em escala industrial. O consumo de produtos químicos também foi reduzido, por exemplo, por recuperação de solvente na destilação.

A avaliação de impacto foi realizada para uso de energia não renovável, mudança climática, acidificação terrestre e eutrofização de água doce. A maioria dos impactos para o Filme 1 devem-se à produção de amido e NCA. Para o Filme 2, o NCC teve uma parcela considerável dos impactos e é o principal contribuidor para o uso de energia não renovável e a acidificação. Foram avaliados cenários de melhoria, nomeadamente alterando o ácido de hidrólise e assumindo rendimentos mais elevados para amido, NCA e NCC, que mostraram que uma grande redução dos impactos pode ser alcançada para ambas as formulações. O Filme 1 teve um desempenho melhor do que o Filme 2 em todas as categorias de impacto analisadas. A análise de cenário para considerações de matéria-prima e técnicas de fabricação de filme do Filme 1 mostrou grandes variações nos impactos. A inclusão das fases agrícola e polpação aumentou os impactos do filme; essas adições foram maiores considerando a alocação mássica

do que a econômica. Duas técnicas de fabricação de filmes foram analisadas: casting (referência) e extrusão. A extrusão do filme teve impactos menores do que o casting.

A comparação do Filme 1 e do PEBD em uma base de 1 kg mostra que o biopolímero teve um desempenho melhor do que o PEBD para energia não renovável; no entanto, o filme de PEBD teve menores impactos de mudança climática, acidificação e eutrofização. Uma combinação de melhorias foi analisada para o biopolímero Filme 1, assim como taxas de substituição com base em uma unidade funcional de 1 m², para atingir impactos na mudança climática equivalentes ao PEBD. Em duas situações, isso foi obtido: 1- Maximizando os rendimentos da extração de amido e NCA e considerando a produção do filme por extrusão e 2- Se um filme de biopolímero suficientemente mais fino fosse alcançado para a mesma aplicação. Os resultados desfavoráveis do biopolímero em relação ao PEBD podem estar relacionados à maior maturidade tecnológica do polímero fóssil; entretanto, o biopolímero tem mais espaço para melhorias. Recomendações foram propostas para a análise de biopolímeros em estágio inicial, no que diz respeito à funcionalidade, aumento de escala, obtenção de dados e desempenho.

Palavras-chave: ACV prospectivo, ex-ante, escalonamento, bioplásticos, nanocristais, resíduos agroindustriais

Table of Contents

<i>Acknowledgements</i>	<i>i</i>
<i>Abstract</i>	<i>ii</i>
<i>Resumo</i>	<i>iv</i>
<i>List of Abbreviations</i>	<i>viii</i>
<i>List of Figures</i>	<i>ix</i>
<i>List of Tables</i>	<i>x</i>
1. Introduction	1
1.1. Motivation	1
1.2. Research questions and objectives	2
1.3. Dissertation outline	3
2. Background	4
2.1. Performing LCA at early R&D stages	4
2.2. Bio-based plastics	6
2.2.1. Starch plastics	7
2.3. LCA of biopolymers	8
2.3.1. Evaluation of starch polymers and nanocomposites	9
2.3.2. Early-stage LCA of novel bio-based polymers	10
3. Materials and methods	12
3.1. Goal and scope definition	12
3.1.1. Description of laboratory processes	14
3.2. Inventory analysis and scale-up	17
3.2.1. Allocation	20
3.3. Impact assessment	20
3.4. Analysis of replacement ratios when comparing biopolymer and LDPE	21
3.5. Scenario analysis	22
4. Results and discussion	24
4.1. Life cycle inventory analysis of the biopolymer film at laboratory and industrial-scales 24	
i) Cellulose and CNC production	24
ii) SNC production	26
iii) Film production	26
4.2. Life cycle impact assessment	27
4.2.1. Biopolymer Film 1	27
4.2.2. Biopolymer Film 2	29
4.2.3. Selecting the best-performing biopolymer formulation	31
4.2.4. Comparing Biopolymer Film 1 and LDPE	32
i) Comparison based on a 1:1 replacement	32
ii) Replacement ratio for equivalent GHG impacts	34
4.3. Scenario and improvement analysis for Biopolymer Film 1	35
4.4. Comparison with other biopolymer LCAs	36
5. Conclusions	39

5.1. Limitations and further research	40
5.2. Recommendations for assessing biopolymers at early R&D stages.....	40
<i>References.....</i>	43
<i>Annexes.....</i>	49
Appendix A – Parameters and equations used in the scale-up.....	49
Appendix B – Detailed life cycle inventories per phase.....	54
Annex A – Inventory data from previous studies	58

List of Abbreviations

CC – Climate change
CNC – Cellulose nanocrystals
CO₂ – Carbon dioxide
FE – Freshwater eutrophication
FU – Functional unit
GHG – Greenhouse gas emissions
GWP – Global warming potential
H₂SO₄ – Sulphuric acid
H₃PO₄ – Phosphoric acid
HCl – Hydrochloric acid
kg – kilogram
kg CO₂-eq – kilogram carbon dioxide equivalent
kg P-eq – kilogram phosphorous equivalent
kg PO₄-eq – kilogram phosphate equivalent
kg SO₂-eq – kilogram sulphur oxide equivalent
LCA – Life cycle assessment
LCI – Life cycle inventory
LCIA – Life cycle impact assessment
LDPE – Low-density polyethylene
MJ – Megajoules
MKS – Mango kernel starch
NREU – Non-renewable energy use
PBAT – polybutylene adipate terephthalate
PBS – Polybutylene succinate
PCL – Polycaprolactone
PE – Polyethylene
PET – Polyethylene terephthalate
PHA – Polyhydroxyalkanoates
PHB – Polyhydroxybutyrate
PLA – Polylactic acid
PP – Polypropylene
PVC – Polyvinyl chloride
PVOH – Polyvinyl alcohol
SNC – Starch nanocrystals
TA – Terrestrial acidification
TPS – Thermoplastic starch
TRL – Technology readiness level

List of Figures

Figure 1: Valorisation of mango processing wastes.....	2
Figure 2: Bio-based, biodegradable and bioplastics. Source: adapted from Spierling et al. (2018) and Endres & Siebert-Raths (2011).....	7
Figure 3: Strategy adopted in the early-stage LCA. Partially adapted from ISO (2006).....	12
Figure 4: Flowchart of the production of biopolymer film - Film 1 and 2	14
Figure 5: Isolation of starch nanocrystals	15
Figure 6: Cellulose production and cellulose nanocrystals isolation	16
Figure 7: Biopolymer film production	17
Figure 8: Plant flowchart including potential heat recovery routes	19
Figure 9: Functionality of polymer films	21
Figure 10: Process contribution for Film 1 (1 kilogram of film)	28
Figure 11: Impacts per process in film production, starch, and SNC production, before (P.0) and after (P.4) improvements	29
Figure 12: Process contribution for Film 2 (1 kilogram of film)	30
Figure 13: Impacts per process in CNC production, before (P.0) and after (P.3) improvements	31
Figure 14: Comparative analysis of biopolymer films 1 and 2 (1 kg of biopolymer film). The bars represent the values of the sensitivity analysis for distillation energy in cellulose production.....	32
Figure 15: Comparative assessment of mango-based biopolymer and LDPE film (1 kilogram of film).....	33
Figure 16: Eco-design strategy for novel biopolymers	42

List of Tables

Table 1: Conceptualisation of ex-ante assessment modes. Source: adapted from Cucurachi et al. (2018)	6
Table 2: Characteristics of the mango-based biopolymer - Films 1 and 2.....	13
Table 3: Data sources for the production of mango waste-based biopolymer film	14
Table 4: Allocation factors used for the stages of fibre production, pulping and seed separation	20
Table 5: Properties of the biopolymer and LDPE	21
Table 6: Inventory of cellulose production at laboratory and industrial-scales	24
Table 7: Inventory of CNC production at laboratory and industrial-scales	25
Table 8: Inventory of SNC production at laboratory and industrial-scales.....	26
Table 9: Inventories of film production at industrial-scale – Film 1 and 2.....	27
Table 10: All scenarios, worst- and best-case results for Film 1, in absolute values and percentage of difference in relation to the reference (P.4).....	36
Table 11: Comparison of LCIA scores of Film 1 and other starch-based polymers.....	37
Table 12: Recommendations for conducting early-stage assessment of bio-based polymers and nanocomposites	41

1. Introduction

1.1. Motivation

Bio-based plastics have emerged as potential substitutes to petroleum-based products. These biomaterials have been traditionally produced from edible crops (e.g. corn), but more recent developments focused on the valorisation of agro-industrial wastes generated in large volumes around the world. Brazil is a major producing country of tropical fruits. It is the 7th largest producer of mangoes in the world (FAO, 2018), having reached a production volume of 1.4 million tonnes in 2018 (IBGE, 2018). The Brazilian semi-arid region has a share of about three-quarters of the national mango production (IBGE, 2018), part of which is used for the industrial production of juice and frozen pulp. It is estimated that around 35-60% of the fruit is wasted in the industry, in the form of peels and seeds (Ayala-Zavala et al., 2011); this residual biomass could be converted in many potential value-added products (Figure 1), amongst them polymeric materials. However, using food waste as raw material for bio-based products is not a guarantee of lower environmental impacts because its conversion processes can have great burdens. Furthermore, the quality of bio-based products still requires improvements when compared to similar fossil-based and mature products.

Thermoplastic starches (TPS) are polymers that became attractive for its cheap, renewable feedstocks and biodegradability property (Broeren et al., 2017a). Poor technical performances have led to TPS reinforcement with nanofillers, yielding nanocomposites (Lambert & Wagner, 2017). Such biomaterials have so far been produced in research and development (R&D) and little is known about their environmental aspects. It is crucial to assess the environmental sustainability of novel products early-on in their development, when there is more flexibility to make changes at low cost, preventing environmental burdens and unsound investments (Buyle et al., 2019; Cucurachi et al., 2018).

Life cycle assessment (LCA) has been applied to evaluate the environmental performance of bio-based plastics, and understand their benefits and trade-offs compared to fossil plastics (Broeren et al., 2017a; 2017b). However, while LCA is a helpful and widely used tool for analysing mature technologies, applying LCA for products at low technology readiness levels (TRL) is not a straightforward task and presents many challenges (Moni et al., 2020). In addition, the direct comparison of mature products, based on large-scale production data, with novel future products, based on laboratory data, can be misleading, due to advantages that industrial production presents (for instance, process optimisation and economies of scale). This usually results in an overestimation of impacts for the novel product in comparison to the commercial product (Piccinno et al., 2016). Furthermore, new technologies and processes typically suffer many modifications during scale-up, which are very difficult to anticipate in the first stages of R&D. To overcome such problems, future-oriented approaches have been proposed for conducting LCA of products at early R&D stages, which involve the application of scale-up modelling and multiple likely scenarios for a future time when the product is forecasted to reach full-scale production.

1.2. Research questions and objectives

Mango seed shells and kernels are the outer and inner parts of the seed (Figure 1), respectively, and currently do not have economic value. R&D projects were carried out at Embrapa Tropical Agroindustry aiming to use these waste materials to develop biopolymer films. Initially, processes were defined at laboratory-scale to extract mango kernel starch (MKS) from seed kernels (Cordeiro et al., 2014) to be used in biopolymers. Starch nanocrystals (SNC) were obtained from MKS and were used as nanofillers to improve film properties (Oliveira et al., 2018). Seed shells, on the other hand, were used to obtain cellulose nanocrystals (CNC) (Silva et al., 2019).

In this thesis, a novel biopolymer film, produced from mango processing wastes, was analysed, considering two alternative formulations: Film 1, developed in laboratory by Oliveira et al. (2018), is composed of a mango kernel starch matrix (MKS) with a 5%wt (starch basis) SNC reinforcement; Film 2, obtained by Silva et al. (2019), is also composed of a MKS matrix but with a 1.5%wt of CNC and 8.5%wt of SNC reinforcement.

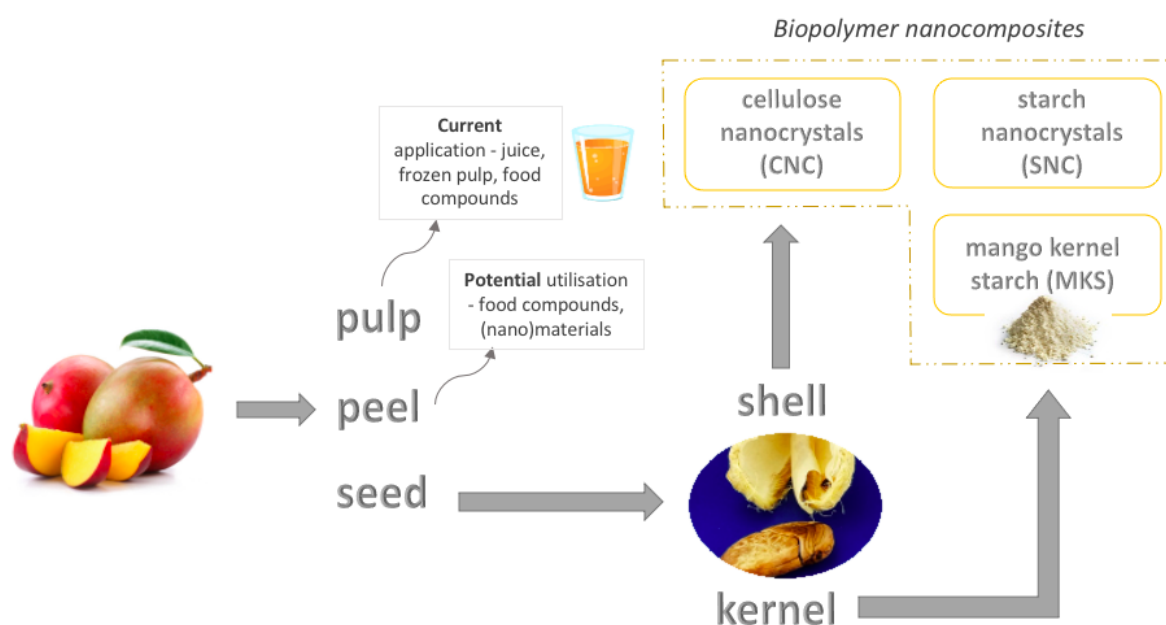


Figure 1: Valorisation of mango processing wastes

The thesis aims to respond to the following research questions:

- How the two biopolymer film formulations, based on mango kernel starch, perform environmentally and how can they be improved?
- How the best-performing biopolymer formulation compares in environmental terms to low-density polyethylene (LDPE), its fossil plastic counterpart?
- Which scenarios, methodological choices, and scale-up assumptions most affect the environmental impacts of the mango-based polymer and its comparison to LDPE?
- What recommendations can be made for assessing bio-based plastics at low TRLs (3-4)?

This study also seeks to contribute to the limited literature on LCA of bio-based plastics performed at early development stages. This is to our knowledge the first early-stage LCA on

100% biologically sourced starch-based polymer film with nanoreinforcement. Previous LCA work on biomaterials derived from mango wastes analysed alternative routes for extracting mango kernel starch (MKS), polyphenols, fat, cellulose, lignin, and pectin from mango seeds and peels (da Silva et al., 2020; de Sá Filho et al., 2020). This thesis builds on these works, delivering four new scaled-up life cycle models: for the production of cellulose and cellulose nanocrystals, for the production of starch nanocrystals, and the production of a biopolymer film based on mango processing wastes in the two formulations.

The aim of this study is to evaluate the potential environmental impacts of a biopolymer film at an early stage of research (TRL 3). More specifically:

- To obtain a scaled-up model for the production of a mango-based biopolymer in two film formulations, and to analyse these formulations, identifying environmental hotspots and improvement opportunities in their production;
- To compare the environmental performance of the best-performing biopolymer formulation and a conventional polymer with similar characteristics – LDPE;
- To analyse which conditions concerning system boundaries, functionality, allocation methods, and manufacturing processes most influence the potential environmental impacts of the biopolymer film, and consequently its comparison to LDPE;
- To identify critical aspects and insights in the life cycle of biopolymers and bionanocomposites that can inform and facilitate future works on early-stage LCA of such materials.

1.3. Dissertation outline

In the next chapter, we provide a background for the thesis work on early-stage LCA and bio-based plastics, and then the state-of-the-art of LCA on biopolymers is discussed, focusing on starch polymers and novel polymers (at early R&D stages). Chapter 3 describes the methods used for obtaining the industrial-scale model, and performing impact assessment and scenario analysis. Chapter 4 presents the results of the study, including laboratory and scaled-up inventories, impact assessment, and scenario and sensitivity analyses. Finally, Chapter 5 presents the conclusions of the study, including limitations and recommendations.

2. Background

In this chapter, concepts and definitions concerning early-stage LCA and bio-based polymers are described, and then a literature review on LCA of biopolymers is presented.

Life cycle assessment (LCA) is a method for analysing the potential environmental impacts associated with a product from a holistic perspective, considering all direct and indirect interactions between product and environment across the product life cycle, from materials acquisition to manufacturing, distribution, use, and final disposal. LCA is applied in four interactive stages: (1) Goal and Scope definition; (2) Life cycle inventory (LCI) analysis; (3) Life cycle impact assessment (LCIA); and (4) Interpretation (Guinee, 2002).

LCA is a useful decision-support tool for sustainable development (Brusseau, 2019), not only for comparing alternatives but also for providing insights for product improvement. For mature technologies, making changes can be very costly and disruptive. Thus, researchers have been moving towards a new approach for assessing products early-on in their development, in a way to anticipate issues before they are consolidated in the product.

2.1. Performing LCA at early R&D stages

Over the course of product development, several decisions are made concerning processing routes, materials, energy sources and so on. These early-on decisions have a far-reaching influence on the future functionality, costs and environmental aspects of the product (Villares et al., 2020); it has been estimated that around 80% of all environmental impacts of a product or process are locked in the design stage (Tischner et al., 2000).

In this context, it becomes clear why it is important for environmental assessments to be performed proactively rather than reactively, i.e. at early development stages. If provided with such information, product developers can prevent regrettable investments, avoid environmental consequences, and make changes without major disruptions (Cucurachi et al., 2018). Besides, LCAs have been increasingly a requirement for funding of new R&D projects (Moni et al., 2020).

Before a new product is ready to be commercialised, it goes through stages of research, development, and deployment. The level of maturity of a technology, i.e. its stage of development can be expressed in terms of Technology Readiness Levels (TRL) (NASA, 2015), in which:

- TRL 1: Basic principle observed and reported;
- TRL 2: Technology concept and/or application formulated;
- TRL 3: Proof of concept in laboratory environment;
- TRL 4: Component and/or system validation in laboratory environment;
- TRL 5: Laboratory-scale system validation in relevant environment (prototyping and modelling of process at pilot- and industrial-scales);
- TRL 6: Engineering/pilot-scale system validation in relevant environment;
- TRL 7: Full scale, similar system demonstrated in relevant environment;
- TRL 8: Actual system completed and qualified through test and demonstration;
- TRL 9: Actual system operated over a full range of expected conditions.

Emerging technologies can be defined as those which are currently at an early stage of their development, hence at TRL below 9 (Buyle et al., 2019; Stahl, 2011). At such stages, products can be assessed implementing a future-oriented LCA, using the so-called ex-ante, prospective and anticipatory LCAs.

Ex-ante LCA was defined by Cucurachi et al. (2018), who stated that ex-ante LCA "explores the future by assessing a range of possible scenarios that define the space in which the technology may operate". Additionally, these authors put forward a second, more specific definition, considering ex-ante studies those that "scale-up an emerging technology using likely scenarios of future performance at full operational scale, and that compare the emerged technology at scale with a mature product serving the same (or similar) function". This definition necessarily entails the upscaling of the emerging technology analysed, thus studies based on laboratory data only are not therein included.

Prospective LCA, in its turn, was defined by Arvidsson et al. (2018) who stated that an LCA is prospective "when the (emerging) technology studied is in an early phase of development (e.g., small-scale production), but the technology is modelled at a future, more-developed phase (e.g., large-scale production)". In the early days of LCA, consequential LCA modelling was sometimes called prospective, and because of that, some authors avoid using this term (e.g. Buyle et al., 2019). On the other hand, in many recent studies, this term was preferred in the context of LCA of emerging technologies (Bartolozzi et al., 2020; Piccinno et al., 2018; Zackrisson et al., 2019), including studies that proposed methodological guidance for prospective LCAs (Thonemann et al., 2020).

At last, anticipatory LCA has been defined by Wender et al. (2014) as a "forward-looking, non-predictive tool that increases model uncertainty through the inclusion of prospective modelling tools and multiple social perspectives". The differential feature of anticipatory LCAs seems to be the integration of decision-theory techniques (Cucurachi et al., 2018); since anticipatory LCA aims is to achieve responsible research and innovation, stakeholders values and social perspectives should be included (Wender et al., 2014).

There is little consensus across the literature on the definition and differentiation of ex-ante, anticipatory, and prospective LCAs. Buyle et al. (2019) concluded that the difference between these assessment types is subtle and not consistent, but suggested that ex-ante and prospective approaches are the same - or at least very similar -, while anticipatory LCA includes social perspectives. For Cucurachi et al. (2018), prospective and anticipatory LCA (and also others, see Table 1) are modes under the broad definition of ex-ante LCA previously mentioned, though with different focus. Furthermore, since these assessments were performed before gaining proper definitions, some authors did not distinguish them, while others abstained from applying any of these terms, using words like 'early-stage', 'early-on', and 'LCA of emerging technology'.

Type	Focus / Operating mode
Prospective	Studies that analyse future technological systems and their environmental implications, as opposed to retrospective ex-post studies dealing with existing information and technologies

Anticipatory	Studies in which a specific focus is placed on integrating in the assessment techniques of decision-theory that should allow for the explicit inclusion of the values of decision-makers in the analysis
Consequential	This approach models the effects determined by changes in the technology landscape, e.g. as a consequence of the introduction of a new technology, or as a consequence of changes in policies
Dynamic	The term stresses the importance of improving the accuracy of LCA by addressing the temporal component not only of technological developments but especially of emissions and the related impacts
Mixed	Applications falling in this category combine criteria and features that cross the boundaries of the single types above defined

Table 1: Conceptualisation of ex-ante assessment modes. Source: adapted from Cucurachi et al. (2018)

Conducting LCA at early stages at times means facing issues in inventory development, definition of functional unit and assumptions required to estimate future developments and uses of the novel product (Cucurachi et al., 2018). Researchers have identified the following attention areas that pose challenges in ex-ante LCA: data availability, scaling issues, comparability, uncertainty and its communication, and assessment time (Hetherington et al., 2014; Moni et al., 2020; Thonemann et al., 2020). To overcome such challenges, it is recommended to use multiple scenarios varying the relevant elements, which can be related to scale-up assumptions, functional units, system boundaries, impact methods and so forth.

2.2. Bio-based plastics

Bio-based plastics are polymers produced from a variety of renewable sources (biomass), and they can be biodegradable or not. Some forms of these materials have been used for decades and even centuries (referred to as 'old economy' bio-based polymers in Figure 2), while others only recently entered the market ('new economy' bio-based plastics). There is conflicting information in the literature about the difference between bioplastics, bio-based plastics and biodegradable plastics; in this work, the classification adopted is shown in Figure 2.

Similarly to biofuels, bio-based plastics or polymers can be produced from three categories of feedstocks: 1st generation feedstock, generally based on edible crops; 2nd generation, obtained from residues and by-products; and 3rd generation, which relates to algal biomass (Lee & Lavoie, 2013).

Food crops such as corn and sugarcane have been traditionally used for the production of bioplastics, but concerns about land use competition and increasing food prices has reduced interest in such feedstocks. Even though only a small portion of available land is used for the production of biomaterials, the growing use of biomass for biofuels and plastics has increased the need for optimal utilisation of biomass (Molenveld et al., 2015), for instance by increasing productivity and valorising side- and waste-streams. The use of residues and by-products as feedstock requires increased knowledge on optimal use of plants (biocascading) and technologies for isolating their various components (biorefining) (Molenveld et al., 2015).

	Durable	Biodegradable	
Bio-based	Cellophane	Natural rubber	Old economy
Bio-based	Bio-PE, Bio-PET	PLA, PHA/PHB, <u>Starch plastics</u>	New economy
Fossil-based	PE, PP, PVC	PBAT, PBS, PCL, PVOH	

Figure 2: Bio-based, biodegradable and bioplastics. Source: adapted from Spierling et al. (2018) and Endres & Siebert-Raths (2011)

Food packaging applications, especially for fresh food, are of particular interest for bio-based materials since technical properties such as breathability and permeability make them suitable for fruit and vegetable packaging. Moreover, if these materials are compostable, they offer advantages for retailers at the end-of-life since expired products and packaging can be discarded together for composting, reducing costs in waste removal and labour (Molenveld et al., 2015).

2.2.1. Starch plastics

Starch plastics are polymers that became attractive for being produced from cheap and renewable sources, besides its potential biodegradability (Figure 2). Pure starch plastics are brittle, absorb moisture, and difficult to process. Therefore, their structure first needs to be disrupted using water, heat, and typically plasticisers to yield thermoplastic starch (TPS), which can be processed like other plastics, e.g. by extrusion, injection moulding, etc. (Avérous, 2004; Broeren, 2017a; Lambert & Wagner, 2017; Le Corre et al., 2010). In comparison to fossil plastics, TPS has several drawbacks, such as water sensitivity and weak mechanical properties. To overcome these issues, two main strategies have been adopted: mixing them with fossil or bio-based polymers, forming starch blends; or reinforcing them with natural fibres (cellulose, lignin), generating biocomposites (Avérous, 2004). More recent efforts have focused in improving the functionality of starch polymers by incorporating nano-sized fillers, forming bionanocomposites (Lambert & Wagner, 2017). Currently commercial forms of TPS appear to be only available in the form of blends, i.e. mixtures with other polymers often fossil-based, resulting in a loss of biodegradability (Lambert & Wagner, 2017). On the other hand, natural fibres and nanofillers do not seem to affect the biodegradability of biopolymers and in some cases can even improve this property (Mousa et al., 2016).

Nanocomposites are composed of a polymer matrix and a nano-sized (1-100nm) filler. Several starch nanocomposites formulations have been tested in R&D (for instance Ilyas et al., 2018; Kargarzadeh et al., 2017; Müller et al., 2011; Silva et al., 2019). Common nanofillers are carbon nanotubes, nanoclays, and nanocellulose. Nanocellulose is a naturally-derived nanomaterial that has been widely used for industrial applications. They are synthesised through bottom-up processes using bacteria (bacterial nanocellulose – BNC), or top-down approaches, which result in cellulose nanofibers (CNF) and cellulose nanocrystals (CNC) (Hubbe et al., 2017; Rana et

al., 2017). The last two have been used as nanofillers in biopolymer matrices; CNC, for instance, has been found to improve strength, elasticity and water vapour barrier of starch films (Silva et al., 2019), as well as thermal stability (Kargarzadeh et al., 2017), swelling and enzymatic degradation (Nessi et al., 2019). Another nanoparticle obtained from biological sources are starch nanocrystals (SNC), which can be produced by acid hydrolysis of starch from various sources; these have also been used to reinforce biopolymers (e.g. Oliveira et al., 2018).

2.3. LCA of biopolymers

Bio-based plastics have been the subject of many LCA studies. In this section, a summary of LCA findings will be presented based on the two most recent review papers on the subject (Spierling et al., 2018; Walker & Rothman, 2020) and then focus will be given to LCA on starch polymers and bionanocomposites.

Spierling et al. (2018) conducted a literature review with the goal of assessing environmental, social and economic aspects of bio-based plastics. Since there were very few studies on the last two, these authors focused on environmental LCA (e-LCA). Their findings are summarised below:

- **Types:** most studies available focus on PLA and PHAs.
- **Feedstock:** majority of polymers were based on 1st generation feedstock - mainly corn, sugarcane. Few studies focused on residues and by-products, mainly corn stover.
- **Boundaries:** cradle-to-gate studies outweighed cradle-to-grave;
- **Functional unit (FU):** predominant is 1 kg of plastic; few studies use a FU applied to a product (e.g. 1000 water bottles);
- **Biogenic carbon:** most studies considered carbon uptake at cradle-to-gate point, for both biodegradable and durable biopolymers;
- **Land use change:** most studies did not include emissions from land use change;
- **Multi-functionality:** various allocation approaches – partitioning (mass, economic, exergetic, starch content); or system expansion;
- **Impact assessment:** global warming potential (GWP) was the most assessed indicator amongst studies, followed by non-renewable energy use (NREU).

Concerning impact assessment, a broad range of results was found for bio-based polymers – e.g. GWP: -0.3-11.9 kg CO₂-equivalent/kg of material and NREU: 1.1-92 MJ/kg material. Spierling et al. (2018) pointed out that there was a large bandwidth of values associated to different feedstock sources, considerations of biogenic carbon uptake, allocation methods and credits, and end-of-life assumptions. Moreover, the non-inclusion of land use change (LUC) emissions and the consideration of biogenic carbon as a negative emission in some studies have resulted in significantly reduced carbon footprints in bio-based materials, even negative values (e.g. Kim & Dale, 2008).

Spierling et al. (2018) also compared bio-based plastics to fossil polymers across different studies and concluded that in general bio-based plastics have lower non-renewable energy use than petroleum-based plastics, but higher acidification and eutrophication. Similar trade-offs were observed by Tsiropoulos et al. (2015), who concluded that even though lower GHG emission reductions can be achieved for bio-based plastics in relation to their fossil

counterparts, this happens at the expense of increased impacts in other impact categories. Furthermore, Spierling et al. (2018) found a considerable variation of impact values due to methodological choices and highlighted that standard guidance and/or joint product category rule (PCR) for fossil and bio-based plastics could enhance the comparability between them.

Walker & Rothman (2020) analysed the state-of-the-art of LCA of bio-based and fossil-based polymers with a focus on the European Product Environmental Footprint (PEF) standards. These authors compared selected studies – those that at least partly complied with the PEF standards, which corresponded to 50 biopolymers and 39 fossil-based polymers. It was noted that even when analysing the same polymer with the same scope, large variations of impact scores were still found (in the order of 200-400%). These variations were associated to several differences in the LCA assumptions, particularly concerning end-of-life treatment, biogenic carbon and allocation of multi-functional processes, even though the selected studies adopted in the most part the methodological choices required in the PEF. Further, these authors concluded that it was not possible to find best performing polymer types nor to suggest whether bio-based or fossil-based performed better in any impact category, in contrast with the conclusions of Spierling et al. (2018).

For Hottle et al. (2013), bio-based and petrochemical plastics performed similarly, partly due to biopolymers being relatively new to the market. They argued that biopolymers have more room for improvement, for example, through productivity gains, thus technological advancement and economies of scale could favour biopolymers in the future.

2.3.1. Evaluation of starch polymers and nanocomposites

Few LCA studies focused on starch plastics, and most of them were based on laboratory synthesis and assessed at lab-scale. Razza et al. (2015) analysed starch foams prototypes obtained from different feedstocks in Thailand and Europe from cradle-to-grave, and compared them to fossil-based foams. They found that using European maize and potato starch increased the burdens associated to the film when compared to Thai cassava, which the authors attributed to the different agricultural practices in Thailand and Europe (e.g. manual labour vs. agricultural machines). In addition, they found that the starch foam performed better than the fossil-based foam in 5 out of 7 environmental indicators, and offered energy and carbon savings in relation to its fossil counterparts, but had higher eutrophication and acidification potentials. De Léis et al. (2017) performed a cradle-to-gate LCA of cassava starch film. In this case, a mixture of small-scale and large scale data was used – for the agricultural production of cassava, the isolation of starch and other inputs, commercial-scale data was used, while for the production of film, experimental data based on the casting film production technique was used. Not surprisingly, the manufacturing of film had substantial contributions in some impact categories (e.g. 73% of GHG emissions), due to a high consumption of electricity from laboratory equipment. Moreover, a sensitivity analysis showed that film production by extrusion improved most (5 out of 6) of the environmental indicators than by casting, which speaks more to the different scales of each process than to the environmental performances of the two techniques. Industrial-scale LCAs analysed TPS mixed with other plastics. Broeren et al. (2017a) studied various starch blends, focusing in comparing two different feedstocks: potato starch and reclaimed starch from potato processing wastewater. Currently, this is the only LCA that

analysed starch plastics from waste-streams. This study found that blends produced from reclaimed starch had lower impacts than from virgin starch, showing small reductions for GWP and NREU (less than 10%), but substantial for eutrophication (up to 40%) and agricultural land use (up to 60%). Additionally, they found that additives (e.g. plasticisers, fillers) which are many times considered negligible in LCA studies could have large contributions to the environmental impacts of biopolymers (up to 40% in this study).

Very few nanocomposites have been assessed in LCA since they are actually very recent products. Lorite et al. (2017) analysed PLA-nanoclay packaging systems for fresh-cut fruits, but based on mixed (laboratory and industrial) data without scale-up implementation.

2.3.2. Early-stage LCA of novel bio-based polymers

To our knowledge there are no early-stage LCAs on novel starch polymers. Concerning novel biopolymers in general, two studies stood out. Fernández-Dacosta et al. (2015) analysed the production of polyhydroxyalkanoates (PHAs) from wastewater in three different systems in an ex-ante LCA combined with techno-economic analysis. These authors used simulation software to scale-up data from lab and pilot-scales to industrial-scale and analysed the projected impacts of the biopolymers on non-renewable energy use and climate change. In addition, Tecchio et al. (2016) proposed a scale-up protocol for novel biopolymers based on five steps: (1) choice of reference polymer; (2) pilot scale production and assessment; (3) industrial assessment of the reference polymer; (4) stoichiometric baseline; (5) scale up function definition. These authors have applied such protocol to analyse the production a bio-based polybutylene succinate (bio-PBS), comparing the potential impacts of pilot-scale and industrial-scale production, and comparing the latter to the production of a commercial plastic (PET). This protocol represented an effective and effortless way to scale-up a pilot-production that can be easily applied to other biopolymers, but requires a pilot plant production, which is only reached at a later stage of development.

Another important methodological contribution was the engineering-based framework proposed by Piccinno et al. (2016) for scaling up chemical processes at laboratory stages (TRL 3-4). The framework consisted of five steps: (1) laboratory protocol (as a starting point); (2) design of plant flowchart; (3) scale-up of each individual process; (4) linkage of process steps; (5) LCA. This method was later applied in case studies by Bartolozzi et al. (2020) and Piccinno et al. (2018).

Even though no ex-ante LCAs were found for bio-based nanocomposites, many have been conducted for nanomaterials, which are potential nanofillers. Thonemann et al. (2020) has identified in the literature 44 case studies of prospective LCA, 11 of which focused on nanomaterials. This included carbon nanotubes, graphene, nanosilver, nanocellulose and so on. Four of these studies focused on nanocellulose (Arvidsson et al., 2015; Bartolozzi et al., 2020; Piccinno et al., 2018; Tan et al., 2018).

Piccinno et al. (2018) analysed a future production of cellulose nanofibers (CNF) produced from carrot waste. According to the authors, this CNF could be used for nanoreinforcement in composites, although they did not consider this application in the model. The scale-up allowed for comparison of CNF to other fibres on same-weight basis and showed that CNF could perform better environmentally than carbon fibres, but had more burdens than glass fibres.

Moreover, the main hotspots of CNF production were solvent, heat and electricity consumption. As for cellulose nanocrystals (CNC), these have so far only been analysed in one study (Tan et al., 2018) but in the form of foams; besides that, only laboratory scale-based LCAs on CNC are available in the literature (e.g. de Figueirêdo et al., 2012), which is also the case for starch nanocrystals (LeCorre et al., 2013).

Currently, LCA can only provide limited information on the life cycle impacts of nanocomposites. Some types of nanoparticles released during usage and disposal of these products are believed to have adverse effects on human health and ecosystems quality, as for instance respiratory issues and toxicity (Roman, 2015), but these effects are yet to be unravelled. Lack of life cycle information and LCIA methods that assess toxicological impacts of nanoparticles are major barriers to performing full-LCAs on nanoenabled products, and to actually capturing their overall benefits and burdens (Bauer et al., 2008; Hetherington et al., 2014). Nevertheless, there is ongoing investigation on the release of nanofillers from polymer matrixes (see Lankone et al., 2017) and including nanoparticles in toxicity models (Salieri et al., 2019) which could increase completeness of such studies.

3. Materials and methods

The research strategy applied in this thesis is described in Figure 3. Following the definition of goal and scope, experimental data was collected from a series of studies (Table 3). Laboratory-scale data was scaled-up using an engineering-based tool (Piccinno et al., 2016). A plant flowchart was drawn and then each unit procedure was calculated, which were then integrated. Once the scale-up was concluded, impact assessment for two biopolymer film formulations (Table 2) was carried out to identify hotspots and improvement opportunities. The biopolymer formulations were compared and the best-performing one was then compared to a fossil polymer, LDPE. A series of scenario and sensitivity analysis were performed. Finally, conclusions and recommendations were presented.

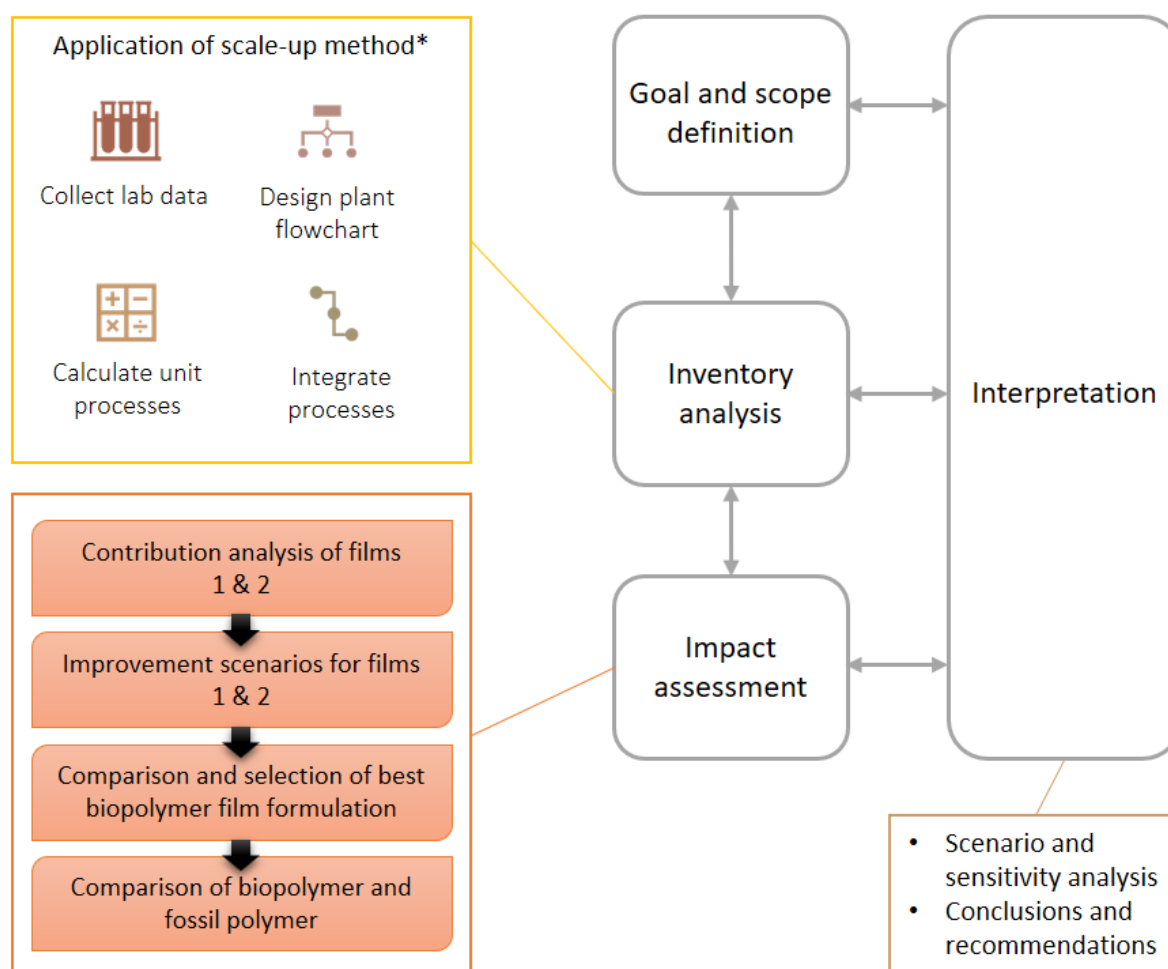


Figure 3: Strategy adopted in the early-stage LCA. Partially adapted from ISO (2006)

3.1. Goal and scope definition

The goal of this study is to assess the potential environmental impacts associated with the future production of a biopolymer film produced from mango wastes, and also to compare this novel biomaterial to its fossil counterpart, LDPE.

Two formulations based on a mango kernel starch (MKS) matrix produced in laboratory (reference in Table 3) were analysed, based on the studies of Oliveira et al. (2018) and Silva et

al. (2019). These formulations contained different nanoreinforcement and had similar properties (Table 2).

	Unit	Film 1	Film 2
Composition			
Starch (MKS)	%	77.4	74.3
Glycerol	%	19.4	18.6
SNC	%	3.9	6.3
CNC	%	-	1.1
Property			
Tensile strength	MPa	17.51	16.68
Elongation at break	%	11.15	10.35
Elasticity module	MPa	1466.2	1299
Water vapour permeability	g.mm.kPa-1.h-1.m-2	1.21	1.27
Source		Oliveira et al. (2018)	Silva et al. (2019)

Table 2: Characteristics of the mango-based biopolymer - Films 1 and 2

The functional unit adopted was of 1 kilogram of biopolymer film for a cradle-to-gate system boundary. For the comparison to LDPE, besides the 1-kg basis comparison, material replacement ratios were also considered (section 3.4). In a reference situation, the processes included for each biopolymer film are shown in Figure 4. For film production, the casting technique was considered as reference.

Alternative scenarios were analysed (section 3.5), considering mango seed as by-products of mango pulping, with the inclusion of crop production and pulping. In addition, another potential film manufacturing technique (extrusion) was considered.

The main data sources used in this study are listed in Table 3.

Process	Source
Experimental data	
Production of cellulose fibres, from mango seed shells, and fibre treatment	da Silva et al. (2020); Silva et al. (2019)
Isolation of cellulose nanocrystals (CNC), from mango seed shell cellulose fibres	Silva et al. (2019)
Production of biopolymer film formulation 1	Oliveira et al. (2018)
Production of biopolymer film formulation 2	Silva et al. (2019)
Production of starch nanocrystals (SNC) from mango kernel starch	Oliveira et al. (2018)
Scaled up data	
Mango washing and pulping	
Separation of seed components	de Sá Filho et al. (2020)
Production of mango kernel starch	
Agro-industrial data	
Mango seedling production	
Mango cultivation	Müller Carneiro et al. (2019)
Other	
Low-density polyethylene	
Film extrusion	Ecoinvent database
Chemicals and plasticiser	

Electricity, heat and steam
 Infrastructure
 Transport
 Waste treatment

Table 3: Data sources for the production of mango waste-based biopolymer film

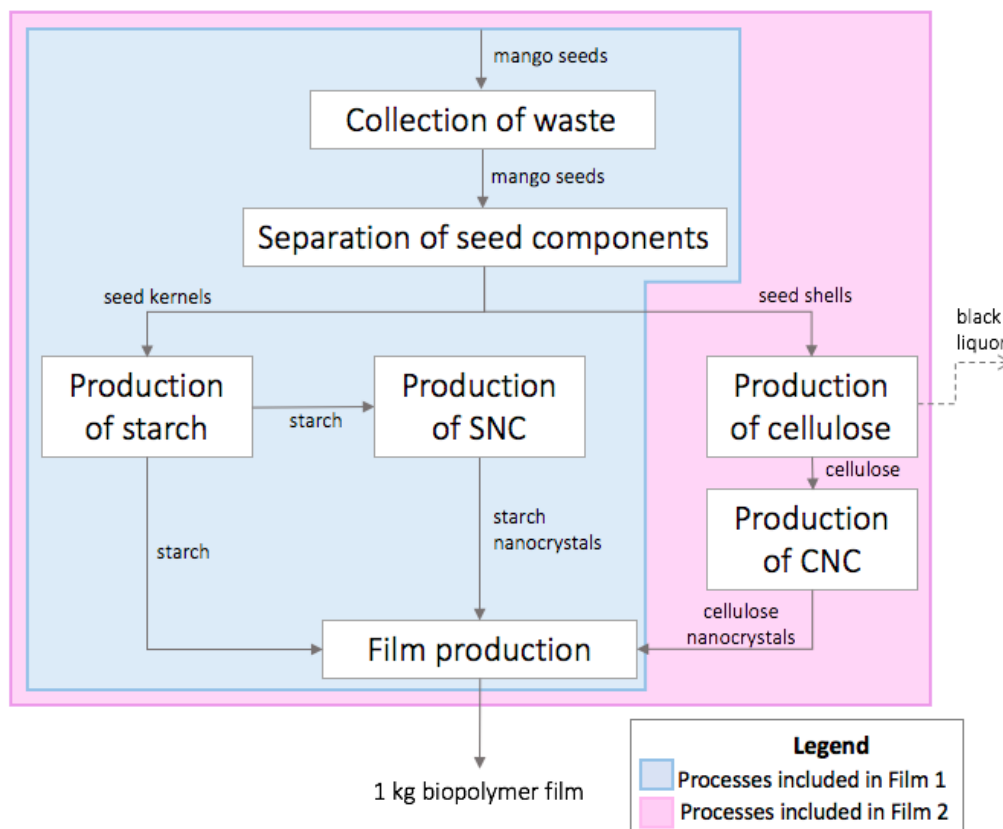


Figure 4: Flowchart of the production of biopolymer film - Film 1 and 2

3.1.1. Description of laboratory processes

Mangoes at ripening stage of the cultivar Tommy Atkins were pulped and their seeds (or stones) decorticated, separating the seed shells (outer layer) and kernels (inner part). Mango kernel starch (MKS) was extracted from kernels as well as SNC, while cellulose and CNC from shells. The film formulations used starch as matrix and CNC and/or SNC as fillers.

To obtain mango kernel starch (MKS), the following steps were taken: oxidation inhibition, drying and grinding, purification, alcohol treatment, and drying (Cordeiro et al., 2014; de Sá Filho et al., 2020).

Part of the MKS produced was used for the isolation of starch nanocrystals (SNC). SNC were obtained by acid hydrolysis (Figure 5), followed by six neutralisation cycles (centrifugation-homogenisation-ultrasonication), dialysis, and final homogenisation (Oliveira et al., 2018). In each stage, there was some loss of nanocrystals – in the effluent for each centrifugation, and as biowaste for the other processes.

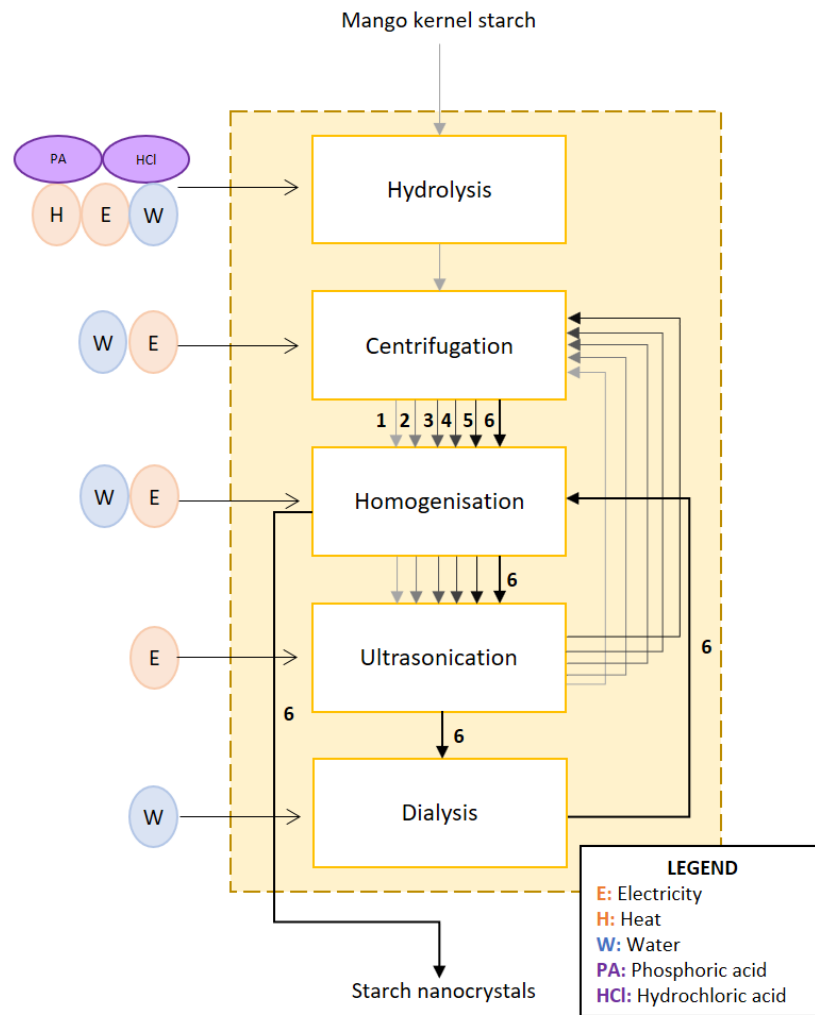


Figure 5: Isolation of starch nanocrystals

For obtaining cellulose nanocrystals from mango seed shells (Figure 6), according to Silva et al. (2019), first cellulose fibres were isolated from lignin, and then fibres were treated to obtain cellulose powder. Cellulose was then hydrolysed with a mixture of sulphuric and hydrochloric acids to remove amorphous regions, obtaining nanocrystals. Then, the CNC suspension was neutralised in cycles of centrifugation and homogenisation. Lastly, CNC was sonicated and the remaining acid was removed by dialysis until the suspension reached constant pH. Similarly to SNC production, losses of cellulose nanocrystals occurred at each stage. At the end, both CNC and SNC were kept in suspensions of 2% and 2.3% in weight, respectively.

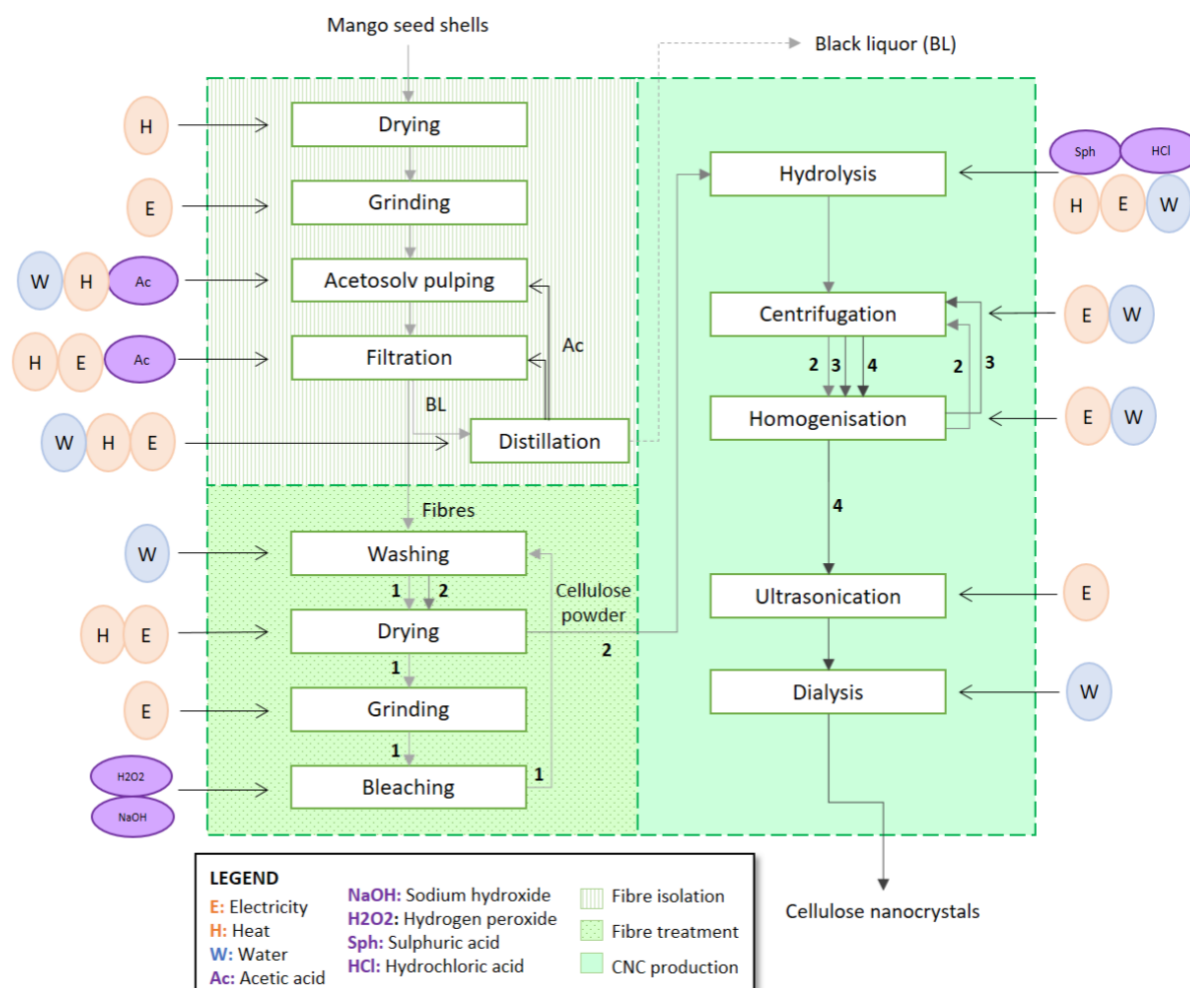


Figure 6: Cellulose production and cellulose nanocrystals isolation

Two formulations developed and selected by Oliveira et al. (2018) and Silva et al. (2019) for having an optimal combination of properties were analysed. This corresponded to a MKS matrix reinforced with 5% SNC (starch basis) - Film 1, and a MKS matrix reinforced with 8.5% of SNC and 1.5% CNC - Film 2, respectively. In line with these authors, for the production of the biopolymer film, the following steps were carried out: gelatinisation, plasticising, homogenisation, addition of nanoparticles, degassing, and film casting (Figure 7). No heating source was used for the casting process, i.e. the film was left to dry naturally.

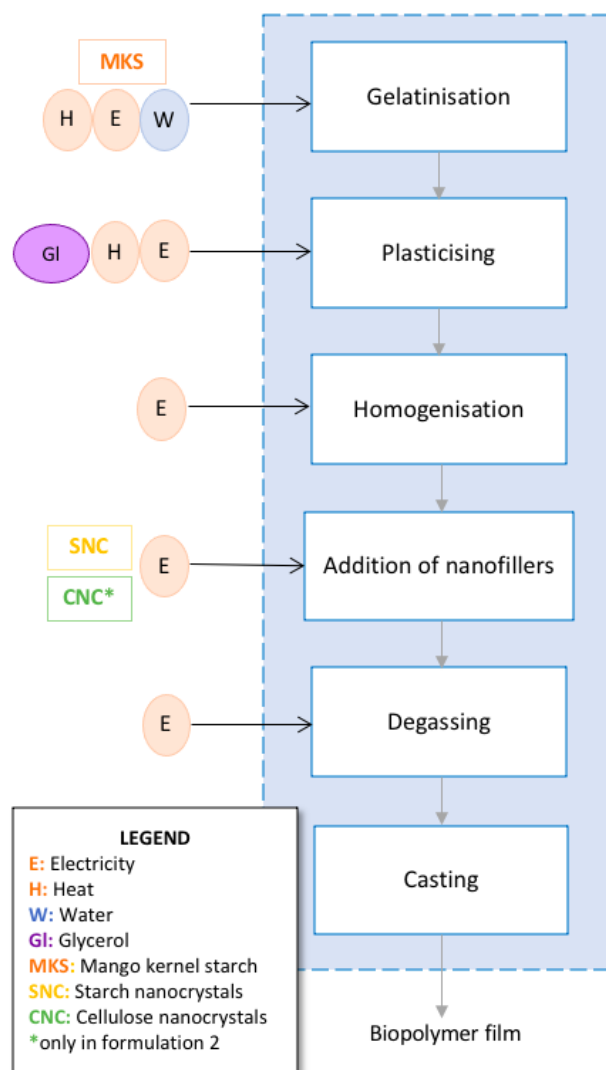


Figure 7: Biopolymer film production

3.2. Inventory analysis and scale-up

The extraction of cellulose and CNC from mango seed shells, the extraction of SNC from mango kernel starch, and the production of biopolymer films were modelled at industrial-scale, following the experiments listed in Table 3. To obtain additional information not available in those studies (i.e. amounts of water added, and effluents and biowaste discarded in each step), interviews were conducted with the respective authors. Inventory data for the production of MKS had been previously scaled-up (reference in Table 3), as well as mango pulping and separation of seed components. This data was used in the SNC and biopolymer film manufacturing models.

The scale-up tool proposed by Piccinno et al. (2016) was used for the industrial-scale modelling. Starting from the laboratory protocols, a plant flowchart was designed (Figure 8), then each unit procedure was scaled-up and then the processes were integrated. Scale-up of unit processes was based on expert opinion, engineering-based calculations or average industrial data. Raw materials were linearly scaled and a 20% reduction of solvent was applied – except for the stages of hydrolysis for SNC and CNC. The same yields obtained in the laboratory were

maintained in the scale-up. Heat and electricity requirement for different processes were calculated using a series of equations provided by Piccinno et al. (2016), including:

- Drying
- Heating (fluid)
- Centrifugation/filtration
- Stirring/homogenizing

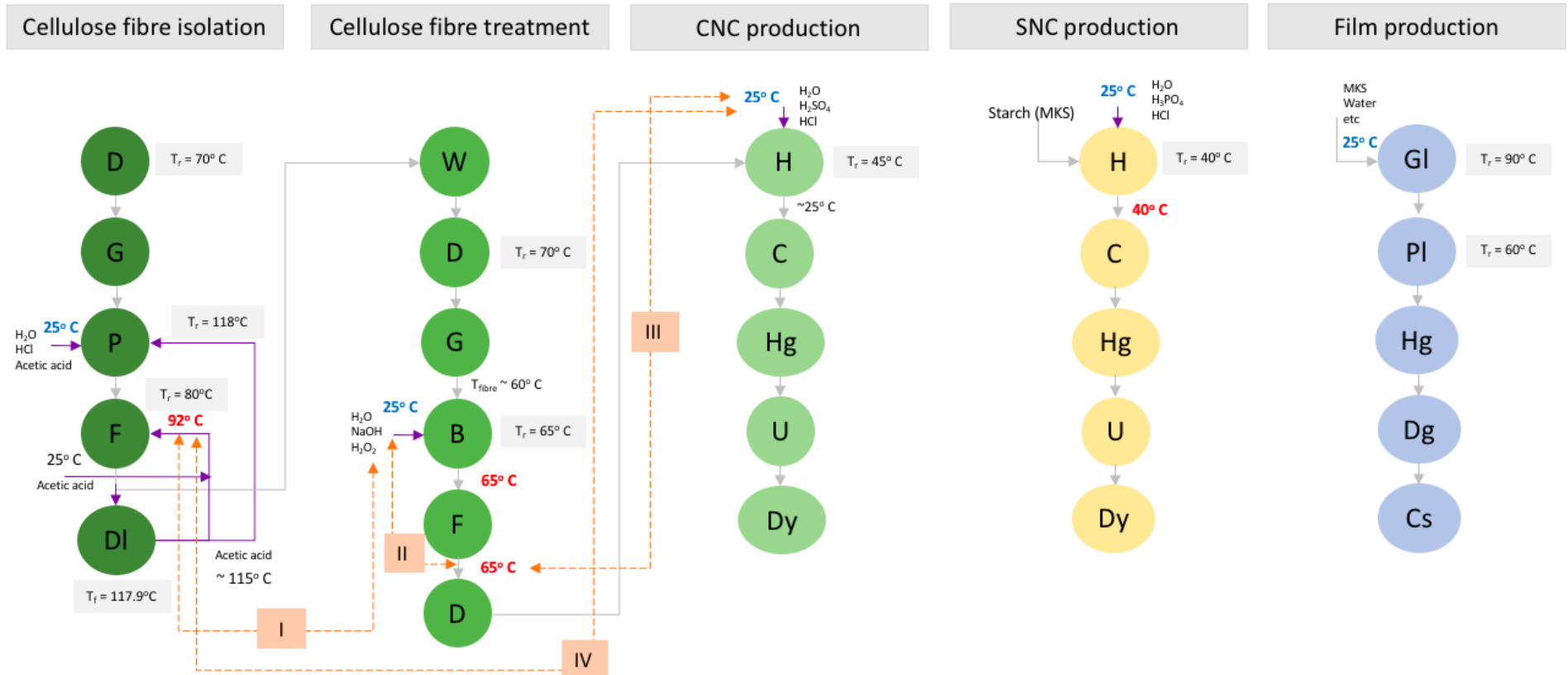
It was assumed that 10% of the mangoes produced in the Sao Francisco valley, the main producing region of this fruit in Brazil, was used for the production of juice in line with de Sá Filho et al. (2020). Hence, about 10,696 tonnes of mango seeds per year was considered available as starting material. That way, a total of 3,600 kg of mango seeds per batch would be processed to obtain cellulose and then cellulose nanocrystals, following the value obtained by de Sá Filho et al. (2020) for the separation of seed components. The cellulose fibre treatment (Figure 6) was slightly modified in the scale-up: in the laboratory, the fibres were washed and dried, but we assumed that there was a filtration step before drying to remove water in excess – the water/fibres ratio was about 17-, since drying is an energy intensive process. It was assumed that the drying process removed a mass of water equal to the mass of dried fibres. Then, for the production of cellulose nanocrystals, it was considered that all cellulose fibres generated in the fibre treatment process were used for the isolation of CNC by acid hydrolysis - a total of 918.5 kg of cellulose per batch. For the two drying steps that occurred in cellulose production, a tray dryer with a 85% energy efficiency was considered (Sanjuán et al., 2014).

To build a large-scale model for the starch nanocrystals production, we assumed only a small part of the starch produced would be further processed to SNC, since starch is needed in larger quantities to compose the film matrix. That way, only the mass of MKS necessary to produce the SNC used in the film formulation ($SNC/MKS = 8.5/100$, in Film 2) entered the SNC scaled-up model, around 530 kg MKS per batch.

After each film component were produced, starch, CNC, SNC, glycerol, and water were mixed together to form the biopolymer. A loss of 3% of film was considered in the large-scale model, based on this information for plastic extrusion in the ecoinvent database.

Two processes could not be scaled-up using this scaled-up method: ultrasonication (in CNC and SNC production) and degassing (film production). For the first, the average power of 225 Watts/Litre obtained from Arvidsson et al. (2014) was applied, while for the second the electricity data considered in Piccinno et al. (2018) for cellulose nanofibers was used as a proxy. All equations and parameters used for upscaling cellulose, CNC, SNC, and film production are presented in appendix A.

Once the energy requirements of each step were calculated, it was time to integrate the unit processes. Two heat recovery routes were considered, routes II and IV in Figure 8. The hot liquid streams that leave distillation (cellulose fibre isolation) and filtration (fibre treatment) were used to preheat the fluid entering filtration (fibre isolation) and bleaching, respectively. The new temperatures of these processes were calculated using thermal equilibrium equations; in both cases, a 75% efficiency heat exchanger was considered.



Legend

D: Drying; G: Grinding; P: (Acetosolv) Pulping; F: Filtration; DI: Distillation; W: Washing; B: Bleaching; H: Hydrolysis; C: Centrifugation; Hg: Homogenising; U: Ultrasonication; Dy: Dialysis; Gl: Gelatinisation; Pl: Plasticising; Dg: Degassing; Cs: Casting. T_r: Temperature required at the stage; Temperatures in **red**: excess heat; Temperatures in **blue**: requires heating. Grey arrows: main product flow; **Purple** arrows: Reagents/water; **Orange** arrows: potential heat recovery routes.

Figure 8: Plant flowchart including potential heat recovery routes

Finally, generic infrastructure data from ecoinvent ('Chemical factory, organics') was included in the model, as well as electricity for pumping whenever there was a fluid being transferred between reactors, as instructed by Piccinno et al. (2016). Furthermore, road transport was considered for delivering mango seeds from the juice factory to the biopolymer factory and for transporting mangoes from the field to the juice factory (only in scenario b - section 3.5).

3.2.1. Allocation

For the processes that generated two or more co-products, mass allocation was applied for the reference scenario. In the process of seed components separation, burdens were divided by seed shells and kernels; in cellulose fibre production, by cellulose fibres and lignin content in the black liquor generated in the filtration step. In scenario b (section 3.5), mass allocation was applied and the burdens from mango pulping and agricultural phase were distributed to pulp, seeds, and peels. Furthermore, economic allocation was also considered in a sensitivity analysis. Since peels and seeds do not have economic value, prices of materials with similar compositions were used: the value of apple peel was used for mango peel as these are both sources of pectin, for seed kernels price of corn (source of starch) was applied, and for seed shells the value of wood sawdust, another source of cellulose, was used. Allocation factors are shown in Table 4.

Co-products	Mass allocation	Economic allocation
<u>Fibre production</u>		
Fibre	64.3%	65.7%
Black liquor (lignin)	35.7%	34.3%
<u>Mango pulping</u>		
Pulp	55.5%	83,3%
Peel	22.5%	8,4%
Seed	22.0%	8,3%
<u>Separation of seed components</u>		
Seed shell	50.1%	40,1%
Seed kernel	49.9%	59,9%

Table 4: Allocation factors used for the stages of fibre production, pulping and seed separation

3.3. Impact assessment

The following impact categories were selected for the impact assessment: climate change (CC), non-renewable energy use (NREU), terrestrial acidification (TA) and freshwater eutrophication (FE). For climate change, the IPCC 2013 100-years method was used and a biogenic carbon neutrality approach was adopted (Pawelzik et al., 2013); for non-renewable energy use, the Cumulative Energy Demand (CED); and for acidification and eutrophication, the ReCiPe Midpoint Hierarchical was applied. The impact categories were selected considering the LCAs on bio-based and fossil-based plastics previously reviewed in this thesis, whereas for the LCIA methods selection, the European Commission Joint Research Centre recommendations (EC-JRC, 2011; Fazio et al., 2018) were taken into account. The impact modelling was performed using the SimaPro software.

In the LCIA phase, first each biopolymer film was analysed separately to understand the contribution of film components and production processes to its potential environmental impacts. Next, some process changes were introduced to improve the performance of the films, and then the two formulations were compared to select the film with best environmental performance. The selected biopolymer film, on its turn, was compared to a commercial polymer (LDPE), on a 1-kg basis and considering material replacement ratios (see 3.4).

3.4. Analysis of replacement ratios when comparing biopolymer and LDPE

To compare the biopolymer film to LDPE considering their technical differences (Table 5), we analysed replacement ratios (RR, in kg biopolymer/kg LDPE) based on a functional unit of 1 m² of film (Figure 9), aiming at identifying for which RR the biopolymer film had the same GWP as LDPE. Equations 1-3 were used to determine this value.

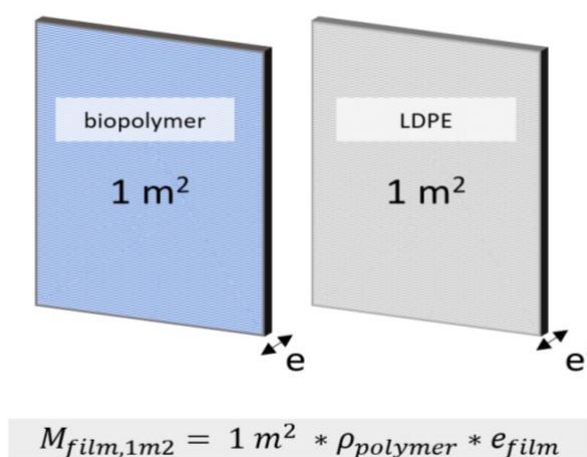


Figure 9: Functionality of polymer films

Polymer	e (μm)	TS (MPa)	EB (%)	EM (MPa)	WVP (g.mm.kPa-1.h ⁻¹ .m ⁻²)	ρ (kg/m ³)	Source
<u>Mango-based film</u>							
Neat TPS	60.0	9.30	22.85	659	1.37		Oliveira et al. (2018)
Reinforced 5%SNC*	60.0	17.51	11.15	1466	1.21		Oliveira et al. (2018)
						1070	Abera et al. (2020)
TPS (other feedstocks)						1190	Müller et al. (2012)
						1130	Average value
<u>Low-density polyethylene</u>							
Sample	636.9	15.34	207	265	0.02		Tested in laboratory
Standard values**	25.4	23.60	205	370	n.a.		ASTM (2000)
						910	Plastics Europe
LDPE (generic)						940	Plastics Europe
						925	Average value

*percentage on starch basis; n.a.: not available; **values for ASTM D882-00; e: Thickness; TS: Tensile strength; EB: Elongation at break; EM: Elasticity modulus; WVP: Water vapour permeability; ρ: Density.

Table 5: Properties of the biopolymer and LDPE

Equation 1:
$$GWP_{polymer, 1m^2} = GWP_{polymer, 1kg} * M_{film, 1m^2}$$

Where:

- $GWP_{polymer, 1m^2}$ – Global warming potential referent to 1 m² of film (kg CO₂eq/m²)
- $GWP_{polymer, 1kg}$ - Global warming potential for 1 kg of polymer film (kg CO₂eq/kg)
- $M_{film, 1m^2}$ - Mass of film used to cover a 1 m² area (kg)

Equation 2:
$$RR = \frac{M_{biopol, 1m^2}}{M_{LDPE, 1m^2}} = \frac{\rho_{biopol} * e_{biopol}}{\rho_{LDPE} * e_{LDPE}}$$

Where:

- RR - Replacement ratio (kg LDPE/kg biopolymer)
- $M_{LDPE, 1m^2}$ - Mass of LDPE film covering a 1 m² area (kg LDPE)
- $M_{biopol, 1m^2}$ - Mass of biopolymer film covering a 1 m² area (kg biopolymer)
- ρ_{LDPE} - Density of LDPE film (kg/m³)
- ρ_{biopol} - Density of biopolymer film (kg/m³)
- e_{LDPE} – LDPE film thickness (µm)
- e_{biopol} – LDPE film thickness (µm)

Equation 3:
$$RR_{equal-GWP} = \frac{GWP_{LDPE, 1kg}}{GWP_{biopol, 1kg}}$$

Where:

- $RR_{equal-GWP}$ – Replacement ratio for which GWP of the biopolymer is at least as good as GWP of LDPE, on a 1-m² basis (kg biopolymer/kg LDPE)
- $GWP_{LDPE, 1kg}$ - Global warming potential for 1 kg of LDPE film (kg CO₂eq/kg)
- $GWP_{biopol, 1kg}$ - Global warming potential for 1 kg of biopolymer film (kg CO₂eq/kg)

3.5. Scenario analysis

The following scenarios were introduced:

- Reference scenario: mango seeds are considered wastes; film production by casting technique;
- Considers mango kernels and seed shells could have economic value in the future and thus should be modelled as by-products (inclusion of cultivation and pulping stages);
- Considers film manufacturing by extrusion.

To build a model for scenario b, mango cultivation and pulping stages inventories were included (references in Table 3). Emissions from direct land use change from native vegetation to mango orchard were considered as in Müller Carneiro et al. (2019). The allocation factors used are described in section 3.2.1.

For scenario c, the following steps were considered for the production of film by extrusion:

- Mixture of components;
- First extrusion: which plasticises starch and combines the components of the polymer, yielding plastic pellets;

- Second extrusion: Converts pellets to film.

For the first step, the stirring energy for mixing the components for the time prior to the first extrusion was calculated using the equations provided by Piccinno et al. (2016). Since extrusion is a continuous process, it was assumed that extruders operated for 24 hours a day, obtaining a production of around 110 kg of film per hour. For the first extrusion, a 100kg/h capacity extruder was considered with an energy consumption of 1.9 MJ/kg of extruded material (Kent, 2018). For the second extrusion, inventory data was retrieved from theecoinvent database. Moreover, following the findings of the impact assessment, we also analysed scenarios aiming to improve the performances of Film 1 (section 4.2.1) and Film 2 (section 4.2.2).

4. Results and discussion

In this chapter, results are presented in three main sections – inventory analysis, impact assessment, and scenario analysis. Life cycle inventories are presented at lab-scale and industrial-scale. In the impact assessment, the biopolymer formulations are analysed and scenarios are introduced to improve their environmental performances. The formulations are compared and then the best-performing one is compared to LDPE. Scenario analysis is performed and, finally, LCIA scores of the mango-based polymer is compared to other biopolymers.

4.1. Life cycle inventory analysis of the biopolymer film at laboratory and industrial-scales

i) Cellulose and CNC production

The laboratory and scaled-up inventories of the production of cellulose from mango seed shells is shown in Table 6 for 1 kg of cellulose.

Product	Unit	Laboratory	Scaled-up	$\Delta(\text{Lab-Scaled-up})$
Cellulose powder	kg	1.00	1.00	
Fibre isolation				
Inputs				
Mango seed shells	kg	3.92	3.92	0%
Water	kg	1.48	1.94	-31%
Acetic acid	kg	52.10	2.85	95%
Hydrochloric acid	kg	0.07	0.05	20%
Electricity	kWh	23.96	1.25	95%
Heat	kWh	-	41.42	-
Outputs				
Fibres	kg	1.09	1.09	0%
Black liquor (lignin)	kg	6.20	6.20	0%
Biowaste	kg	0.08	0.08	0%
Water vapour	kg	1.52	1.52	0%
Fibre treatment				
Inputs				
Fibres	kg	1.09	1.09	0%
Water	kg	77.20	67.53	13%
Sodium hydroxide	kg	0.07	0.06	20%
Hydrogen peroxide	kg	1.77	1.42	20%
Heat	kWh	-	3.22	-
Electricity	kWh	6.17	0.02	100%
Outputs				
Wastewater	L	55.60	67.64	-22%
Biowaste	kg	0.07	0.07	0%
Water vapour	kg	22.68	2.86	87%

Table 6: Inventory of cellulose production at laboratory and industrial-scales

For the production of cellulose from seed shells, it was noted that there was a large electricity consumption in the laboratory, while at large-scale this was much lower but there was a

considerable use of heat (provided by steam from industrial boilers). Most of the heat requirement was associated to the distillation for acetic acid recovery. For most chemicals used (e.g. hydrogen peroxide), there was a 20% reduction in the large-scale model, as suggested in the scale-up method. However, for acetic acid a much higher reduction was observed since it was assumed that this reactant was largely recovered by distillation. At the laboratory, distillation was also performed but no energy data was available for this step, therefore it was not considered. As a result, a large consumption of acetic acid was observed (52.10 kg per kg of cellulose generated), in contrast to the 2.85 kg obtained in the large-scale model.

For the production of cellulose nanocrystals (Table 7), the amount of chemicals were linearly scaled, since the hydrolysis reaction might be affected if the ratio of reactant/cellulose is changed. As a result, at both scales there was a very high consumption of acids in the hydrolysis step (e.g. 105 kg sulphuric acid per kg CNC produced). This is worsened by the low yield of CNC (15.8% kg CNC/kg cellulose), assumed the same at both scales. Furthermore, by analysing the amount of these chemicals by kilogram of cellulose that enters the hydrolysis stage, this was still very high - around 18 kg of sulphuric and hydrochloric acid together (without water). It was also observed that the energy consumption was much higher at the laboratory, even if comparing with the summation of electricity, heat and cooling energy at industrial-scale. The most energy intensive steps at the laboratory were centrifugation and hydrolysis (electricity providing heat and agitation). At industrial-scale, centrifugation had minor electricity usage whereas the most electricity intensive procedure was ultrasonication. Considering total energy (summing heat, electricity, and cooling energy), hydrolysis was the most energy consuming stage in the CNC scaled-up model.

Product	Unit	Laboratory	Scaled-up	$\Delta(\text{Lab-Scaled-up})$
Cellulose nanocrystals	kg	1.00	1.00	
Inputs				
Cellulose powder	kg	6.33	6.33	0%
Water	L	1687.79	1687.79	0%
Hydrochloric acid	kg	9.23	9.23	0%
Sulphuric acid	kg	105.22	105.22	0%
Electricity	kWh	117.69	0.45	100%
Heat	kWh	-	2.43	-
Cooling energy	kWh	-	9.30	-
Outputs				
Biowaste	kg	7.11	7.11	0%
Wastewater	L	1772.98	1772.98	0%

Table 7: Inventory of CNC production at laboratory and industrial-scales

Furthermore, heat integration reduced the heating requirements in the cellulose and CNC production. Two heat integration routes were considered (Figure 8); in route II, the excess heat of the liquid that exits the filtration step is used to preheat the reagents used in the bleaching stage. This way, the initial temperature of the mixture became 40°C (instead of the room temperature), reducing the energy requirement for the bleaching step by 37%. In addition, route IV considered that the excess heat of the acetic acid that leaves distillation is used preheat CNC

hydrolysis reagents, increasing the initial temperature of the hydrolysis mixture from 25°C to 36°C and reducing the heating requirement of hydrolysis by 59%.

ii) SNC production

In Table 8, a summarised LCI of the production of starch nanocrystals from MKS is shown at laboratory and industrial-scales.

Product	Unit	Laboratory	Scaled-up	$\Delta(\text{Lab-Scaled-up})$
Starch nanocrystals	kg	1.00	1.00	
Inputs				
Starch	kg	3.16	3.16	0%
Water	L	248.10	248.10	0%
Hydrochloric acid	kg	1.24	1.24	0%
Phosphoric acid	kg	3.33	3.33	0%
Electricity	kWh	1342.78	0.65	100%
Heat	kWh	-	1.15	
Outputs				
Biowaste	kg	3.09	3.09	0%
Wastewater	L	211.87	211.87	0%

Table 8: Inventory of SNC production at laboratory and industrial-scales

Starch nanocrystals were obtained by acid hydrolysis, similarly to CNC. The acids used were phosphoric and hydrochloric acids, and in much smaller quantities per kg of starch than the reactants used in cellulose hydrolysis - less than 1.5 kg of concentrated acids per kg starch. Moreover, SNC production has a higher yield (31.67% on a starch basis) than CNC, reducing the amount of resources required per kg of output. Electricity usage at the laboratory was very high, especially at the stage of hydrolysis in which it was used for heating and stirring the SNC dispersion for 5 days of reaction. At industrial-scale, this was much lower, which can be associated to better insulation and more efficient agitation. Furthermore, centrifugation at the laboratory had an electricity consumption more than 1000 times higher than at industrial-scale, while these differences were smaller for homogenising and stirring processes (between 2 and 6.5 times).

iii) Film production

Concerning film production, the scaled-up inventories for each film formulation are depicted in Table 9.

Product	Unit	Film 1	Film 2
Biopolymer film	kg	1.00	1.00
Inputs			
Starch	kg	0.80	0.77
SNC	kg	3.2E-02	6.5E-02
CNC	kg	-	1.1E-02
Glycerol	kg	0.20	0.19

Water	kg	6.38	6.13
Heat	kWh	0.82	0.80
Electricity	kWh	2.3E-02	2.5E-02
Outputs			
Water vapour	kg	9.70	11.03
Losses	kg	0.03	0.03

Table 9: Inventories of film production at industrial-scale – Film 1 and 2

In the film production model, all mass components were linearly scaled. Glycerol was used to plasticise the starch in the second step of film production. Electricity consumption data for stirring the mix and removing bubbles (degassing) were obtained, as well as steam for heating the mixture at the stages of gelatinisation and plasticising. The most energy intensive process of film production was the gelatinisation of starch, which required heating a large volume of fluid to the temperature of 90°C. Since energy data for film production was available at the laboratory, only inventories at industrial-scale were obtained.

Detailed inventories of cellulose and CNC production, SNC, and film production, describing inputs and outputs of each process stage, are shown in appendix B.

4.2. Life cycle impact assessment

4.2.1. Biopolymer Film 1

The impact assessment results for Film 1 are shown in Figure 10 (Performance - P.0).

Mango kernel starch production had the largest contributions on non-renewable energy use, climate change, and terrestrial acidification, with a share of 58% approximately. On the other hand, the production of starch nanocrystals had the largest freshwater eutrophication emissions (36%), and a considerable share of the impacts in the other indicators (22%-29%). Film manufacturing contributions were between 10% and 23%, whereas the transport of mango waste and separation of seed components had minor contributions to Film 1 impacts, in the range of 3%-6%.

Most of Film 1 impacts on NREU and CC are associated to energy consumption, especially heat, with shares of 60% and 54%, respectively. For FE and TA, this was also important, however, the use of chemicals was the main hotspot with 50% and 44%, respectively; ethanol (starch production), phosphoric and hydrochloric acids (SNC production), and glycerol (plasticiser for film production) were the main contributors.

Figure 11 details the impacts of starch, SNC and film production by process. For starch production, the stage of drying and grinding had the largest contributions to the impacts due to the consumption of industrial steam. As for SNC production, the impacts occurred mainly in the hydrolysis stage due to the consumption of phosphoric and hydrochloric acids. For film manufacturing, the stages of plasticising and gelatinisation had the largest contributions, due to glycerol consumption and heating, respectively.

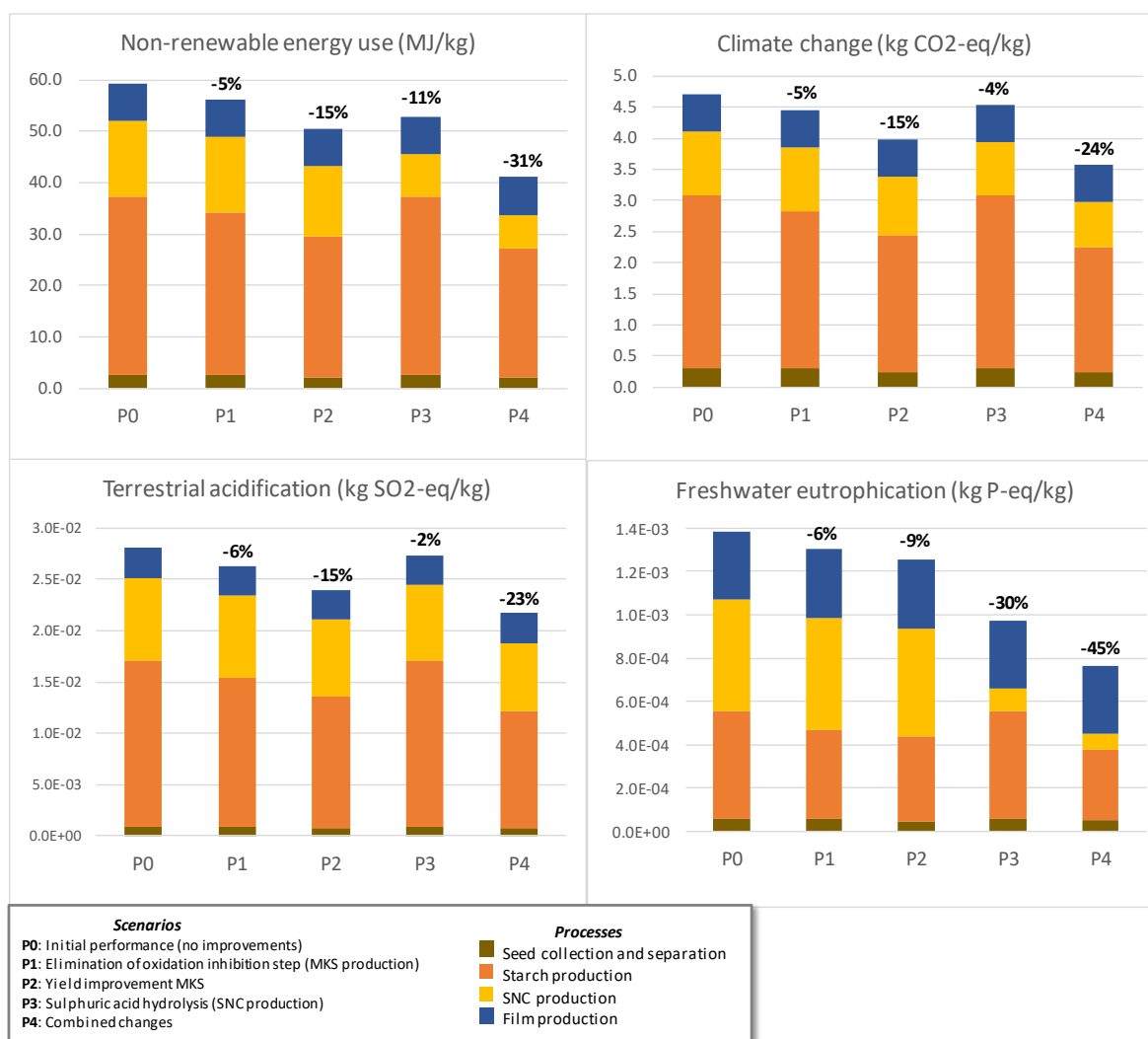


Figure 10: Process contribution for Film 1 (1 kilogram of film)

Considering the hotspot identified above, improvement scenarios were analysed for Film 1. Since most of the impacts were related to MKS and SNC production, three changes in these processes were analysed. First, for the MKS production, as per de Sá Filho et al. (2020), the oxidation inhibition step was eliminated (Performance – P.1), which should not impair the technical performance of the film but produces a brownish film instead of a transparent one. Second, a higher yield was assumed for the MKS production (Performance – P.2), which was achieved by Silva et al. (2019) (38.8%wt, instead of the 30% obtained in the simulation of de Sá Filho et al., 2020). Third, it was assumed that sulphuric acid was used for SNC isolation (Performance – P.3), which is the most commonly used acid in hydrolysis for obtaining both SNC and CNC (e.g. Angellier et al., 2004; LeCorre et al., 2013; Qing et al., 2020; Gu et al., 2015; Tan et al., 2018).

The first process change (P.1) showed that impact reductions of 5%-6% could be achieved (Figure 10), while P.2 showed reductions between 9% and 15%. P.3 had a considerable improvement was for FE (-30%), but minor for acidification (-2%). Combining all three (P.4), overall impact reductions ranged from 23% to 45%, and the biggest improvements were observed in freshwater eutrophication.

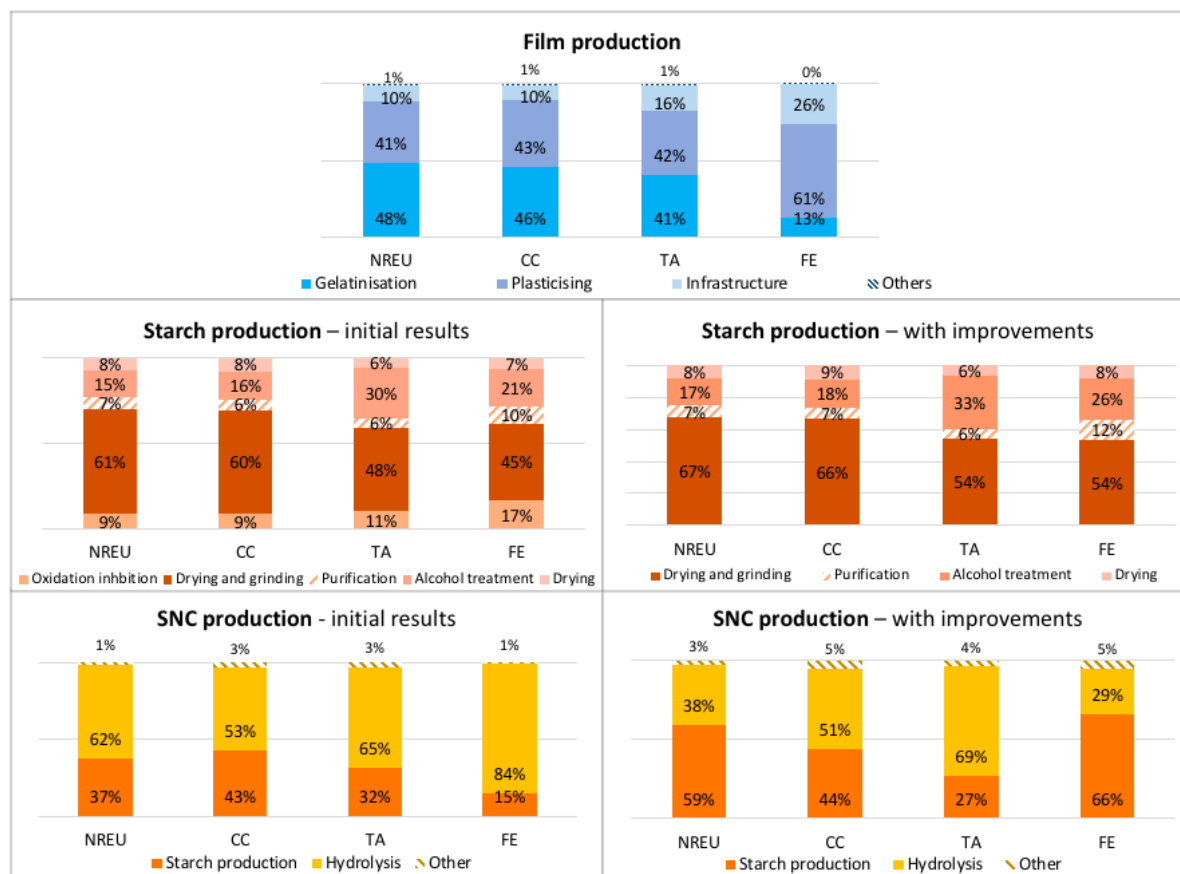


Figure 11: Impacts per process in film production, starch, and SNC production, before (P.0) and after (P.4) improvements

4.2.2. Biopolymer Film 2

The impact results obtained for Film 2 are depicted in Figure 12 (Performance – P.0), for 1 kilogram of biopolymer film.

The impacts of this formulation were well distributed between starch, SNC, and CNC production. Starch production had the majority of GHG emissions, while SNC production the highest share of eutrophication emissions. On the other hand, CNC was the major contributor to the film impacts on NREU and TA.

The main differential of Film 2 was the additional nanofiller, cellulose nanocrystals, besides a higher percentage of nanoreinforcement (twice as much as in Film 1). CNC had a much larger impact per unit of mass than SNC and MKS; it was applied in small quantities in the film (about 1% wt), but it carried a large share of the film impacts, ranging between 25% and 36%. The impacts of CNC production come from both core (hydrolysis) and upstream processes (cellulose production, Figure 13). In the hydrolysis stage, sulphuric and hydrochloric acids held the vast majority of the impacts (90%-95%), whereas in cellulose production, impacts were mostly associated with acetic acid consumption and recovery (distillation). In cellulose extraction, a large amount of acetic acid was used in the stages of acetosolv pulping and filtration (about 35 kg per kg of cellulose), and 92% was recovered. Distillation is an intensive process, requiring around 38 MJ of heat per kg of cellulose (about 93% of the heat used in the fibre isolation stage). The energy requirement for distillation used in this model was, however,

based on average industry data; this value could be 60% lower or twice as much. These values were considered in section 4.2.3 in a sensitivity analysis.

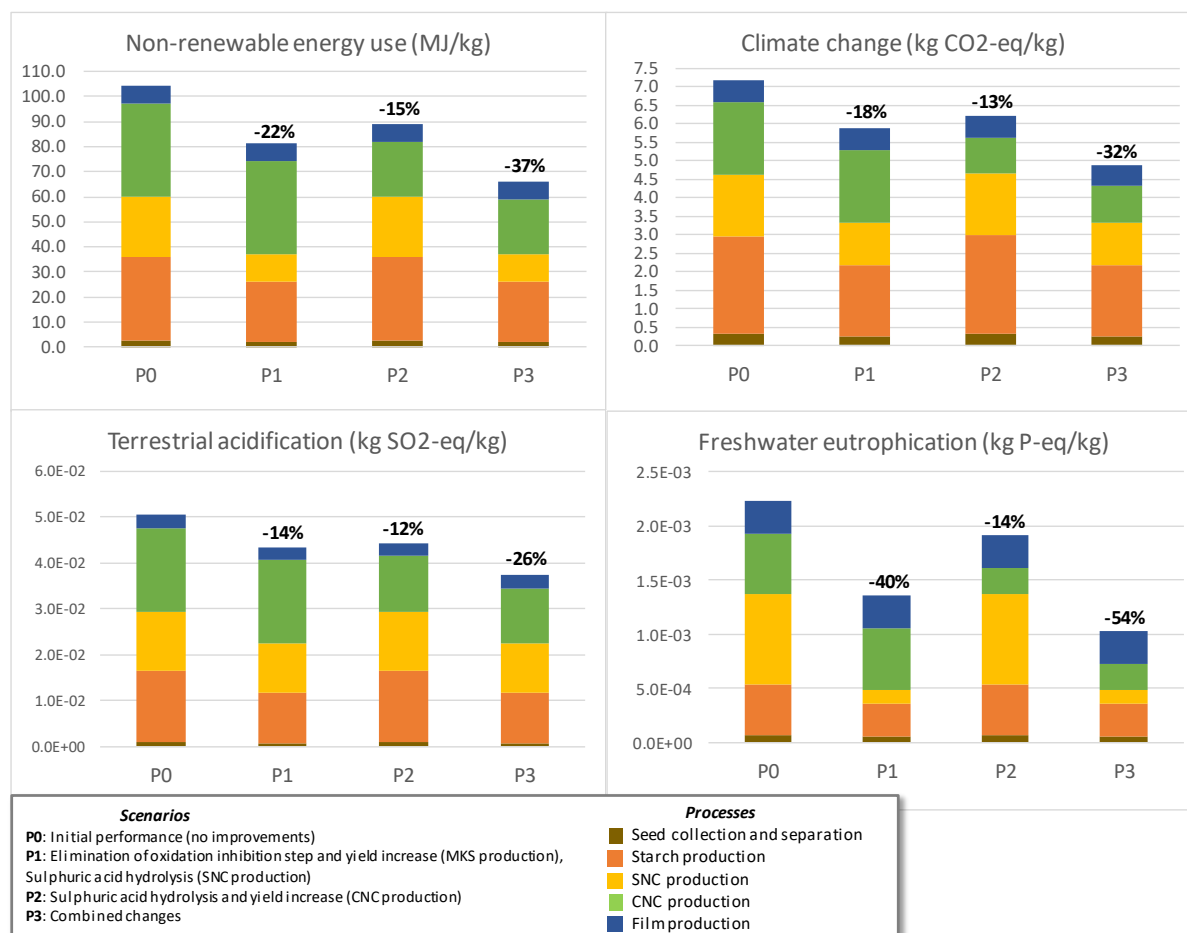


Figure 12: Process contribution for Film 2 (1 kilogram of film)

For Film 2, three improvement scenarios were considered. First, we considered the same changes of Film 1 combined (Performance – P.1 in Figure 12). Additionally, we considered another situation (P.2) in which we CNC was produced by sulphuric acid alone (instead of a mix with hydrochloric acid) and that a higher yield was achieved (22.8%), considering the cellulose nanocrystals obtained by Henrique et al. (2013) also from mango seed shells. Finally, in the third improvement scenario (P.3) considered all changes combined.

P.1 showed impact reductions from 14% to 40%, whereas P.2 showed smaller deductions in the range of 12%-15%. Combining all process changes and performance improvements (P.3), the impacts of Film 2 were reduced by up to 53%. Performance P.3 was taken as the reference scenario for the following analyses.

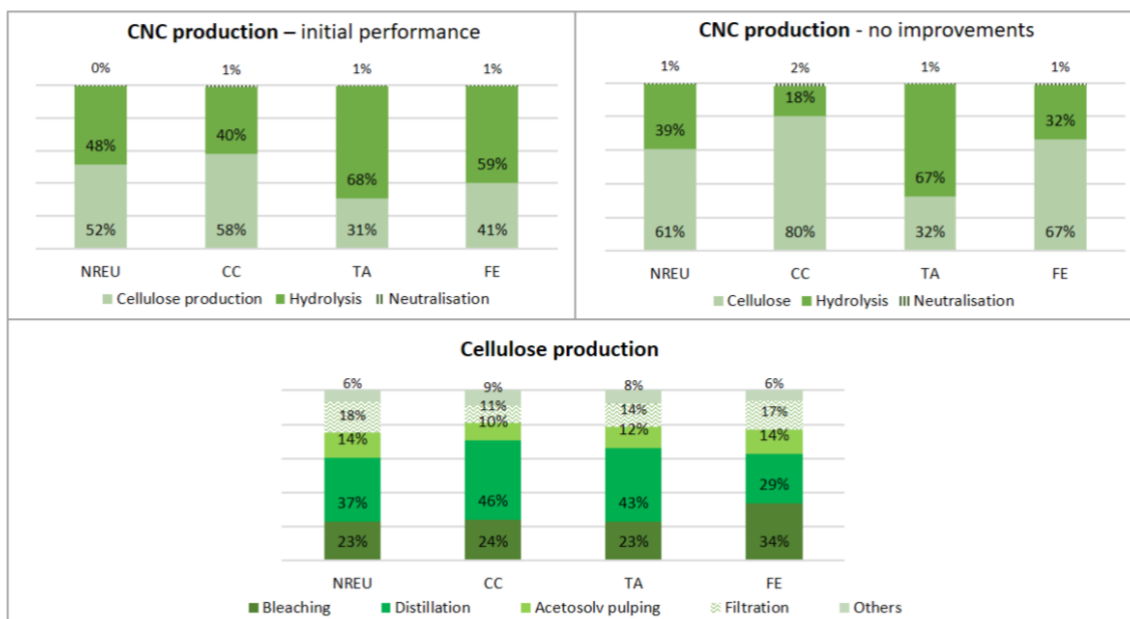


Figure 13: Impacts per process in CNC production, before (P.0) and after (P.3) improvements

4.2.3. Selecting the best-performing biopolymer formulation

In this section, the mango waste-based biopolymer film formulations were compared to select the material with best environmental performance. For this analysis, both the performance of the films before (P.0) and after improvements (P.4 for Film 1 and P.3 for Film 2) were considered. Since a major hotspot of Film 2 was the energy used in distillation in cellulose isolation, the minimum and maximum values for steam consumption obtained by Capello et al. (2005) for distillation were considered in a sensitivity analysis. The results are shown in Figure 14.

It was found that Film 2 performed worse than Film 1 for each of the four impact categories analysed. This is true for both the initial performances and after impact reductions. When considering the minimum energy value for distillation, Film 2 still had considerably larger impacts than Film 1 - at least 21% higher. Moreover, considering the maximum values, Film 2 impacts could be up to 46% higher than Film 1. Therefore, Film 1 was selected as the most promising biopolymer formulation, in terms of environmental performance, and will be compared to a commercial polymer film in the next section.

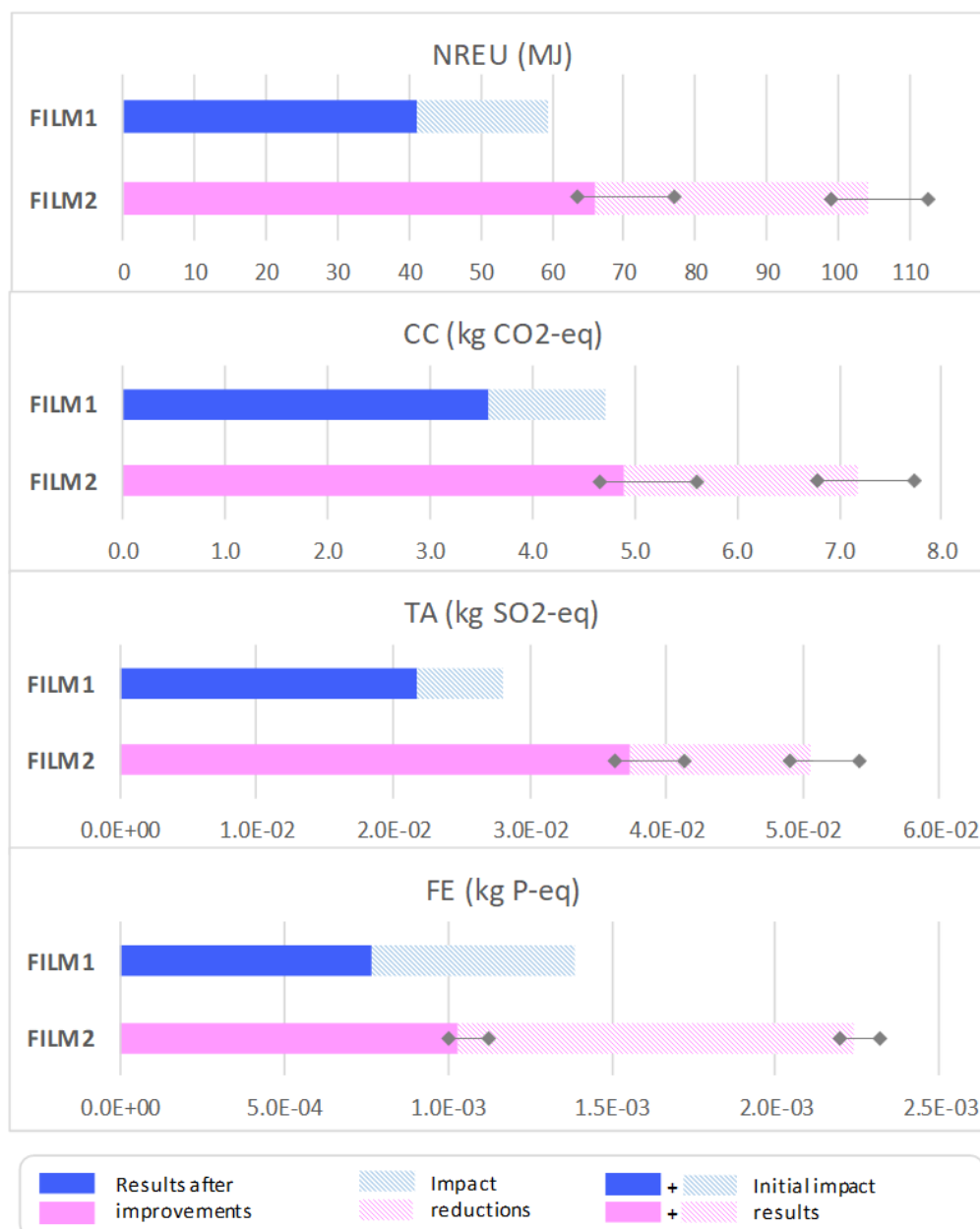


Figure 14: Comparative analysis of biopolymer films 1 and 2 (1 kg of biopolymer film). The bars represent the values of the sensitivity analysis for distillation energy in cellulose production

4.2.4. Comparing Biopolymer Film 1 and LDPE

It is critical to assess if the mango-based film selected can compete, from an environmental standpoint, to a current material, in this case low-density polyethylene (LDPE). In this section, these materials were compared on a 1-kilogram basis and then material replacement ratios were also considered.

i) Comparison based on a 1:1 replacement

The comparative assessment on a same weight-basis (1 kg) is depicted in Figure 15, considering the reference situation for the biopolymer Film 1 as well as alternative scenarios b and c (section 3.5). For this analysis, Film 1 was considered, after improvements (P.4 in 4.2.1).

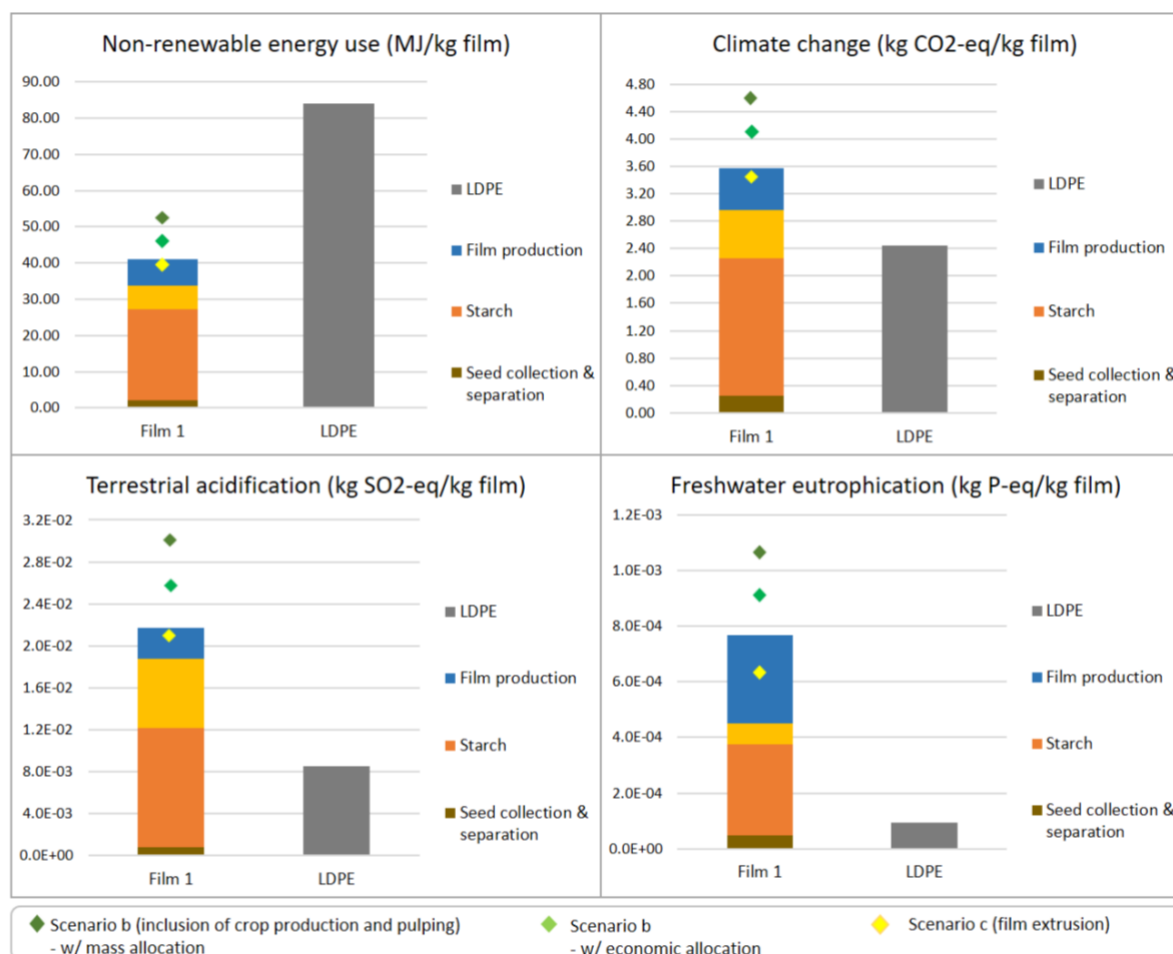


Figure 15: Comparative assessment of mango-based biopolymer and LDPE film (1 kilogram of film)

The biopolymer performed better than LDPE for non-renewable energy, in all four situations – reference case (scenario *a*), inclusion of crop production and pulping (*b*) with mass or economic allocation and film extrusion (*c*). However, the biopolymer film showed worse environmental performance than LDPE film for climate change, freshwater eutrophication, and terrestrial acidification, regardless of feedstock consideration and film manufacturing technique.

The biopolymer film had a score of 41.05 MJ/kg film, whereas LDPE score was about twice as much (83.9 MJ/kg). In contrast, we obtained a GWP of 3.57 kg CO₂-eq/kg for the biopolymer, whereas LDPE had a score of 2.45 kg CO₂-eq/kg, 31% lower. The better performance of mango-based film on NREU is partly associated to the high share of renewable electricity in Brazil. On the other hand, the high score of LDPE on NREU was related to the use of crude oil and natural gas as feedstock. Even though these fossil substances were not used to produce energy, they were accounted as consumed energy resources. Hence, there was a high consumption of fossil resources, which did not result in carbon emissions at the production stage.

The performance of the biopolymer film on freshwater eutrophication was the worst in comparison to LDPE, with an impact approximately nine times as much in the reference scenario. Eutrophication emissions were mainly associated to the consumption of industrial steam, for heating, and to the production of glycerol from soybean oil, used as a plasticiser in

the film formulation. For acidification, heat consumption was also significant, as well as emissions from biowaste composting.

Furthermore, it is highlighted that depending on the end-of-life treatment of these polymers, their relative performances could change. For instance, if both biopolymer and LDPE films were incinerated after consumption, the GWP of LDPE would increase and while the GWP of biopolymer would remain the same, since the biogenic carbon uptake would offset the GHG emissions from waste burning. Therefore, this comparison is limited due to the boundaries of the study.

ii) Replacement ratio for equivalent GHG impacts

Even though most LCA studies on polymers also adopted the functional unit of 1 kilogram, many authors agree that this does not reflect the functionality of a material (e.g. Spierling et al., 2018; Broeren et al., 2017a; Ita-Nagy et al., 2020). Some suggested the functional unit of 1 m² (e.g. Leceta et al., 2014) for films, which seems adequate but requires that the dimensions of the film are known and that film thickness is optimised or properly determined for a specific product.

The previous section showed that the mango-based biopolymer selected performed worse than LDPE for three out of four impact categories for the 1 kilogram FU. If two films with identical dimensions were compared considering an area of 1 m², it is possible that the gap between their performances would be even greater, due to the higher density of the biopolymer film (Table 5). However, since the biopolymer is nanoreinforced, it could also be possible to obtain thinner films.

Therefore, the replacement ratio (in kg LDPE/kg biopolymer) for which the film would perform at least as well as LDPE on climate change was determined, since the difference in performances for this indicator was not so great (differently than for eutrophication and acidification). The equations used for these calculations are indicated in section 3.4, applying the GWP scores obtained in section 4.2.4 - 3.57 kg CO₂-eq/kg for the biopolymer and 2.45 kg CO₂-eq/kg for LDPE.

It was found that for a replacement ratio of 0.68 kg biopolymer/kg LDPE the fossil and bio-based polymer would have had the same performance on climate change. This means that a mango-based biopolymer packaging would have to be 32% lighter than a LDPE packaging for a same product. Further, the biopolymer film would have to be 44% thinner than LDPE for a same packaging application.

As Table 5 shows, there are LDPE films with different thicknesses, which depend on the application; it is possible to find 0.15 mm LDPE films in the market, as well as thicker films (0.60 mm) and very thin films (25 µm). For the latter, it is unlikely that a sufficiently thinner (13 µm) substitute biopolymer film could be achieved, but the thicker film LDPE tested in laboratory (636.9 µm) showed similar tensile strength than the 60 µm thick biopolymer film.

It is worth noticing that the development of such thinner films could have influence on its properties and be limited by the manufacturing technique used. According to de Moraes et al. (2013), the thickness of a film influences its basic properties. However, experts were consulted, who stated that in the case of bionanocomposite films these effects should be minor. Furthermore, the casting technique used in the laboratory (batch process) has a limited capacity

of thickness control, besides being a slow process and likely unfit for commercial production. The extrusion technique, in its turn, could completely alter the properties of the film in comparison to those produced by casting. Experts suggested that at large-scale the most appropriate technique for obtaining these films would be continuous tape casting, which offers a better control of film thickness and have the same working principle as the technique used in laboratory, operating at moderate temperatures. The thickness of films produced by tape casting usually range between 20 μm and 1 mm (de Moraes et al., 2013). Even though tape casting is a well-established technique in industry for the production of ceramics (Vogelsang et al., 2014), it has yet to be optimised for biopolymer film production (Karki et al., 2016).

Therefore, for some applications it could be possible to attain a satisfactory biopolymer film that is much thinner in a way that it would have lower GHG emissions than its fossil counterpart, differently than what the 1-kg basis comparison showed. However, it is necessary to use a film manufacturing technique that can produce sufficiently thin films while guaranteeing properties similar to those the films produced in the laboratory. Nevertheless, it is highlighted that the mango-based films have worse barrier to water vapour than LDPE, therefore such films could have limited food-packaging applications.

4.3. Scenario and improvement analysis for Biopolymer Film 1

Further impact reductions could be reached for the biopolymer production at industrial-scale by improving the yields of starch and starch nanocrystals extraction. Laboratory experiments on which our model was based obtained yields of 38.8%wt (kg dry starch/kg dry kernels) and 31.67%wt (kg SNC/kg dry starch). However, other authors reached yields of up to 59.8% for MKS from the same mango variety (Silva et al., 2013). For starch nanocrystals, according to Angellier et al. (2004), the maximum yield that could be achieved corresponds to the relative crystallinity of starch granules, which according to Saeaurng & Kuakpetoon (2018) was 37% for MKS. Considering these values, impact reductions in the order of 22% to 29% were achieved, in relation to the reference results for Film 1 ('S.Max_yield', Table 10). It is possible that not all MKS and SNC content is extractable, not to mention that distinct or additional processes may be needed to optimise process yield. Nonetheless, this shows how gains in process yield could largely reduce the burdens of novel biomaterials.

Moreover, since the Film 1 was selected instead of Film 2, seed shells were not used, which could be used in the factory for energy production in biomass boilers. This material has a higher heating value of 18.05 MJ/kg and good quality for heat generation, besides offering carbon benefits in comparison to other fuels (Perea-Moreno et al., 2018). Considering that the total heating requirement of the biopolymer factory was 43.42 MJ/kg film, that for each kilogram of biopolymer film produced 3.3 kg (dry mass) of seed shells are generated, the heating needs of the system could be largely offset. Heat consumption was a major contributor to all impact categories analysed, therefore this could be largely enhance the environmental performance of the biopolymer film.

Throughout this thesis, various situations were considered – different feedstock considerations, manufacturing techniques, allocation methods, process changes, and performance improvements. These resulted in a wide variation in impact scores, as depicted in Table 10.

Scenario	NREU	GWP	TA	FE	NREU	GWP	TA	FE
	MJ	kg CO ₂ -eq	kg SO ₂ -eq	kg P-eq				
P.0	59.33	4.72	2.80E-02	1.38E-03	43%	31%	28%	78%
P.1	56.16	4.46	2.63E-02	1.30E-03	35%	24%	20%	68%
P.2	50.48	3.99	2.40E-02	1.25E-03	22%	11%	10%	61%
P.3	52.81	4.53	2.74E-02	9.74E-04	27%	26%	25%	25%
P.4 (reference)	41.05	3.57	2.17E-02	7.66E-04	0%	0%	0%	0%
S.b_MA	52.51	4.60	3.01E-02	1.07E-03	27%	28%	38%	38%
S.b_EA	46.61	4.08	2.56E-02	9.13E-04	12%	13%	17%	18%
S.c	39.33	3.45	2.07E-02	6.16E-04	-5%	-3%	-4%	-19%
S.Max_yield	29.38	2.58	1.59E-02	6.07E-04	-29%	-28%	-27%	-22%
Combined scenarios								
Best case*	27.66	2.45	1.49E-02	4.58E-04	-33%	-31%	-31%	-40%
Worst case**	70.79	5.75	3.65E-02	1.69E-03	72%	61%	68%	120%

P.0: initial performance of the film (no improvements); P.1: elimination of MKS oxidation inhibition; P.2: Improved MKS yield; P.3: Sulphuric acid hydrolysis in SNC production; P.4: Combined improvements (reference scenario); S.b_AM: Scenario b (including pulping and agricultural phase) with mass allocation; S.b_AE: Scenario b with economic allocation; S.c: Film extrusion; S.Max_yield: Maximised SNC and MKS yield. *No improvements & inclusion of cultivation and pulping (w/ mass allocation) **Improved & Max. Yields & Extrusion

Table 10: All scenarios, worst- and best-case results for Film 1, in absolute values and percentage of difference in relation to the reference (P.4)

In relation to the reference (P.4) the inclusion mango pulping and cultivation (scenario b) increased the impacts by 27%-38%, with mass allocation, and 12%-18%, when applying economic allocation. The highest additions occurred in eutrophication and acidification, due to agricultural field emissions. Considering film production by extrusion (scenario c), there were impact reductions (between 3% and 19%) in relation to the casting technique. Furthermore, results could be up to 78% higher if improvements were not incorporated (P.0).

Combining the results in best- and worse-case scenarios, the minimum impacts were achieved combining yield improvement (S_Max.yield) and film extrusion (S.c), while the maximum scores were attained by combining the initial results (P.0) and scenario b_AM, which considered processes upstream from the collection of waste (mango cultivation and pulping) with mass allocation. The ratio between maximum and minimum scores was between 2.33 and 3.67. Freshwater eutrophication was the indicator that showed the highest variations (-40% and +120%).

Moreover, it is worth noticing that in the best-case scenario GWP was 2.45 kg CO₂-eq, which is the same score obtained for LDPE. Further, in the worst-case scenario NREU was 70.79 MJ, which is still lower than the score obtained for LDPE (83.90 MJ).

4.4. Comparison with other biopolymer LCAs

The selected mango-based biopolymer film (Film 1) was compared to other biopolymers assessed in LCA. For this comparison, we used the study of Broeren et al. (2017a) on various starch blends (partly bio-based) and of De Léis et al. (2017) on a cassava starch film (Table 11).

In addition, we used the distribution of biopolymers impact scores presented in the reviews of Walker & Rothman (2020) and Spierling et al. (2018).

		This study	De Léis et al., 2017	Broeren et al., 2017a (min/max)		
Type/feedstock		MKS	Cassava starch	Potato starch*		
Functional unit		1 kg film	1 kg film	1 kg plastic granules		
Type/scale of data		Scaled-up	Mixed**	Industrial data		
Impact category	Unit	Method	Impact scores			
Non-renewable energy use	MJ	CED	41.05	44.84	33	72
Climate change	kg CO ₂ -eq	IPCC 2013 100-y	3.57	4.31	1.8	3.7
Terrestrial Acidification	kg SO ₂ -eq	ReCiPe Midpoint (H)	2.17E-02	1.73E-02	-	-
Freshwater eutrophication	kg P-eq	ReCiPe Midpoint (H)	7.66E-04	2.56E-03	-	-
Eutrophication	kg PO ₄ -eq	CML 2002	7.36E-03	-	3.79E-03	6.00E-03

*Partly bio-based

**Large-scale data for the agricultural production, starch production and background processes, laboratory-scale data for film production (casting)

Table 11: Comparison of LCIA scores of Film 1 and other starch-based polymers

For climate change, we obtained a score of 3.57 kg CO₂-eq/kg film, which was higher than most of the values obtained by Broeren et al. (2017a) for different potato-based starch blends (between 1.8 and 3.7 kg CO₂-eq/kg), only slightly better than a starch/PLA/PBAT formulation. However, these authors analysed 1 kilogram of plastic granules and the stage of conversion or film manufacturing was not included in the boundaries. On the other hand, the cassava film assessed by De Léis et al. (2017) had higher emissions (4.31 kg CO₂-eq/kg film), however a large part of these emissions (73%) were due to film production by casting technique in the laboratory, which was not optimised. These authors analysed film production by extrusion in a scenario but, curiously, GWP reduction was minor (-7%), with a resulting score of 4.0 kg CO₂-eq/kg. Furthermore, the cassava starch film had much lower tensile strength than the mango-based film (3.96 MPa, whereas Film 1 had a value of 17.51 MPa). Moreover, compared to the impact score distributions presented in the review of Walker & Rothman (2020), our GWP scores were higher than most LCA studies on biopolymers. Nevertheless, many of the reviewed LCAs also did not consider plastic conversion and, more importantly, a large portion of them deducted the biogenic carbon uptake from the GWP scores, considerably reducing the net GWP of the biopolymers.

Concerning freshwater eutrophication, we obtained a better performance than the biopolymer film analysed by De Léis et al. (2017), which was expected since this was based on cassava and therefore had emissions from agriculture. In addition, to compare eutrophication impacts to the other studies, we obtained impacts scores using the CML 2002 method (Guinee, 2002) for total

eutrophication (terrestrial and aquatic). We obtained a value of 7.36×10^{-3} kg PO₄-eq/kg film, which was higher than the maximum value obtained by starch blends by Broeren et al. (2017a) (6.0×10^{-3} kg PO₄-eq) and higher than most biopolymers analysed in the reviews of Walker & Rothman (2020) and Spierling et al. (2018). A large portion (34%) of the impact of the mango-based film on eutrophication was associated to the use of glycerol, mostly due to soybean cultivation. Moreover, it was noted that in most of the studies biopolymers were analysed in primary forms (pellets), not including film production or other conversion.

For non-renewable energy use, we obtained a value of 41.05 MJ/kg biopolymer film, which is very similar to the values found by Broeren et al. (2017a) for starch/PLA and starch/PBS/fibre blends, and to the cassava film analysed by De Léis et al. (2017). Moreover, this score is lower than those of most fossil-based polymers, ranging from 55.5-115.9 MJ/kg plastic pellets (Spierling et al., 2018).

For terrestrial acidification, we obtained a score of 2.17×10^{-2} kg SO₂-eq/kg biopolymer film. This was higher than the score obtained by De Léis et al. (2017), 1.73×10^{-2} kg SO₂-eq/kg, and also higher than most literature values shown in Walker & Rothman (2020). A considerable part of the acidification emissions occurred in SNC production (27%), used to reinforce the film. Consequently, the mango-based film had higher acidification impacts per kilogram, but also better mechanical performance than the cassava starch film analysed by De Léis et al. (2017).

In addition, we compared the results of our study with two ex-ante LCAs on biopolymers – Fernández-Dacosta et al. (2015) for PHAs from wastewater and Tecchio et al. (2016) for bio-PBS from maize starch, for 1 kilogram of plastic pellets from cradle-to-gate. In the first study, the model was scaled-up using simulation software, while in the second a scale-up tool proposed by the same authors was applied. Concerning GHG emissions, PHAs showed scores between 4.10 and 6.34 kg CO₂-eq/kg pellets (disregarding biogenic carbon uptake) for different production routes; these were higher than the values obtained for the mango-based polymer, and did not include plastic conversion. Some of the hotspots of the PHAs system were the use of electricity, chemicals, and nutrients for the fermentation microorganisms. Moreover, this study included credits for avoided wastewater treatment. As for the Bio-PBS study, a value of 6.35 kg CO₂-eq/kg pellets was obtained. Different feedstocks and production processes were analysed and a best-case scenario of 4.17 kg CO₂-eq/kg was found for sugarcane starch, which was still worse than the mango-based biopolymer. For NREU, bio-PBS had a score of 138.5 MJ/kg, while for PHAs a value of 106 MJ/kg was found in the best scenario, both of which are much higher than the results found in this study.

There were no LCAs on nanoreinforced biopolymer films, to which we could compare our material. The somewhat unfavourable results of the mango-based polymer can be partly explained by the use of nanoreinforcement, since nanomanufacturing processes are often energy and resource intensive, due to e.g. low yields, intensive purification procedures, etc. (Bartolozzi et al., 2020). Increasing the percentage of bio-based nanofillers enhances the performance of the film to a certain point as shown in Oliveira et al. (2018), Silva et al. (2019), and others, but it may increase the impacts per kilogram of film, due to these intensive conversions. Nevertheless, the use of nanofillers could also reduce the material usage in packaging, thus for a fair comparison between this material and other polymers it is necessary to know more about the future functionality of bionanocomposites.

5. Conclusions

In this thesis, we analysed the potential environmental impacts of a nanoreinforced biopolymer film produced from mango wastes at an early research stage. Two film formulations based on mango kernel starch (MKS) were analysed - Film 1 with a reinforcement of starch nanocrystals (SNC) and Film 2, filled with SNC and cellulose nanocrystals (CNC).

We obtained a scaled-up model for the production of SNC, CNC, and biopolymer film using an engineering-based tool. Scaling up had major effects on electricity usage, which was largely reduced but also partly replaced by the use of steam (for heating) at industrial-scale. The biopolymer formulations were analysed at industrial-scale to identify hotspots and improvement opportunities. Most Film 1 impacts were due to starch production, but production of starch nanocrystals had a considerable share of the impacts. For Film 2, the addition of cellulose nanocrystals increased the film impacts. Improvement scenarios were proposed for these two formulations, involving changes in hydrolysis reactant and yield increase, which decreases the environmental impacts of both films. Film 1 was the best-performing biopolymer formulation across different scenarios and was therefore compared to its fossil counterpart, LDPE.

A comparative analysis of Film 1 and LDPE on a 1-kg basis showed that the biopolymer performed better than the fossil polymer for non-renewable energy use, but worse for climate change, terrestrial acidification, and freshwater eutrophication. Considering material replacement ratios, it was found that the biopolymer could have the same performance of LDPE on climate change if a sufficiently thinner film was achieved for the same application.

Various scenarios were analysed for the biopolymer, considering different manufacturing techniques (casting and extrusion), system boundaries (considering mango seeds as a waste - reference - or as a co-product of mango pulping), and allocation methods (mass and economic), besides the abovementioned improvement scenarios. The inclusion of crop production increased considerably the impacts, especially when applying mass allocation, whereas with economic allocation additions were smaller. Film extrusion had lower impacts than casting. Regarding the improvement scenarios, increasing yields reduced impacts considerably in all impact categories analysed, while changing hydrolysis acid was the most effective measure to reduce eutrophication emissions. Overall, large variations in the impact results were found, especially for freshwater eutrophication. In the best-case scenario - combining all process improvements, maximised yields, and film extrusion -, Film 1 had the same GHG emissions than LDPE on a 1-kg basis. Moreover, even in the worse-case scenario Film 1 had lower non-renewable energy use than the fossil film.

Although the results were mostly unfavourable for the biopolymer film, it is noted that there might be significant performance gains in the industry that were not considered in this study. Petrochemical polymers are mature products that have been produced and improved for decades, whereas biopolymers are fairly new materials with production processes that can still significantly evolve over time. In the next section, the limitations of this thesis are discussed, and suggestions for future work are provided; then, recommendations for early-stage assessments of biopolymers are presented in 5.2.

5.1. Limitations and further research

A large number of processes were modelled at industrial-scale, most of them by applying a simple scale-up framework. However, there were limitations in the scale-up concerning process yield, reaction emissions, solvent recycling (by other means than distillation), and the proportion between reactant and raw materials. Beyond that, in future products and systems, the ‘preferred’ production processes are often not yet defined, and there may be a wide range of possible paths (i.e. unit procedures) to attain a product. Moreover, the lack of knowledge regarding the functionality of the nanoreinforced biopolymer was a barrier to the comparison to other materials. These limitations, when overcome, may change the impact results for the mango-based polymer.

Regarding process scale-up, it was assumed that laboratory yields remained the same in the industrial-scale model, though it is possible that these would be improved in industry. Similarly, the proportion between reactant/starch and reactant/cellulose in hydrolysis, respectively, were maintained in the industrial-scale model; in CNC hydrolysis, that totalled 18 kg of acid per kg of cellulose, which was about 4.7 higher than the values found in a pilot-scale study for CNC production from dissolving pulp (Reiner & Rudie, 2013). Moreover, regarding solvent recycling, the recommendations of the scaled-up method followed in this study were only applicable for recovering chemicals that had a boiling point below 200°C, which was not the case for the sulphuric acid. However, several authors indicate that in sulphuric acid hydrolysis there can be a large recovery of this acid (e.g. Boo Chen Qing et al., 2020; Tan et al., 2018).

Furthermore, in general it was assumed that same processes used in the laboratory would be used in the industry, but there could be different processes with different environmental burdens. For instance, the neutralisation of nanocrystals suspension following acid hydrolysis, is customarily done in the laboratory using centrifugation-sonication cycles; however, some suggest that industrial hydrolysis would be followed by membrane separation (e.g. LeCorre, Bras, & Dufresne, 2011; Gu et al., 2015; Reiner & Rudie, 2013).

Functionality and comparability between alternative products and across studies is a recurrent issue when comparing a product at low TRL to an established one (Moni et al., 2020). For the mango-based polymer, considering a 1-kilogram FU, there was an increase in the impacts due to the incorporation of nanofillers, since they go through more conversion processes and have low yields. Nevertheless, there is a potential for reducing material usage for this nanoreinforced film that must be investigated, which could favour their environmental performance in relation to other packaging materials. Moreover, to reduce film thickness in starch-based nanocomposites, it is necessary to consider appropriate large-scale manufacturing techniques that do not affect its technical performance and behaviour, such as continuous tape casting.

Furthermore, the cradle-to-gate boundary of this LCA limited its findings. Hence, it is suggested that end-of-life scenarios are analysed for the mango-based biopolymer and LDPE, since these materials have with distinct degradation behaviours and treatment options. Future work should also include uncertainty analysis to increase robustness of the model.

5.2. Recommendations for assessing biopolymers at early R&D stages

From this research, a number of lessons arose regarding: i) functionality; ii) scale up; iii) data completeness; and iv) performance. For functionality, it was observed that for conducting an

LCA of biopolymer at an early R&D stage it is crucial to understand the probable applications of the material and the relationship between its dimensions (in the case of films, its thickness) and technical performance; in the case of nanoreinforced biopolymers, functionality is particularly important because there can be large mass reductions in relation to unfilled biopolymers, but this is not reflected in the LCIA results in 1-kg analyses. Concerning performance, it was observed that process yields could have a large influence on reducing the impacts of biopolymers, even though these are difficult to predict. Regarding data, it was noted that important data had not been obtained at the time of the experiments (e.g. discarded fluid at each stage). Finally, for the scale-up, we observed that the method used offered an agile option for assessing products that involve a large number of production steps and components, as it is the case for multi-phase polymers and especially nanocomposites. Nevertheless, it is likely that other methods (e.g. simulation software) could give estimations that are more accurate and that capture the complexity of the systems more thoroughly, but these also require more time, financial resources and expertise. Furthermore, it is also critical to identify alternative production processes, since there can be many routes to attain a product. Based on these learnings, the following recommendations were proposed for evaluating novel biopolymers at low TRL (Table 12).

Functionality	Scale-up
<ul style="list-style-type: none"> Analyse materials beyond a 1-kg FU (e.g. 1 m²) or consider replacement ratios in comparative analyses Find optimal dimensions (e.g. thickness) based on probable application and/or a reference material 	<ul style="list-style-type: none"> Map and analyse probable production processes For agile assessment, use engineering-based scale-up tools For more detailed analysis and/or with less components, use simulation software (e.g. Super Pro Designer, Aspen Plus)
Data completeness	Performance
<ul style="list-style-type: none"> Determine biopolymer density and dimensions Measure sample volume or mass at each process stage 	<ul style="list-style-type: none"> Identify process changes that influence yields Consider best- and worse-case scenarios for process yield

Table 12: Recommendations for conducting early-stage assessment of bio-based polymers and nanocomposites

Moreover, to consider production processes beyond the ones considered in the laboratory experiment, we propose the eco-design strategy in Figure 16. This consisted on identifying possible alternative processes or modifications in the process used (e.g. hydrolysis acid) and assessing if they have positive or negative influences on both environmental and technical performances of the biopolymer film. In case trade-offs are observed between impact categories (e.g. reduction on climate change and increase on eutrophication), it is suggested that multi-criteria decision analysis (MCDA) be used to define if there is an overall improvement. It is highlighted that this strategy is to be used for experiments that are in course to integrate LCA in the development of biopolymer films.

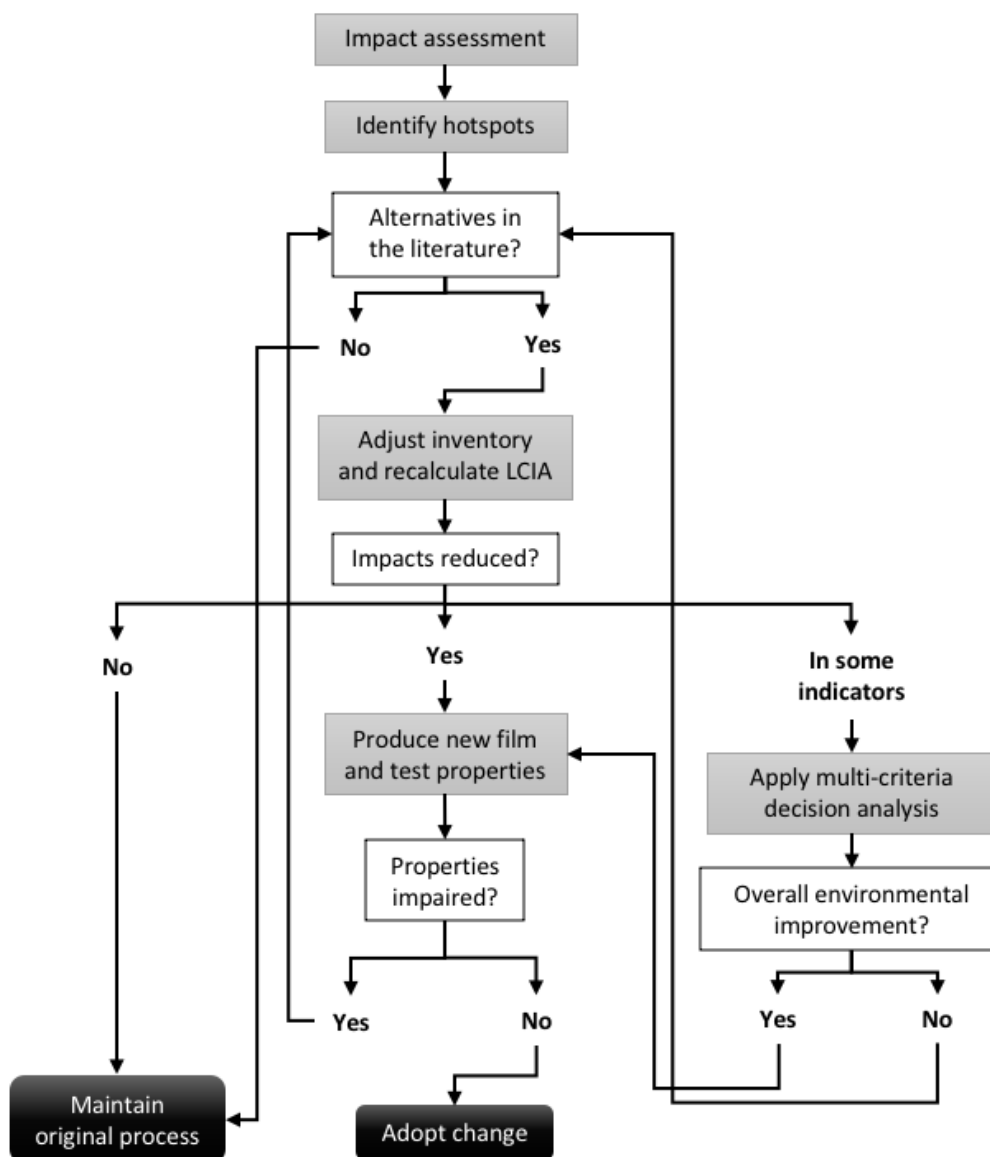


Figure 16: Eco-design strategy for novel biopolymers

Furthermore, it was noted that the absence of a LCA practitioner accompanying the experiments resulted in a lack of information biopolymer developers do not judge important. Considering the increasing relevance of environmental aspects in product development, it is suggested that research centres have a LCA analyst follow laboratory experiments whenever a new product is being developed, to identify critical data to be collected.

We also suggest the research team of Embrapa Tropical Agroindustry that Film 1 is produced again, integrating the changes suggested in this thesis, and that its properties are tested to assure there were no performance losses nor changes in process yield. Furthermore, we suggest that film thickness is optimised and that tape casting technology is explored for the production of thin films.

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Annexes

Appendix A – Parameters and equations used in the scale-up

Parameter	Value	Unit	Description	Data source
Drying of seed shells				
Heat for drying				
<u>Equation 1</u>	$Q_{dry} = \frac{C_{p_{liq}} * m_{liq} * (T_{boil} - T) + \Delta H_{vap} * m_{vap}}{n_{dry}}$			Piccinno et al. (2016)
Cp_liq	4.2	kJ/kg.°C	Sensible heat of water	
ΔHvap	2256.4	kJ/kg	Enthalpy of vaporisation	Laboratory experiment
m_vap	1394.9	kg	Mass of water evaporated	Assumed same as above
m_liq		kg	Total water content	Assumed same as above
T_boil	100	°C	Boiling point	
T	25	°C	Temperature of the mix	Assumed
T_out	25	°C	Temperature outside of reactor	Assumed
n_dry	0.85	-	Efficiency of dryer (tray dryer)	Sanjuán et al. (2014)
Grinding				
Energy for grinding				
E_grinding	12	kWh/ton	Energy per ton of ground material (average)	Piccinno et al. (2016)
Acetosolv pulping				
Solvent				
Reduction of 20% of solvent				Piccinno et al. (2016)
Heating energy				
<u>Equation 2</u>	$Q_{react} = \frac{C_p * m_{mix} * (T_r - T_0) + A * \frac{ka}{S} * (T_r - T_{out}) * t}{n_{heat}}$			Piccinno et al. (2016)
m_mix		kg	Mass of the mix	Laboratory experiment
Cp	4.2	kJ/kg.°C	Sensible heat of water	
T_r	118	°C	Temperature of reaction	Laboratory experiment
T_0	52.5	°C	Initial temperature of sample	Calculated
t	90	min	Reaction time	Laboratory experiment
Scale dependent parameters				
Volume	17187	kg	Volume of the mix	Laboratory experiment
Equipment selected: 2 x 10'000 L reactors				
A	27.981	m ²	Area of reactor	Piccinno et al. (2016)
ka	0.042	W/m.k	Thermal conductivity of insulation	Piccinno et al. (2016)
S	0.075	m	Insulation thickness	Piccinno et al. (2016)
n_heat	0.79	-	Efficiency of heating device	Piccinno et al. (2016)
Stirring energy				
<u>Equation 3</u>	$E_{stir} = \frac{N_p * \rho_{mix} * N^3 * d^5 * t}{n_{stir}}$			Piccinno et al. (2016)
Np	0.79	-	Power number of impeller (axial)	Piccinno et al. (2016)
ρ_mix	1.07	kg/L	Density of mixture	Laboratory experiment
N	0.658	1/s	Rotational speed of agitator	Piccinno et al. (2016)
d	0.803	m	Diameter of agitator	Piccinno et al. (2016)
Filtration				
Solvent				
Reduction of 20% of solvent (acetic acid)				Piccinno et al. (2016)
Filtration energy				

E_filt	5.5	kWh/ton dry material	Electricity for filtration	Piccinno et al. (2016)
Heating energy				
For heating acetic acid only				
Cp	2.05	kJ/kg.°C	Sensible heat of acetic acid	
n_heat	0.79	-	Efficiency of heating device	Piccinno et al. (2016)
T	80	°C	Final temperature of acetic acid	Laboratory experiment
T_0	25	°C	Initial temperature of acetic acid	Calculated (w/out heat exchange)
Distillation				
Energy and cooling water for acetic acid recovery				
Ratio of recovered acid	0.92	kg/kg	Amount of recovered acid/total acid applied	Laboratory experiment
E_distil	0.03	kWh/kg	Electricity use for distillation	Capello et al. (2005)
Steam	1,4	kWh/kg	Steam for distillation (average)	Capello et al. (2005)
Cooling water	0.027	kWh/kg	Cooling water	Capello et al. (2005)

Table 1: Parameters for cellulose fibre isolation scale-up

Parameter	Value	Unit	Description	Data source
Drying of fibres				
Heat for drying				
Calculated using Equation 1				
m_vap	1709	kg	Mass of water evaporated	Laboratory experiment
m_liq	1709	kg	Total water content	Assumed same as above
Parameters: same as in table 3.				
Fibre grinding				
Grinding energy				
E_grinding	12	kWh/ton	Energy per ton of ground material (average)	Piccinno et al. (2016)
Bleaching				
Solvent				
Reduction of 20% of solvent				Piccinno et al. (2016)
Heating energy				
Calculated using Equation 2				
Equipment selected: 2 x 10'000 L reactors				
T_r	65	°C	Temperature of reaction	Laboratory experiment
T_0	25	°C	Initial temperature of sample	Calculated (w/out heat exchange)
t	2.5	hours	Reaction time	Laboratory experiment
Other parameters: same as in table 3.				
Stirring energy				
Calculated using Equation 3				
p_mix	1.09	kg/L	Density of mixture	Laboratory experiment
Other parameters: same as in table 3.				
Washing, filtration & drying				
Filtration energy				
E_filt	7	kWh/ton dry material	Electricity for filtration	Piccinno et al. (2016)
Heat for drying				
m_vap	918.5	kg	Mass of water evaporated	Assumed
m_water	918.5	kg	Total water content	Assumed
Other parameters: same as in table 3.				

Table 2: Parameters for cellulose fibre treatment scale-up

Parameter	Value	Unit	Description	Data source
Hydrolysis				
Heating energy				
Calculated according to Equation 2				
m _{mix}		kg	Mass of the sample	Laboratory experiment
T _r	45	°C	Temperature of reaction	Laboratory experiment
T ₀	25	°C	Initial temperature of sample	Calculated (w/out heat exchange)
t	60	min	Reaction time	Laboratory experiment
Scale dependent parameters				
Equipment selected: 3 x 10'000 L reactors				
Other parameters: same as in table 3.				
Stirring energy				
Calculated using Equation 3				
ρ _{mix}	1,15	kg/L	Density of mixture	Laboratory experiment
t	60	min	Reaction time (under stirring)	Laboratory experiment
Other parameters: same as in table 3.				
Centrifugation				
Centrifugation energy				
Average value of 8 kWh/ton of dry material				
M _{centrif1}	832.54	kg	Solids in centrifugation 1	Piccinno et al. (2016) Calculated from laboratory data
M _{centrif2}	660.68	kg	Solids in centrifugation 2	Idem
M _{centrif3}	488.83	kg	Solids in centrifugation 3	Idem
Homogenisation				
Homogenising energy				
Calculated using Equation 3				
Parameters for 10'000 power impeller				
N _p	2.39		Power number of impeller	Piccinno et al. (2016)
N	20	1/s	Rotational speed of agitator	Piccinno et al. (2016)
d	0.288	m	Diameter of agitator	Piccinno et al. (2016)
Homogenisation 1: 2 homogenisers/power impellers				
ρ _{mix1}	1.13	kg/L	Density of mixture	Laboratory experiment
Homogenisation 2: 2 homogenisers/power impellers				
ρ _{mix2}	1.06	kg/L	Density of mixture	Laboratory experiment
Homogenisation 3: 1 homogeniser/power impeller				
ρ _{mix2}	1.03	kg/L	Density of mixture	Laboratory experiment
t	60	s	Time	Laboratory experiment
n _{homog}	0.9		Efficiency of agitator	Piccinno et al, 2016
Ultrasonication				
Electricity use in ultrasonication				
Between 150 and 300 W per liter solvent				
P _{ultrason}	225	W/L	Average power use in ultrasound per L of solvent	Arvidsson et al. (2014)
t	1	minute	Time	Laboratory experiment
V	11.48	m ³	Volume of sample	Laboratory experiment

Table 3: Parameters for cellulose nanocrystals scale-up

Parameter	Value	Unit	Description	Data source
Hydrolysis				
Heating energy				
Calculated according to Equation 2				
m _{mix}		kg	Mass of the sample	Laboratory experiment
T _r	40	°C	Temperature of reaction	Laboratory experiment
T ₀	25	°C	Initial temperature of sample	Assumed
t	5	days	Reaction time	Laboratory experiment
Volume	4579.6	L	Volume of sample	Laboratory experiment
Scale dependent parameters (5'000 L reactor)				
ka	0.042	W/m.k	Thermal conductivity of insulation	Piccinno et al. (2016)
S	0.075	m	Insulation thickness	Piccinno et al. (2016)
n _{heat}	0.77		Efficiency of heating device	Piccinno et al. (2016)
Other parameters: same as in table 3.				
Stirring energy				
Calculated using Equation 3				
ρ _{mix}	1.25	kg/L	Density of mixture	Laboratory experiment
t	5	days	Reaction time (under stirring)	Laboratory experiment
Np	0.79		Power number of impeller (axial)	Piccinno et al. (2016)
ρ _{mix}		kg/L	Density of mixture	Laboratory experiment
N	0.828	1/s	Rotational speed of agitator	Piccinno et al. (2016)
d	0.638	m	Diameter of agitator	Piccinno et al. (2016)
Centrifugation				
Centrifugation energy				
Average value of 8 kWh/ton of dry material				
M _{centrif1}	650.04	kg	Solids in centrifugation 1	Piccinno et al. (2016) Calculated from laboratory data
M _{centrif2}	584.38	kg	Solids in centrifugation 2	Idem
M _{centrif3}	518.73	kg	Solids in centrifugation 3	Idem
M _{centrif4}	453.07	kg	Solids in centrifugation 4	Idem
M _{centrif5}	387.41	kg	Solids in centrifugation 5	Idem
M _{centrif6}	321.76	kg	Solids in centrifugation 6	Idem
Homogenisation				
Homogenising energy				
Calculated using Equation 3				
Homogenisation 1: 3 x 1'000L homogenisers				
ρ _{mix1}	1.36	kg/L	Density of mixture	Laboratory experiment
Homogenisation 2: 3 x 1'000L homogenisers				
ρ _{mix2}	1.2	kg/L	Density of mixture	Laboratory experiment
Homogenisation 3: 3 x 1'000 L homogenisers				
ρ _{mix3}	1.21	kg/L	Density of mixture	Laboratory experiment
Homogenisation 4: 3 x 1'000 L homogenisers				
ρ _{mix4}	1.21	kg/L	Density of mixture	Laboratory experiment
Homogenisation 5: 2 x 1'000 L homogenisers				
ρ _{mix5}	1.18	kg/L	Density of mixture	Laboratory experiment
Parameters for 1'000 power impeller				
Np	2.39		Power number of impeller	Piccinno et al. (2016)
N	48.333	1/s	Rotational speed of agitator	Piccinno et al. (2016)
d	0.139	m	Diameter of agitator	Piccinno et al. (2016)
Homogenisation 6: 10'000 L homogeniser				
ρ _{mix6}	1.01	kg/L	Density of mixture	Laboratory experiment
Final homogenisation: 10'000 L homogeniser				
ρ _{mixf}	1.03	kg/L	Density of mixture	Laboratory experiment
Parameters for 10'000 power impeller				

Np	2.39		Power number of impeller	Piccinno et al. (2016)
N	20	1/s	Rotational speed of agitator	Piccinno et al. (2016)
d	0.288	m	Diameter of agitator	Piccinno et al. (2016)
For all homogenisation steps				
t	60	s	Time	Laboratory experiment
n_homog	0.9		Efficiency of agitator	Piccinno et al. (2016)
Ultrasonication				
Electricity use in ultrasonication				
Between 150 and 300 W per litre solvent				Arvidsson et al. (2014)
Power_ultrason	225	W/L	Average power use in ultrasound per L of solvent	Arvidsson et al.(2014)
t	1	min	Ultrasonication time	Laboratory experiment
V1	2.29	m ³	Volume in ultrasonication 1	Calculated from laboratory data
V2	2.74	m ³	Volume in ultrasonication 2	Idem
V3	2.29	m ³	Volume in ultrasonication 3	Idem
V4	2.06	m ³	Volume in ultrasonication 4	Idem
V5	1.83	m ³	Volume in ultrasonication 5	Idem
V6	9.14	m ³	Volume in ultrasonication 6	Idem

Table 4: Parameters for SNC process scale-up

Parameter	Value	Unit	Description	Data source
Gelatinisation				
Heating energy				
Calculated using Equation 2				
m_mix		kg	Mass of the sample	Laboratory experiment
T_r	90	°C	Temperature of reaction	Laboratory experiment
T_0	25	°C	Initial temperature of sample	Assumed room temperature
t	30	min	Reaction time	Laboratory experiment
Scale dependent parameters (2 x 10'000 L reactors) - same as in table 3.				
Stirring energy				
Calculated using Equation 3				
ρ_mix	1.1	kg/L	Density of mixture	Laboratory experiment
t	30	min	Stirring time	Laboratory experiment
Equipment: 3 x 1'000L power impellers				
Other parameters: same as in table 3.				
Plasticising				
Heating energy				
Only the heat to maintain desired temperature				
T_r	65	°C	Temperature of reaction	Laboratory experiment
T_out	25	°C	Temperature outside of reactor	Assumed room temperature
t	15	min	Plasticising time	Laboratory experiment
Scale dependent parameters (2 x 10'000 L reactors) - same as in table 3.				
Stirring energy				
Calculated using Equation 3				
ρ_mix	1.1	kg/L	Density of mixture	Laboratory experiment
t	15	min	Stirring time	Laboratory experiment
Equipment: 2 x 1'000L power impellers				
Other parameters: same as in table 3.				
Homogenisation				
Homogenising energy				
Calculated using Equation 3				
ρ_mix	1.1	kg/L	Density of mixture	Laboratory experiment
t	15	min	Homogenising time	Laboratory experiment

Equipment: 2 x 1'000L homogenisers
 Other parameters: same as in table 5 (CNC).

Addition of nanoparticles

Stirring energy

Calculated using Equation 3

ρ_{mix}	1.08	kg/L	Density of mixture	Laboratory experiment
t	30	min	Stirring time	Laboratory experiment

Equipment: 3 x 1'000L power impellers

Other parameters: same as in table 3.

Degassing

Electricity use for degassing

Industry data for nanocellulose production process (used as proxy) Piccinno et al. (2018)

Table 5: Parameters for film production by casting scale-up

Appendix B – Detailed life cycle inventories per phase

Product	Unit	Value
Starch nanocrystals	kg	1.00
<i>Hydrolysis</i>		
Inputs		
Starch	kg	3.16
Water	kg	15.61
Hydrochloric acid	kg	1.24
Phosphoric acid	kg	3.33
Electricity	kWh	0.14
Heat	kWh	1.15
Output		
Biowaste	kg	0.21
<i>Centrifugation</i>		
Inputs		
Water	L	172.22
Electricity	kWh	0.11
Output		
Wastewater	L	186.04
<i>Homogenising</i>		
Inputs		
Water	kg	32.29
Electricity	kWh	0.03
Output		
Biowaste	kg	1.24
<i>Ultrasonication</i>		
Inputs		
Electricity	kWh	0.36
Output		
Biowaste	kg	1.24
<i>Dialysis</i>		
Inputs		
Water	L	25.83
Electricity	kwh	6.44E-04
Output		

Biowaste	kg	0.21
Wastewater	kg	25.83
<i>Final homogenisation</i>		
Inputs		
Water	kg	2.15
Trichloromethane	kg	0.01
Electricity	kWh	4.95E-03
Output		
Biowaste	kg	0.21

Table 6: Scaled-up life cycle inventory of the production of starch nanocrystals from mango kernel starch

Reference product	Unit	Value
Cellulose powder	kg	1.00
<i>Fibre isolation</i>		
<i>Drying of shells</i>		
Inputs		
Mango seed shells	kg	3.92
Heat	kWh	1.28
Outputs		
Water vapour	kg	1.52
<i>Grinding</i>		
Inputs		
Electricity	kWh	0.03
Outputs		
Biowaste	kg	0.08
<i>Acetosolv pulping</i>		
Inputs		
Water	kg	0.85
Acetic acid	kg	1.35
Hydrochloric acid	kg	0.18
Electricity	kWh	2.9E-04
Heat	kWh	1.95
<i>Filtration</i>		
Inputs		
Acetic acid	kg	1.56
Electricity	kWh	0.01
Heat	kWh	0.07
Outputs		
Black liquor (by-product)	kg	6.20
Fibres	kg	1.09
<i>Distillation</i>		
Inputs		
Electricity	kWh	1.21
Steam	kg	49.90
Water (cooling)	kg	1.09
Fibre treatment		
<i>Washing of fibres</i>		
Input		
Fibres	kg	1.09
Water	L	7.75

Output		
Wastewater	L	6.20
<i>Drying</i>		
Input		
Heat	kWh	1.56
Output		
Water vapour	kg	1.86
<i>Grinding</i>		
Input		
Electricity	kWh	0.01
Output		
Biowaste	kg	0.07
<i>Bleaching</i>		
Input		
Water	L	18.35
Sodium hydroxide 50%	kg	0.11
Hydrogen peroxide 50%	kg	2.83
Electricity	kWh	4.9E-04
Heat	kWh	0.82
<i>Washing, filtration & drying</i>		
Input		
Water	L	41.43
Electricity	kWh	8.0E-03
Heat	kWh	0.84
Output		
Water vapour	kg	1.00
Wastewater	L	61.44

Table 7: Scaled-up life cycle inventory of the cellulose production from mango seed shells

Product	Unit	Amount
Cellulose nanocrystals	kg	1.00
<i>Hydrolysis</i>		
Input		
Cellulose powder	kg	6.33
Water	L	58.06
Water (cooling)	L	379.74
Hydrochloric acid	kg	9.23
Sulfuric acid	kg	105.22
Electricity	kWh	2.0E-03
Heat	kWh	2.43
Cooling energy	kWh	9.30
Output		
Biowaste	kg	1.18
<i>Centrifugation</i>		
Input		
Water	L	411.39
Electricity	kWh	1.2E-01
Output		
Wastewater	L	9.86E+02
<i>Homogenisation</i>		
Input		

Water	l	79.11
Electricity	kWh	3.0E-02
Output		
Biowaste	kg	3.55
<hr/> <i>Ultrasonication</i> <hr/>		
Input		
Electricity	kWh	15.16
Output		
Biowaste	kg	1.18
<hr/> <i>Dialysis</i> <hr/>		
Input		
Water	L	759.49
Electricity	kWh	1.2E-03
Output		
Biowaste	kg	1.18
Wastewater	L	787.40

Table 8: Scaled-up life cycle inventory of the production of cellulose nanocrystals

Product	Unit	Film 1	Film 2
MKS film	kg	1.00	1.00
<hr/> <i>Gelatinisation</i> <hr/>			
Inputs			
Water	kg	6.25	6.13
Heat	kWh	0.68	0.66
Electricity	kWh	3.63E-05	3.65E-05
<hr/> <i>Plasticising</i> <hr/>			
Inputs			
Glycerol	kg	0.20	0.19
Heat	kWh	0.13	0.13
Electricity	kWh	1.82E-05	1.83E-05
Output			
<hr/> <i>Homogenising</i> <hr/>			
Inputs			
Electricity	kWh	9.17E-03	9.22E-03
Output			
Starch, plasticised	kg	7.23	7.09
<hr/> <i>Addition of nanoparticles</i> <hr/>			
Inputs			
Electricity	kWh	5.23E-05	5.25E-05
Output			
Starch, plasticised with nanoparticles	kg	10.14	10.52
<hr/> <i>Degassing</i> <hr/>			
Inputs			
Electricity	kWh	1.53E-02	1.58E-02
Output			
Dispersion	kg	10.14	10.52

Casting			
Inputs			
Heat	kWh	0.00	0.00
Output			
MKS film	kg	1.00	1.00
Water vapour	kg	10.68	11.03
Losses	kg	0.03	0.03

Table 9: Scaled-up life cycle inventory of film manufacturing (Film 1 and 2)

Annex A – Inventory data from previous studies

Product	Unit	Value
Mango pulp	kg	2.52
Mango peels	kg	1.02
Mango seeds	kg	1.00
Mango washing		
Input		
Mangoes	kg	4.55
Water	kg	9.23
Sodium hypochlorite 10%	kg	0.92
Electricity	kWh	4.9E-03
Output		
Mangoes	kg	4.82
Wastewater	L	70.36
Pulping		
Input		
Mangoes	kg	4.82
Electricity	kWh	0.44
Output		
Wastewater	L	0.27

Table 10: Simulation inventory data for mango pulping, obtained from de Sá Filho et al. (2020)

Product	Unit	Value
Mango seed kernels	kg	0.499
Mango seed shells	kg	0.501
Input		
Mango seeds	kg	1.00
Electricity	kWh	0.21

Table 11: Simulation inventory data for the separation of mango seed shells and kernels, obtained from de Sá Filho et al. (2020)

Product	Unit	1 kg starch
Mango kernel starch	kg	1
<i>Input</i>		
Kernels	kg	5.85
Water	kg	42.15
Sodium pyrosulphite	kg	0.14
Sodium hydroxide	kg	0.02
Hydrochloric acid	kg	0.04
Ethanol	kg	0.33
Electricity	kWh	1.49
Heat	kWh	7.24
<i>Output</i>		
Biowaste	kg	0.41
Wastewater	L	44.45
Sulphuric acid (to water)	kg	0.14
Water vapour	kg	4.63

Table 12: Simulation inventory data for the production of mango kernel starch (MKS), obtained from de Sá Filho et al. (2020)