Diplomarbeit

Modelling and Life-Cycle Assessment of Pretreatment Strategies for the Bioconversion of Lignocellulosic Biomass

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Seewalchen am Attersee, am 09.Juli 2021

Patrick Emeder

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Patrick Emeder

Abstract

Over the past few years, the European Union has been strongly supporting sustainable economic concepts such as the Circular Bioeconomy (CBE). The focus of a CBE is the sustainable, resource-efficient use of biomass (such as lignocellulosic residues) and its conversion into value-added energy and material products via biorefineries. From these perspectives, lignocellulosic biomass (LCB) has enormous potential as a feedstock for the sustainable production of chemicals and fuels, as it consists mainly of the polymeric component's cellulose, hemicellulose and lignin, which can be converted into a wide range of bio platform molecules. Due to the resistant nature of LCB (biomass recalcitrance), these components must first be separated from each other in suitable pretreatment steps to enable their simultaneous valorization. However, fractionation is a major challenge, as the pretreatment steps are often very energy- and resource-intensive and cannot be considered sustainable and valuable *per se*. Therefore, this master's thesis aimed to simulate and perform an ecological analysis of three pretreatment scenarios for processing wheat straw to determine the technical-ecological performance at an early stage of the process design. For this purpose, Organosolv (OS) extraction (Scenario 1) and the combination of OS and Liquid Hot Water (LHW) extraction (Scenario 2: OS-LHW; Scenario 3: LHW-OS) were modelled using the Aspen Plus® process simulation software based on data from laboratory trials. The determined mass and energy balances served as the basis for carrying out the life-cycle assessment (LCA). The results from the process simulation and the LCA were used for decision-making to identify the scenario that ultimately leads to the "best" quality platform products (colloidal lignin particles, cellulose-rich solid, sugar-rich liquid stream) and to the lowest ecological impact. It turns out that the combination of LHW and OS (scenario 3: LHW-OS) has the lowest ecological impact with the same or better quality of intermediate products. These findings can be used as decision-making support for further developing the concept at pilot and industrial scale.

Abstract (German)

Die Europäische Union hat in den letzten Jahren nachhaltige Wirtschaftskonzepte wie die Circular Bioeconomy (CBE) stark gefördert. Im Mittelpunkt einer CBE steht die nachhaltige, ressourceneffiziente Nutzung von Biomasse (z.B.: lignozellulosehaltige Reststoffe) und deren Umwandlung in energetische und stoffliche Produkte in Bioraffinerien. Unter diesen Gesichtspunkten hat lignozellulosehaltige Biomasse (LCB) ein enormes Potenzial als Rohstoff für die nachhaltige Produktion von Chemikalien und Kraftstoffen, da sie hauptsächlich aus den polymeren Bestandteilen Zellulose, Hemizellulose und Lignin besteht, die in eine breite Palette von Bio-Plattformmolekülen umgewandelt werden können. Aufgrund der widerstandsfähigen Natur von LCB (Biomasse-Rekalzitranz) müssen diese Komponenten zunächst in geeigneten Vorbehandlungsschritten voneinander getrennt /fraktioniert werden, um ihre gleichzeitige Verwertung zu ermöglichen. Die Fraktionierung stellt jedoch eine große Herausforderung dar, da die Vorbehandlungsschritte oft sehr energie- und ressourcenintensiv sind und nicht *per se* als nachhaltig und wertvoll angesehen werden können. Ziel dieser Masterarbeit war es daher, drei Vorbehandlungsszenarien für die Aufbereitung von Weizenstroh zu simulieren und zu analysieren, um die technisch-ökologische Performance bereits in einem frühen Stadium des Prozessdesigns zu bestimmen. Zu diesem Zweck wurde der Organosolv (OS)-Aufschluss (Szenario 1) und die Kombination aus OS- und Liquid Hot Water (LHW)-Aufschlüssen (Szenario 2: OS-LHW; Szenario 3: LHW-OS) mit der Prozesssimulationssoftware Aspen Plus® auf der Basis von Daten aus Laborversuchen modelliert. Die ermittelten Massen- und Energiebilanzen dienten als Grundlage für die Durchführung der Ökobilanz (LCA). Die Ergebnisse aus der Prozesssimulation und der Ökobilanz wurden zur Entscheidungsfindung herangezogen, um das Szenario zu identifizieren, das letztlich zu den qualitativ „hochwertigsten" Plattformprodukten (kolloidale Ligninpartikel, cellulosereicher Feststoff, zuckerreicher Flüssigkeitsstrom) und zu den geringsten ökologischen Auswirkungen führt. Es zeigt sich, dass die Kombination von LHW und OS (Szenario 3: LHW-OS) die geringsten ökologischen Auswirkungen bei gleicher oder höherwertiger Qualität der Zwischenprodukte hat. Diese Erkenntnisse können als Entscheidungshilfe für die weitere Entwicklung des Konzepts im Pilot- und Industriemaßstab genutzt werden.

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List of Abbreviations

BE	Bioeconomy
BtL-fuels	Biomass to Liquid Fuels
CAPEX	Capital and Expense Costs
CBE	Circular Bioeconomy
CE	Circular Economy
CLP	Colloidal Lignin Particles
DP	Degree of Polymerization
DDS	Distiller`s Dried Grain & Solubles
EU	European Union
FU	Functional Unit
GaBi	Ganzheitliche Bilanz; Life Cycle Assessment Software from Sphera™
GUIDE	Globally Unique Identifier
pH	Hydrogen Potential / "Hydrogen Power" -> scale for indicating the acidity or basicity of an aqueous solution
H_3O^+	Hydronium Ions
HMF	Hydroxymethylfurfural
IEA	International Energy Agency
LCA	Life Cycle Assessment
LCB	Lignocellulosic Biomass
LCI	Life-cycle Inventory
LCIA	Life-cycle Impact Assessment
LHW	Liquid Hot Water
NREL	National Renewable Energy Laboratory
NRTL	Non-Random Two-Liquid model
OS	Organosolv

PFD	Process Flow Diagram
RQ	Research Question

1 INTRODUCTION

1.1 State of the field / research problem

Since the industrial revolution about 250 years ago, humankind has followed a resource-wasting, linear production path of "take, make and dispose" (Hassan, Williams, & Jaiswal, 2018, p. 310). This linear economic model, which consumes scarce resources, especially fossil raw materials, and degrades their value-added products into waste, is mainly responsible for several global crises such as climate change, biodiversity loss, and food, water and energy shortages (Keijer, Bakker, & Slootweg, 2019, p. 190).

Considering these aspects, it is clear that the current model is by nature unsustainable, and many voices are calling for a change to reverse this development trend (Sillanpää & Ncibi, 2019, chap. 1). In this alarming context, the European Union (EU) has adopted the European Green Deal, with the target of zero net greenhouse gas emissions by 2050, decoupling economic growth from resource use and ensuring that no person, and no place is left behind (European Commission, 2019).

To achieve these ambitious goals, renewable resources (biomass) and their resource-efficient, sustainable use will play a key role (Ubando, Felix, & Chen, 2019, p.3). In this sense, the EU is focusing on sustainable concepts such as the Circular Economy (CE), the Bioeconomy (BE) and the combination of these two concepts, a Circular Bioeconomy (CBE).

According to Stegmann, Londo, & Junginger (2020), CBE is defined as follows:

> “The circular bioeconomy focuses on the sustainable, resource-efficient valorization of biomass in integrated, multi-output production chains (e.g. biorefineries) while also making use of residues and wastes and optimizing the value of biomass over time via cascading.”(Stegmann, Londo, & Junginger, 2020, p.5).

Figure 1 illustrates the concept of CBE. In this concept, biomass is sustainably and resource-efficiently utilized in a biorefinery to produce value-added products by using the entire waste streams, recycling secondary products and upgrading by-products. In addition, diluted sub-streams that cannot be used economically for material production are used to generate energy. The energy required in the process is generated, for example, by burning unused biomass.

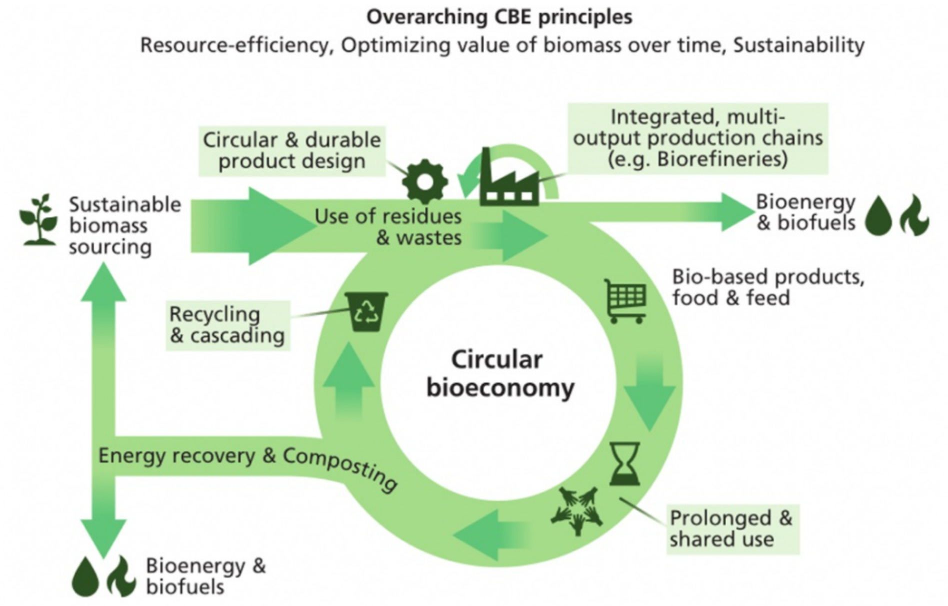

Figure 1. Graphical representation of the "Circular Bioeconomy" concept, inputs, outputs and processing steps. (from Stegmann et al., 2020, p.6)

Under these aspects, lignocellulosic biomass (LCB) is of particular importance as a raw material in CBE. LCB has enormous potential for the sustainable production of chemicals and fuels, as it consists mainly of the polymeric components cellulose, hemicellulose and lignin, which can be converted into a wide range of bio-platform molecules (building block chemicals with potential use in the production of numerous value-added chemicals) (Cherubini, 2010, p. 1418).

Despite the obvious benefits and the EU's support for CBE development, lignocellulosic biorefineries are not yet at the development stages of full industrial application. One reason for this is the complex structure and resistant nature of LCB. These inherent properties make it resistant to enzymatic and chemical degradation and pose a challenge for conversion into high-value chemicals. In order to fulfil the CBE concept that all valuable streams can be valorized, the lignocellulosic matrix must be separated into its different components in an adequate pre-treatment step. Key in this respect is the selective fractionation of the lignocellulosic biomass into separate cellulose-, hemicellulose- and lignin-rich streams. (Ferreira, Brancoli, Agnihotri, Bolton, & Taherzadeh, 2018; p. 1; Isikgor & Becer, 2015, p. 4498).

Therefore, research has focused on developing pretreatment steps that are simple, environmentally friendly, cost-effective and economical, and do not lead to undesired compounds or losses in the fraction of interest. More recent approaches in this field also include the combination of two or more pretreatment strategies, as this can significantly increase the selectivity and yield of the process with a uniform quality (Hassan et al., 2018, p. 312).

For most of the biorefineries, the pretreatment stage is generally the most energy and resource-intensive (from a gate-to-gate perspective); hence, it is not considered to be intrinsically sustainable and opens the possibility to optimize this stage to make it more sustainable. Consequently, the identification of critical hotspots and suitable process parameters is of great importance. In addition, the technical, economic and environmental performance of different technologies is a key activity to identify suitable pretreatment strategies.

Reliable computer-aided models and the balancing of the processes up to a complete life cycle assessment (LCA) are necessary to compare the pretreatment steps from an ecological point of view and to identify optimization potentials. In this way, key parameters can be identified already in the early phase of process development in order to find more advantageous process routes in terms of environmental impact. These steps are necessary to advance the development of biorefineries into fully sustainable circular multiproduct refineries.

1.2 Purpose of the thesis / scientific question

The scope of this master thesis focuses on the modelling and Life Cycle Assessment of different pretreatment strategies for the bioconversion of LCB. The specific study case used within this work consists of the production of colloidal lignin particles (CLP) from wheat straw (Beisl, Loidolt, Miltner, & Friedl, 2018; Beisl, Loidolt, Miltner, Harasek, & Friedl, 2018), already being developed in a pilot phase. Currently, the process valorizes only the lignin fraction of the raw material and research has been focused on the simultaneous valorization of the lignin and hemicellulose fractions, aiming to convert the process into a multi-product biorefinery. This implicates a combination of pretreatment stages and therefore, this work will focus specially in evaluating the different pretreatment strategies from an ecological point of view.

The data base consist of previous findings and results from practical laboratory experiments and laboratory analyses already conducted on the combinations of Organosolv (OS) and Liquid Hot Water (LHW) extractions to hydrolyze the lignin and hemicellulose fractions (Serna-Loaiza, Zikeli, Adamcyk, & Friedl, 2020). In this context, it is of particular interest to find out which pretreatment combination has a better technical and ecological performance and what influence the addition of an additional pretreatment technology has. To evaluate this, three different scenarios were proposed:

- ***Scenario 1:*** Pretreatment of the wheat straw by OS extraction; referred as *base case scenario*

- ***Scenario 2:*** Pretreatment of wheat straw by OS extraction (as the first step), followed by LHW extraction (as the second step), where the solid residue from the first step is retreated; referred as *OS-LHW scenario*
- ***Scenario 3:*** vice versa to Scenario 2; Pretreatment of wheat straw by LHW extraction, followed by OS extraction; referred as *LHW-OS scenario*

Based on the experimental data, these three scenarios were simulated in a process simulation software and LCA software and evaluated for the technical and environmental performance. From the comprehensive overall picture of these models, important key parameters can then be identified, which are summarized in the following research question (RQ):

RQ: *How do the ecological hot spots, the environmental impact, the composition of the individual fractions and the potential for further processing into valuable products change when:*

- *the solid residues of the OS extraction are further treated with a LHW extraction?*
- *the technological treatment strategy arrangement is changed (OS-LHW / LHW-OS)?*

1.3 Methods & academic approach

To achieve the research objectives and to answer the research question, a cradle-to-gate LCA was carried out according to the DIN EN ISO 14040 and 14044 standards. In the process, data from laboratory experiments were collected, displayed in an MS Excel model and scaled up through additional simulations. For the balance of all process steps involved, an additional process simulation was carried out with the simulation software Aspen Plus V10 (36.0.0.249, Aspen Technology Inc.). During this process, missing data were supplemented with literature data. The mass and energy balances obtained from the process simulations have been used to prepare the life cycle inventory.

Based on the life cycle inventories, a life cycle assessment was performed according to ISO standards 14040 and 14044 using the life cycle assessment software GaBi (v.10.0.0.71, Sphera Solution GmbH). From the comprehensive overall picture of the models obtained, the possible environmental impacts were then analyzed and evaluated based on various impact categories.

1.4 Thesis structure

This Master's thesis is divided into five chapters and their subchapters. After the introduction of the research focus (state of the field, research object including the problem and the aim), chapter 2 deals with the theoretical background by describing the concept of biorefinery. In this context, the definition, systematics, classification and process chain of biorefineries are addressed, and the concept of the lignocellulosic biorefinery is explained in more detail (extraction process for the separation of biomass components and their potential for the subsequent conversion and refinement steps into value products). Furthermore, the theoretical background of the LCA and process simulation methods is explained. Chapter 3 summarizes the cradle-to-gate LCA of the research object (three pre-treatment strategies for the bioconversion of LCB) carried out in the context of this Master thesis according to the DIN EN ISO 14040 and 14044 standards. The process of data collection and evaluation, i.e., from the generation of the laboratory data, to the representation of the data in an MS Excel model, as well as their modelling in the process simulation tool Aspen Plus® and the subsequent realization of the LCA in the software GaBi (v.10.0.0.71, Sphera Solution GmbH), is systematically described. Chapter 4 then presents the data resulting from the process simulation and LCA. The most important findings from the results are summarized in Section 4.3, and the research question is answered. This section also points out the limitations associated with the study. The master thesis is concluded with the findings from the study and the outlook for future research.

2 THEORETICAL BACKGROUND

2.1 Biorefinery

Since the launch of the European Bioeconomy Strategy (European Commission, 2018) and the CE Action Plans (European Commission, 2015, 2020), CBE has gained tremendous attention from scientists and industry practitioners. The key in this model is on the development and implementation of material transforming basic product systems (called biorefinery concepts), which follows the CE concept (Ubando et al., 2020, p.3). Therefore, biorefinery concepts are crucial for the sustainable and economic viability of biomass conversion and are discussed in more detail as follows.

2.1.1 Definition and classification

Definition

The concept of a biorefinery is discussed by scientists and practitioners for a long time, and several definitions have been formed, which differ only slightly. Among the best-known definitions are those of Task Group 42 of the International Energy Agency (IEA) and the U.S. National Renewable Energy Laboratory (NREL):

> “Biorefinery is the sustainable processing of biomass into a spectrum of marketable products (food, feed, materials, chemicals) and energy (fuels, power, heat).” (de Jong, 2020, p. 10)
>
> “A biorefinery is a facility that integrates biomass conversion processes and equipment to produce fuels, power, and chemicals from biomass.”

A much more detailed description is provided by the German Biorefinery Roadmap (Wagemann & Tippkötter, 2018, p.3-4). The roadmap was developed to promote the further development and utilization of biorefineries on a national level.

> „A biorefinery is characterized by an explicitly integrative, multifunctional overall concept that uses biomass as a diverse source of raw materials for the sustainable generation of a spectrum of different intermediates and products (chemicals, materials, bioenergy/biofuels) allowing the fullest possible use of all raw material components. The co-products can also be food and/or feed. These objectives necessitate the integration of a range of different methods and technologies.” (BMELV, 2012, p.8)

All these definitions have the same objective, namely the creation of "developed biorefineries”, so-called "Phase III biorefineries" (Kamm, Kamm, Gruber, & Kromus, 2005, p.19). This keyword refers to the stage of development and the degree of flexibility of the biorefineries.

"Phase I biorefineries" have almost no flexibility in processing, which means that the operation of such refinery is only possible for a specific feedstock and a defined primary product. According to the German Biorefinery Roadmap's strict definition, these do not qualify as biorefineries, as the sustainable integration of all material flows is not sufficiently ensured. Nowadays, such biorefineries are also no longer aspired to because there is no desire to generate waste streams in the sense of the circular economy. An example of this type is the dry mill ethanol production, where the amount of grain as raw material and the produced amount of ethanol is fixed (Kamm et al., 2005, p.19).

In a *"Phase II biorefinery"*, only one feedstock is used, but unlike a *"Phase I biorefinery"*, it is able to produce a broader range of products. Thus, depending on the current market demand, the process management can react flexibly and produce one of the possible products in larger quantities. An example of this would be the wet milling technology, where grain is converted into starch, corn syrup, ethanol, corn oil and cornflour (Kamm et al., 2005, p.19-20).

The preferred *"Phase III biorefinery"* can process different feedstocks (feedstock mix) in different process modules (technology mix) and thus produce a variety of different high-quality products (Kamm et al., 2005, p.20). With the degree of diversification of feedstocks and marketable end products, the economic and production advantage increases as well (Dumeignil, 2012, p.2).

Classification

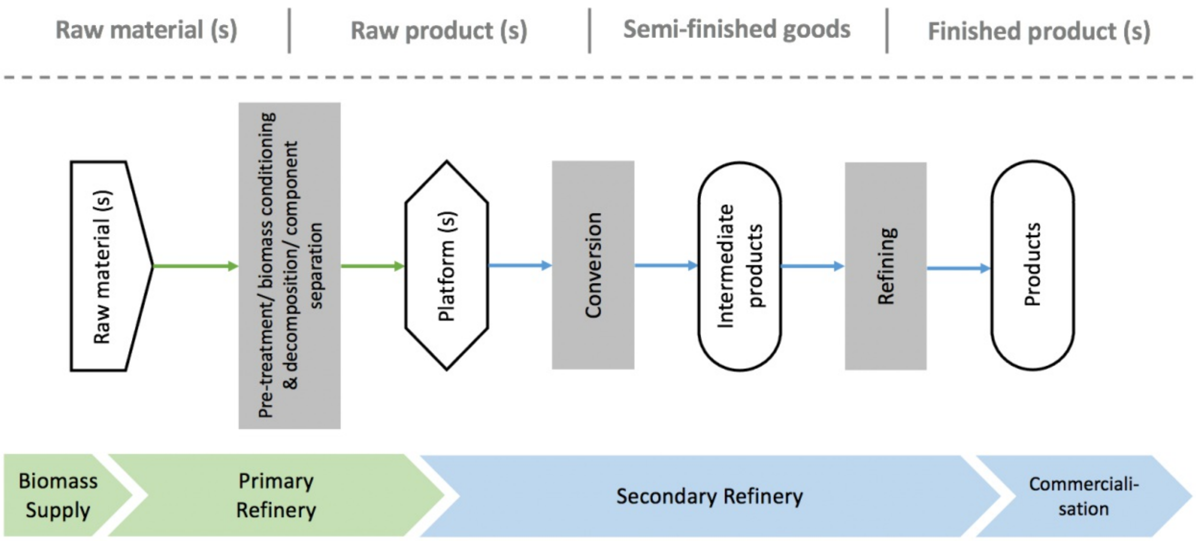

Figure 2. Schematic representation of the biorefinery process chain. (adapted from BMELV, 2012, p.22)

With the development of *"Phase III biorefineries"*, the complexity and number of different biorefinery types increase. Therefore, their classification into standard types is necessary for a better understanding and comparison. To classify them systematically, one primarily refers to the biorefinery process chain (see Figure 2).

The process chain is quite simple in structure and basically consists of biomass supply, primary refinery, and secondary refinery. In the primary refinery, facilities are used for the pretreatment and preparation of the biomass as well as for the separation of the biomass components, while in the secondary refinery, facilities are used for the subsequent conversion and refining steps. Therefore, the primary refining involves the separation of biomass components into usable platforms (intermediate products) (BMELV, 2012, p.22), linking feedstocks and final products (Cherubini et al., 2009, p.538). In the secondary refinery, the platforms from the primary refinery (e.g., cellulose, starch, sugar, vegetable oil, lignin, plant fibers, biogas, syngas) are then converted into a variety of secondary compounds and products via further conversion and upgrading steps (BMELV, 2012, p.22).

The systematic classification system of the IEA Bioenergy Task 42 is, therefore, based on four main characteristics (Cherubini et al., 2009, p.538): *1. Platforms 2. Products 3. Feedstock 4. Processes*, which are listed in more detail in Table 1 and described in the following paragraphs.

Table 1.
Elements (and relative subgroups) of the biorefinery classification

	Agricultural Biomass	**Aquatic Biomass**	**Biogenic Residual- & Waste Materials**
Raw material	Oil Crops	Algae	Agricultural and Forestry Residues (e.g., Straw, Manure, Wood Residues, Fruit Peel, Slurry)
	Starch Crops		
	Sugar Crops		
	Grasses		Biogenic Residual Materials from Processing (e.g., Whey, Pulp, Stillage, Spent Grains)
	Wood		Biogenic Waste Materials (e.g., Yellow Grease, Waste Wood)
	Woody Biomass		
Platforms	Low Molecular Weight Carbohydrates (e.g., Lactose, Sucrose)		
	Polymeric Carbohydrates (e.g., Starch, Inulin, Pectin)		
	Lignocellulose Components (Lignin / Cellulose / Hemicellulose)		
	Proteins		
	Plant Fibers		
	Vegetable Oils, Lipids		
	Pyrolysis Oil		
	Press Juice		
	Biogas		
	Syngas		

Products	**Materials**	**Bioenergy**
	Chemicals	Solid, Liquid, Gaseous Source of Bioenergy
	Materials	Electricity
	Feed	Heat
	Food	
Processes	Physical, including Mechanical Processes	
	Thermochemical Processes	
	Chemical Processes	
	Biotechnological Processes	

Note. From BMELV, 2012, p.32

Platforms

Biorefinery platforms form the basis of the classification system. The platforms are intermediate products, produced during primary refining and used as a feedstock for subsequent secondary refining. This approach is similar to the petrochemical industry, where the feedstock (crude oil) is fractionated in a rectification plant into a variety of intermediates (platforms), which are then processed in liquid catalytic crackers or catalytic reformers into final energy and chemical products (Cherubini et al., 2009, p.538).

Theoretically, all the petroleum refinery's platform chemicals could also be produced from biomass but with lower yields and higher costs. Therefore, biorefinery concepts are based only on a limited number of platforms which are listed in the Table 1 (Cherubini, 2010, p. 1417-1418). Under the biorefinery concepts, five main types have basically emerged, which are essentially distinguished by their platforms and consequently also by the type of secondary refining (BMELV, 2012, p.8; Cherubini et al., 2009, p.536):

- sugar biorefinery or starch biorefinery
- vegetable oil biorefinery or algal lipid biorefinery
- lignocellulose (cellulose, hemicellulose and lignin) biorefinery - green biorefinery
- synthesis gas biorefinery
- biogas biorefinery

Products

The products obtained from secondary refining through conversion and upgrading steps are broadly divided into two main classes (BMELV, 2012, p.29; Cherubini et al., 2009, p.539):

1) Material-driven biorefinery systems that produce biobased chemicals and materials as products for material use.

- Basic chemicals and chemical intermediates.
- Fine and specialty chemicals (e.g., crop protection products, pharmaceutical bases, dyes).
- Bio-based polymers, materials and composites
- Bio-based man-made fibers, natural fibers
- Natural fiber and wood fiber reinforced materials and composites
- Adhesives, coatings and inks
- Detergents and personal care products
- Fertilizers

2) Energy-driven biorefinery systems that produce secondary energy sources for energy use.

- Biofuels (e.g., ethanol, biodiesel, BtL fuels, biomethane, hydrogen)
- Electricity
- Heat

The material and energy use paths are often coupled, so that a strict distinction is not possible. In practice, however, it has been shown that, for economic reasons, a biorefinery is either material- or energy-oriented.

Feedstock

The raw material used for biorefineries is biomass. Biomass is formed according to the photosynthesis reaction (Kamm et al., 2005, p.12):

$$n(CO_2) + nH_2O \rightarrow (CH_2O)n + nO_2$$

Atmospheric carbon dioxide is converted into sugar together with water and sunlight. Plants then use the sugar to form the complex materials of terrestrial biomass (Cherubini, 2010, p. 1414). In aquatic systems, algae and cyanobacteria fulfil this purpose (BMELV, 2012, p.27).

Because of their synthesis, biomass is considered the only renewable source of organic carbon on earth and the ideal petroleum equivalent for producing sustainable, valuable products with net-zero carbon emission (Isikgor & Becer, 2015, p.4498).

From a chemical point of view, the biomass has a relatively high content of oxygen and a relatively low content of hydrogen besides the high organic carbon content. In addition, nitrogen, sulphur and other elements are present in small quantities. The biomass's main components can be roughly divided into the following components: Carbohydrates (cellulose, hemicelluloses, starch, pectin, inulin and sucrose); lipids; proteins; lignin; and inorganics in the form of ash. The proportion of these components varies depending on the origin of the biomass (BMELV, 2012, p.27).

In addition to the biomass's chemical composition, the characteristics of its supply (e.g. quantity, yield, availability, harvesting time, purity, transportability, storage stability and long-term quality) are also relevant for the sustainable and economic operation of the biorefinery (BMELV, 2012, p.27).

To provide biomass, industrial or energy crops are cultivated, or the residues and co-products from primary production or from industrial processing steps in secondary refining, or the waste after the use phase of the finished products are used. They can be roughly divided into the following sectors (BMELV, 2012, p.27-28; Cherubini et al., 2009, p.540):

- renewable resources (from agriculture and forestry, which are not used as food or animal feed, including aquatic biomass)
- biogenic residues from agriculture and forestry (residues from production such as straw, beet leaf, forest residues, liquid manure and biogenic residues from primary refining)
- industrial biogenic residues (processing and production residues; residual biomass from fermentation (e.g., stillage, fermentation residues) or biogenic residues from food production such as whey, spent grains, fruit peel)
- biogenic waste materials that result after the use of finished products (e.g., used cooking fats, waste from food consumption, bio-based oils, bio-based packaging plastics, used wood).

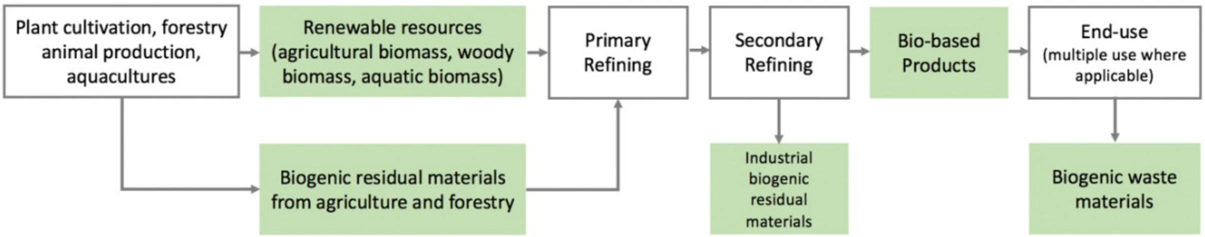

Figure 3. Illustration of the sources of biobased raw materials. (adapted from BMELV, 2012, p.28)

Processes

In the biorefinery process (primary refining, secondary refining), several technological processes can be used to convert biomass feedstocks into marketable products. These are roughly divided into four main groups (Cherubini et al., 2009, p.541):

- Mechanical/physical processes
  Basic operation for altering material properties while maintaining the chemical structure (e.g., pressing, milling, drying, heating, cooling,) as well as purification and separation processes (e.g., filtration, distillation, extraction, crystallization, adsorption) and extraction processes.
- Thermochemical processes
  Biomass is exposed to extreme conditions such as high temperature and/or pressure (e.g., pyrolysis, gasification, hydrothermal refinement, combustion).
- Chemical processes
  Basic operations for material conversion in which the substrate is chemically altered (e.g., hydrolysis, transesterification, hydrogenation, oxidation, digestion)
- Biochemical processes
  Biomass is broken down under mild conditions with the help of enzymes and microorganisms (e.g., aerobic and anaerobic fermentation, enzymatic conversion).

These processes have advantages and disadvantages that can be compensated by combining them. Special attention must be paid to the utilities (e.g. energy) and reagents needed in the process. The aim should be minimizing the demand and generate from renewable sources such as hydropower, solar, and biomass process residues. In addition, the issues of waste, wastewater and pollution have to be considered in the balancing of biorefinery plants (BMELV, 2012, p.31).

The Figure 4 shows the schematic, graphic implementation of the classification system.

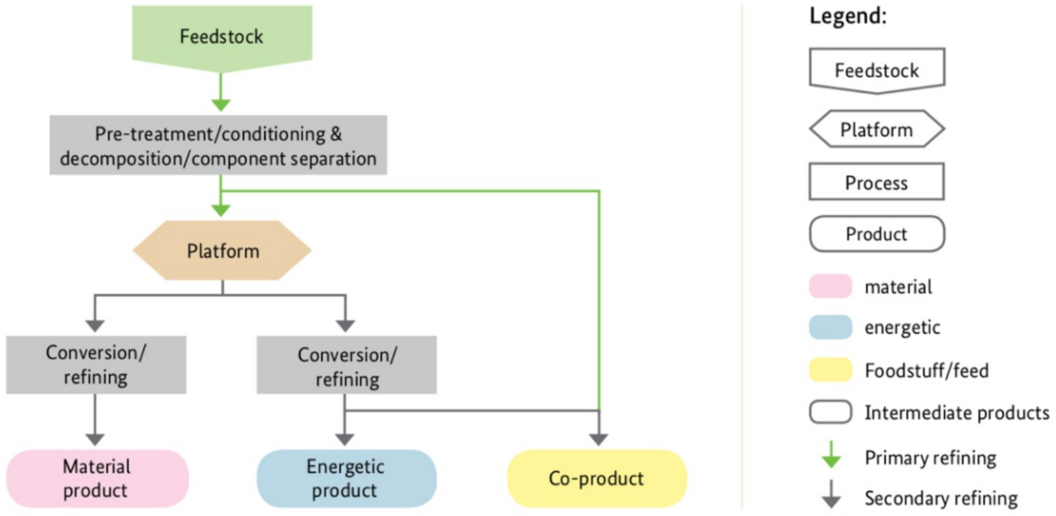

Figure 4. Schematic, graphical presentation of the classification system. (from BMELV, 2012, p.26)

2.1.2 Lignocellulosic biorefinery

Since the thesis is based on experiments with the lignocellulosic biomass (LCB) feedstock wheat straw, the LCB-biorefinery, which is one of the five main types of biorefinery concepts, that have been established (Chapter 2), it will be discussed in more detail.

2.1.2.1 Lignocellulosic biomass as raw material

LCB is the most abundant renewable biomass on earth, and unlike other biomass sources, it does not compete with food production. In addition, forestry residues, agricultural residues and agro-industrial lignocellulosic waste are produced in large quantities every year and are therefore also a favorable raw material from an economic point of view (Isikgor & Becer, 2015, p.4498). However, the differences in availability between forestry residues and agricultural residues must be taken into account. Forest residues can be procured year-round, while agricultural residues are only available at harvest time. To operate an LCB biorefinery year-round, agricultural residues have to be stored.

Among agricultural residues (corn straw, wheat straw, sugarcane straw, bagasse), wheat straw is the largest biomass feedstock in Europe (Talebnia, Karakashev, & Angelidaki, 2010, p.4744).

It is produced as a by-product of wheat harvesting at a ratio of 1.3 (residue to harvested crop). Thus, from one ton of harvested wheat, about 1.3 tons of wheat straw is theoretically available as feedstock for the LCB-biorefinery. However, complete removal of wheat straw from the field results in losses of organic matter and resulting in undesirable soil erosion. Consequently, depending on the climate zone, crop rotation, current soil condition, and field treatment, some wheat straw must remain on the field (Talebnia et al., 2010, p.4745).

According to a study by Kim & Dale (2008, p.363), at least 30% of the straw should be used to cover the cropland to prevent soil erosion. Considering this aspect, the potentially usable wheat straw quantity, based on one ton of harvested wheat, is reduced to around 0.9 tons.

Structure of lignocellulosic biomass

LCB has a complex structure and consists predominantly of the polymeric component's cellulose, hemicelluloses, lignin, and some smaller amounts of ash and extractives. Together, they form the skeleton of the plant cell wall (Kamm, Kamm, Schmidt, Hirth, & Schulze, 2005, p.103). Depending on the plant species and the prevailing growth conditions, these polymers' composition varies (Isikgor & Becer, 2015, p.4500). To show these differences, the compositions of different LCB are given in Table 2. Furthermore, the composition of the three-dimensional, heterogeneous structure of LCB is illustrated in Figure 5.

Table 2.
Chemical composition of different lignocellulosic biomass types

Lignocellulosic biomass		**Cellulose [%]**	**Hemicellulose [%]**	**Lignin [%]**
Hardwood	Poplar	50,8–53,3	26,2–28,7	15,5–16,3
	Oak	40,4	35,9	24,1
	Eucalyptus	54,1	18,4	21,5
Softwood	Pine	42,0–50,0	24,0–27,0	20,0
	Douglas fir	44,0	11,0	27,0
	Spruce	45,5	22,9	27,9
Agricultural waste	Wheat Straw	35,0–39,0	23,0–30,0	12,0–16,0
	Barley Hull	34,0	36,0	13,8–19,0
	Barley Straw	36,0–43,0	24,0–33,0	6,3–9,8
	Rice Straw	29,2–34,7	23,0–25,9	17,0–19,0
	Rice Husks	28,7–35,6	12,0–29,3	15,4–20,0
	Oat Straw	31,0–35,0	20,0–26,0	10,0–15,0
	Ray Straw	36,2–47,0	19,0–24,5	9,9–24,0
	Corn Cobs	33,7–41,3	31,9–36,0	6,1–15,9
	Corn Stalks	35,0–39,6	16,8–35,0	7,0–18,4
	Sugarcane Bagasse	25,0–45,0	28,0–32,0	15,0–25,0
	Sorghum Straw	32,0–35,0	24,0–27,0	15,0–21,0
Grasses	Grasses	25,0–40,0	25,0–50,0	10,0–30,0
	Switchgrass	35,0–40,0	25,0–30,0	15,0–20,0

Note. From Isikgor & Becer, 2015, p.4500

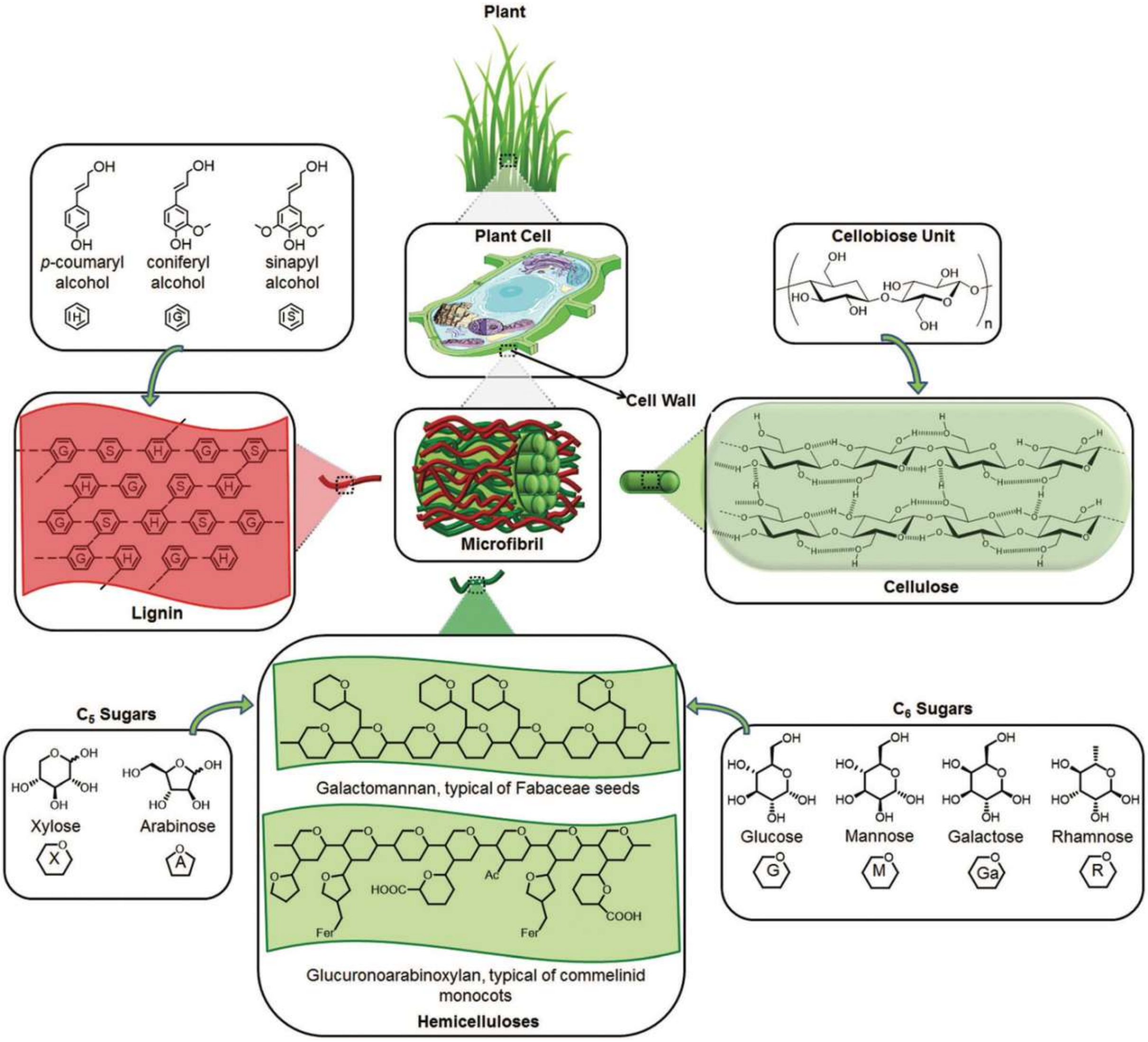

Figure 5. A structural section of lignocellulosic biomass showing the main components. (Isikgor & Becer, 2015, p.4499)

Structure of cellulose

Cellulose $(C_6H_{10}O_6)_n$ is the major component of LCB (Isikgor & Becer, 2015, p.4499). Cellulose is a long-chain, linear polysaccharide consisting of a few hundred to a thousand D-glucose units (C6 sugars) linked entirely by β-1,4-glycosidic bonds. The repeating unit in this process is the disaccharide cellobiose $(C_{12}H_{22}O_{11})_n$ (see Figure 5). The intramolecular and intermolecular hydrogen bonds link the adjacent cellulose chains together, resulting in a solid, ordered (crystalline) structure. Due to this ordered structure, neither an enzyme nor a water molecule can penetrate between the cellulose chains. The connected cellulose chains form the elementary fibrils. In addition to the highly ordered crystalline regions, the elementary fibrils also contain some disordered amorphous regions. These are more reactive and are the first to be hydrolyzed during pretreatment. Thus, an increase in the size of the amorphous region leads to an increase in the hydrolysis rate and thus increases the digestibility of the cellulose (Steinbach, Kruse, & Sauer, 2017, p.250).

Structure of hemicellulose

In addition to cellulose, a significant portion of the LCB is composed of hemicellulose $(C_5H_8O_5)_n$, making it the second most abundant polymer. Hemicelluloses are complex (much more complex than cellulose), amorphous, branched heteropolymers whose composition depends on the plant species. Hemicelluloses can be divided into xylans, mannans, and galactans. The biomass network of these three amorphous polymers consists of pentoses (C5 sugars) such as xylose and arabinose; hexoses (C6 sugars) such as glucose, mannose and galactose; and sugar acids such as glucuronic acid, galacturonic acid, methylgalaturonic acid. In addition, the hemicellulose chains contain acetyl, formyl or other ester groups. In the LCB, hemicelluloses are part of the cell wall and provide structural strength by cementing the elementary cellulose fibrils together to form microfibrils and linking them to lignin via covalent bonds. Hemicelluloses thus act as a binder between lignin and cellulose building blocks. The microfibrils are surrounded by a layer of lignin and hemicellulose and are thus strongly protected against degradation. This stable structure must first be released before any degradation can take place (Isikgor & Becer, p.4499, 2015; Steinbach et al., 2017, p.254).

Structure of lignin

Lignin $(C_9H_{10}O_2(OCH_3)_n)$ is a highly complex three-dimensional amorphous polymer composed of various phenolic compounds and is the main component of cell walls. Lignin acts as a cell glue connected to carbohydrates (cellulose, hemicellulose) by covalent bonds. It thus holds the cellulose and hemicellulose building blocks together. It gives support to the plant fabric and the individual fibers, rigidity to the cell wall, and resistance and impermeability to insects and pathogens (Decina & Crestini, 2012, p.169; Isikgor & Becer, 2015, p.4500).

The lignin structure is formed by the oxidative coupling of three different phenylpropane building blocks, the monolignols: p-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol (Isikgor & Becer, 2015, p.4500). In this process, the monomeric units p-hydroxyphenylpropane- (H), guaiacylpropane (G) syringylpropane (S) are linked to each other via various ether and C-C bonds, such as β- O-4-aryl ether, β-β-, β-5- and α-O-4-aryl ether bonds (Liu et al., 2019, p.2635).

2.1.2.2 LCB-biorefinery platforms

As already described, LCB is generally composed of the three biopolymers, cellulose, hemicellulose, and lignin (Den, Sharma, Lee, Nadadur, & Varma, 2018, p.3), which form the LCB biorefinery platforms (see figure 6). Due to the crystalline structure of cellulose, lignification and the structurally heterogeneous and complex composition of the cell wall, LCB is resistant to chemical and biological degradation (Baruah et al., 2018, p.2). This property is known as biomass recalcitrance and has the consequence that the three polymers cannot be utilized in a valuable way without pretreatment. For this reason, the biopolymers must first be fractionated from the complex structure of LCB. Selective fractionation is a crucial step and represents the main task of the primary refining process. Once these polymers are isolated, a variety of other commercially viable base and bulk chemicals can be obtained from these three platforms in a secondary refining process (Isikgor & Becer, 2015, p.4498). LCB biorefineries, therefore, have high potential for the sustainable production of energy and value-added chemicals.

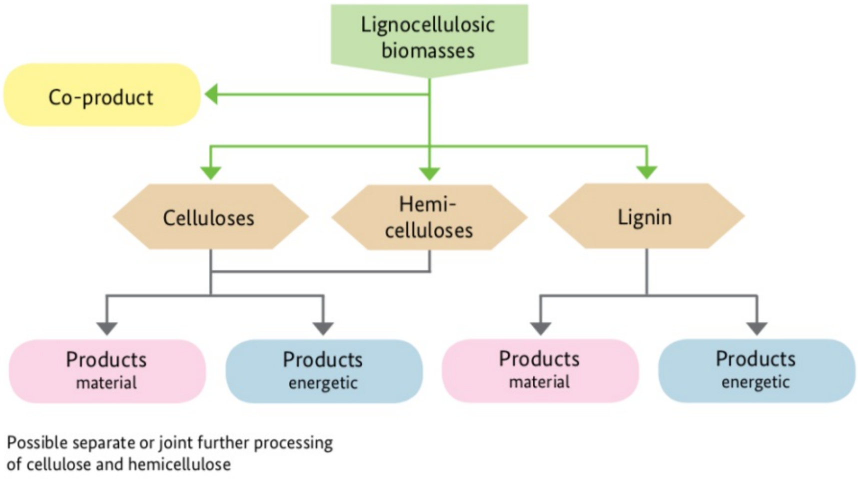

Figure 6. Schematic representation of a LCB biorefinery. (BMELV, 2012, p.26)

Despite the high potential of LCB, relatively few valuable materials (energy and value-added chemicals) have been produced out of them so far. This is mainly due to the high production costs of the biomass pretreatment steps. Due to the naturally recalcitrant structure of rigid polymers, complex pretreatment processes are required to fractionate the components (cellulose, hemicellulose, and lignin) (Den et al., 2018, p.2).

This is also one of the main reasons why LCB biorefineries still face bottlenecks and are not yet at the development stage of full industrial application. Therefore, the focus of science and research is on the selective and economical primary fractionation of LCB (Ferreira & Taherzadeh, 2019, p.1).

2.1.2.3 Biomass pretreatment: separation of cellulose, hemicellulose, & lignin

The pretreatment is one of the first and most important steps in the process chain to get access to the individual components (cellulose, hemicellulose and lignin) (Galbe & Wallberg, 2019, p.5). During the pretreatment process, the complex structure of LCB is generally disturbed, resulting in the breakup of the lignin shield as well as the degradation of the hemicelluloses and the decrystallization of the cellulose, leading to partial depolymerization (Baruah et al., 2018, p.2). This process is shown schematically in Figure 7.

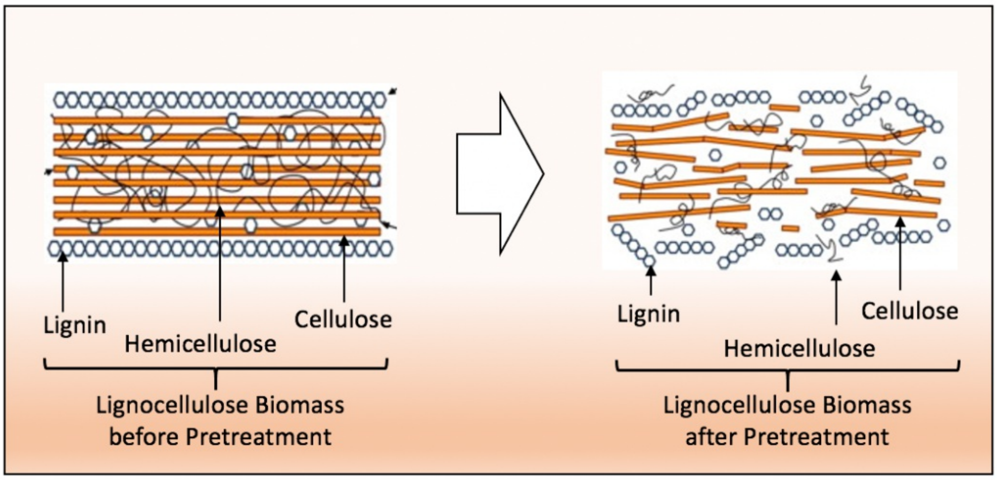

Figure 7. Schematic process of LCB pretreatment. (adapted from Haghighi Mood et al., 2013, p.79)

A successful pretreatment process should meet the following important characteristics: It should leave a digested, hydrated substrate that can be easily hydrolyzed and optimized to meet subsequent conversion steps' requirements. Optimization includes the avoidance/mitigation of the formation of inhibitory compounds and the minimization of carbohydrates' degradation to avoid yield losses during conversion. Further important indicators are the selective separation and recovery of the components cellulose, hemicellulose and lignin; as well as the reduction of the consumption of auxiliary and input materials (e.g. pretreatment additives and energy) as well as the reduction of the footprint of the process (in terms of waste disposal, low toxicity, resource consumption) (de Jong & Gosselink, 2014, p.286; Den et al., 2018, p.6).

To this end, various pretreatment processes have been developed that can be classified on the basis of mechanical/physical, chemical, physicochemical, and biological effects. The most widely used processes are discussed in the following sections with respect to the above properties.

2.2 Biomass pretreatment methods

2.2.1 Physical including mechanical pretreatment

The physical and mechanical processes are often placed before other pretreatment methods. The purpose of these processes is to reduce the particle size (Hendriks & Zeeman, 2009, p.11). The reduction in particle size leads to an increase in porosity and an increase in specific surface area, as well as a reduction in the crystallinity and degree of polymerization (DP) of the cellulose (Behera et al., 2014, p.93), without changing the chemical structure of the LCB. This makes subsequent processes simpler and more efficient (Baruah et al., 2018, p.3). The used processes are milling, grinding, extrusion, pulverization, and/or irradiation (gamma rays, electron beams, ultrasound, and microwave) (Raspolli Galletti & Antonetti, n.d., p. 102). However, these pretreatment processes require high energy input and are therefore expensive. Moreover, the purely physical modification of LCB does not remove lignin which is another disadvantage (Den et al., 2018, p.5).

2.2.2 Chemical pretreatment

Chemical pretreatment removes lignin and/or hemicellulose. As a result, the ability of cellulose to degrade is increased. Furthermore, the degree of polymerization and the crystallinity of the cellulose is reduced. For chemical pretreatment, various oxidizing agents, alkali, acids, and salts can be used (Behera et al., 2014, p. 93).

2.2.2.1 Alkaline pretreatment

The alkaline pretreatment is based on the hydrolytic effect at high pH (Galbe & Wallberg, 2019, p.8), whereby the lignin is solubilized in the alkaline solution (Baruah et al., 2018, p.6). The bases commonly used are sodium hydroxide, calcium hydroxide, sodium carbonate, and liquid ammonia, whereby sodium hydroxide has proven to be the most commonly used and effective base (Den et al., 2018, p.7). During the pretreatment, a saponification reaction occurs that causes a breakdown of the intermolecular ester compounds between hemicellulose and lignin. As a result, the lignin and part of the hemicellulose are solubilized, leaving the cellulose largely intact. However, the structure is altered as the cellulose swells, reducing DP and crystallinity.

In addition, acetyl and various acid substitutions of hemicellulose can also be removed, increasing the accessibility of the cellulose surface (Baruah et al., 2018, p.6).

Unlike other pretreatments, alkaline pretreatment can be carried out at lower temperatures and pressures but then requires long reaction times and high base concentrations, especially at room temperature. The yield/effectiveness of the treatment depends on the feedstocks and treatment conditions. For example, agricultural residues such as wheat straw can be treated more effectively by this method than woody biomass due to their lower lignin content (Raspolli Galletti & Antonetti, n.d., p.109).

2.2.2.2 Acid pretreatment

By acid pretreatment, primarily hemicellulose is hydrolyzed, while cellulose and lignin are generally less affected (Galbe & Wallberg, 2019, p.8). During the acid treatment, the glycosidic bonds between hemicellulose and cellulose are cleaved by the formed hydronium ions (H_3O^+), which breaks down the long cellulose and hemicellulose chains (Baruah et al., 2018, p.6). For this purpose, organic and inorganic acids (e.g., sulfuric acid, hydrochloric acid, nitric acid, phosphoric acid, acetic acid, and maleic acid) are used, whereby sulfuric acid and hydrochloric acid (de Jong & Gosselink, 2014, p.289) are the most commonly used ones (Den et al., 2018, p.7). These acids can be used in different concentrations in the pretreatment process; either diluted acids are used at high temperature or concentrated acids are used at low temperature (Den et al., 2018, p.7). Depending on these conditions (pretreatment severity), the extent of solids dissolution varies. Under sharp conditions (high concentrations and high temperatures), not only hemicellulose is hydrolyzed, also cellulose is converted to oligosaccharides or monosaccharides. At extremely high acid concentrations, carbohydrates are degraded to inhibitory compounds, such as furfural, HMF, and levulinic acid (Galbe & Wallberg, 2019, p.8). Another disadvantage of concentrated acids is that they are toxic and corrosive, requiring high operating and maintenance costs (Baruah et al., 2018, p.6).

2.2.2.3 Organosolv pretreatment

In this process, various organic solvents (organosolv (OS)) or their aqueous solutions are used at high temperatures (100-250°C) to separate lignin and hemicellulose. The most important feature in this respect is the ability to dissolve the biomass (Galbe & Wallberg, 2019, p.13). LCB is thereby fractionated into a cellulose-rich solid stream and a liquid stream rich in lignin, hemicellulose and monomeric C5 and C6 sugars (Ferreira & Taherzadeh, 2019, p.2). During the process, delignification (by cleavage of ether compounds) and solubilization of hemicellulose lead to an increase in the pore volume and accessible surface area of cellulose (Baruah et al., 2018, p8).

A variety of different solvents can be used for the pretreatment. These vary from short-chain aliphatic alcohols (e.g., methanol and ethanol), to polyhydric alcohols (e.g., glycerol, ethylene glycol, triethylene glycol), to alkylene carbonates, organic acids, etc. (Ferreira & Taherzadeh, 2019, p.2). Catalysts (e.g.: mineral acids, bases and salts) can be added to improve the delignification rate and or lower the pretreatment temperature (Baruah et al., 2018, p.8). The process parameters (solvent catalyst type; solvent catalyst concentration; temperature, residence time; solid/liquid ratio (S/L)) need to be optimized for selective fractionation (Ferreira & Taherzadeh, 2019, p.2).

OS pretreatment's advantages lie in obtaining a relatively pure cellulose residue and an isolatable valuable lignin fraction. In addition, the solvents can be recovered relatively easily by distillation and recycled back into the process. This is also necessary because most of the organic solvents are expensive. However, the disadvantage of the recovery process is that it is very energy-intensive and causes considerable additional costs. In addition, due to the high flammability and volatility of the organic solvents, the processes must be carried out under particularly controlled conditions (Baruah et al., 2018, p8).

2.2.2.4 Ozonolysis

Ozonolysis is used to reduce the lignin content in LCB. The lignin is oxidized and degraded during the ozone treatment. It is characteristic of this process that the hemicellulose is only minimally attacked, and the cellulose is not attacked. The pretreatment is carried out at room temperature and atmospheric pressure and has the advantage that no inhibitory compounds are formed. However, the process requires high ozone concentrations and thus requires a large amount of ozone and is therefore relatively expensive (Behera et al., 2014, p.98).

2.2.3 Physical-chemical pretreatment

The pretreatment method combines chemical and physical processes. Such processes include steam explosion, liquid hot water (LHW) treatment, ammonia fiber/freeze explosion, wet oxidation, ammonia recycle percolation, aqueous ammonia, CO_2-explosion and ionic liquids.

2.2.3.1 LHW pretreatment

LHW pretreatment aims primarily to completely hydrolyze the hemicellulose and separate it from the rest of the solid while reducing the formation of inhibitors (de Jong & Gosselink, 2014, p.286; Hendriks & Zeeman, 2009, p.12).

Liquid water at elevated temperature (160-240°C) and pressure is used for this method (Galbe & Wallberg, 2019, p.12). The time of the treatment ranges from a few minutes to an hour (de Jong & Gosselink, 2014, p.288). These severe conditions cause the water to have different physical and chemical properties (decrease in density, weakening of hydrogen bonds, dielectric constant decreases leading to a decrease in polarity). LHW then has similar properties to organic solvents (Cybulska, Chaturvedi, & Thomsen, 2019, p.154).

The mechanism behind hydrolysis is the autoionization of water. The H_3O^+ ions from the autoionization of water catalyze hemicellulose depolymerization through the glycosidic bonds and acetyl groups' selective hydrolysis. Organic acids are formed in the process (e.g., acetic acid), from which further H_3O^+ ions are formed, acting then act as catalysts and increase the reaction rate (Galbe & Wallberg, 2019, p.12; Zhuang et al., 2016, p.69). In addition to hemicellulose, some lignin is also dissolved and degraded to phenolic compounds. At the end of the process, the fractions can be divided into two product streams: the solubilized hemicellulose-rich slurry and the cellulose-rich solids fraction (de Jong & Gosselink, 2014, p.288).

LHW pretreatment offers several advantages, such as the relatively low cost, as no catalysts or chemicals are needed; due to the low corrosivity, the reactor requirements are low. Furthermore, the formation of inhibitory compounds can be virtually eliminated if the pH is kept between 4 and 7 (Baruah et al., 2018, p.11; de Jong & Gosselink, 2014, p.288). However, the process is very energy-intensive due to a large amount of water involved (Baruah et al., 2018, p.11).

2.2.3.2 Steam explosion

Steam pretreatment is an (autocatalytic) hydrothermal process (de Jong & Gosselink, 2014, p.287) in which the LCB is treated with steam for several minutes at high temperatures (up to 240 °C) and high pressures. As in the LHW pretreatment, parts of the hemicellulose hydrolyze and form acids that can catalyze the hemicellulose's hydrolysis. At the end of the treatment, there is an abrupt release of pressure and cooling, resulting in an explosive escape of the water in the biomass (Behera et al., 2014, p.96). The advantages of steam explosion are low environmental impact, limited use of chemicals, high energy efficiency, no recycling costs, and complete recovery of sugars (Baruah et al., 2018, p.10). However, these advantages are offset by the high thermal energy input (Baruah et al., 2018, p.11).

2.2.3.3 Ammonia fiber explosion (AFEX)

In the AFEX process, the LCB is treated with liquid anhydrous ammonia for a few minutes under moderate temperatures (60-100°C) and high pressure. The liquid ammonia is used in a mass ratio of 1:1 (1g LCB per 1g dissolved ammonia). After the residence time, the pressure is abruptly reduced. The harsh conditions (high temperatures, pressures and expansion of the ammonia gas) cause the LCB to swell. As a result, the hemicellulose is hydrolyzed, and the lignin-carbohydrate bond is disrupted. The subsequent rapid pressure reduction then breaks the fiber structure, reducing the cellulose's crystallinity and increasing the accessible surface area. Like the steam explosion, the disadvantages of this process are the high thermal energy requirements and the ammonia's highly corrosive properties and the harmful environmental effects (Baruah et al., 2018, p.10; de Jong & Gosselink, 2014, p.290).

2.2.4 Biological pretreatment

Biological digestion involves the use of fungi (white rot, brown rot, and musty rot fungi) that can produce specific enzymes that degrade the components (lignin, hemicelluloses, and polyphenols) of LCB. The advantages of the digestion process are substrate and reaction specificity, environmental friendliness (no formation of toxic compounds), energy savings, and high yield of desired products. The disadvantages of biological pretreatment are the slow process, careful control of growth conditions, and loss of cleaved carbohydrates from the biomass due to consumption of the microorganisms used (Behera et al., 2014, p. 94-95).

2.2.5 Combination of pretreatment methods

From the discussion of the different pretreatment methods, it is clear that they have different effects on the composition of LCB and each of these methods has its advantages and disadvantages (Baruah et al., 2018, p12). A pretreatment method that can completely fractionate LCB into its major components has not yet been realized. For this reason, combining one or more pretreatment methods may be a way to improve selective fractionation and eliminate possible disadvantages (Galbe & Wallberg, 2019, p.21).

Process combinations have to be found in this context, resulting in process streams optimized for all components (cellulose, hemicellulose, lignin). For example, the hemicellulose can be pre-extracted in an acid treatment and the lignin and cellulose recovered in a subsequent OS treatment (Galbe & Wallberg, 2019, p21). The LHW and OS processes represent another possible combination, as lignin and hemicellulose can also be hydrolyzed in different fractions in these two processes, with higher overall yields and cellulose remaining available for further processing (Serna-Loaiza et al., 2020, p.1).

Due to the high number of pretreatment methods, there are also many possibilities to improve substrate efficiency by combinations. However, combining several pretreatment methods involves additional costs. Therefore, it is important to find coordinated combinations to avoid additional complications in terms of process design, capital and expense costs (CAPEX), and environmental impact (Galbe & Wallberg, 2019, p.21).

Therefore, it is of importance to analyze and evaluate the pretreatment combinations with all related plant components and process conditions in a planned biorefinery concept. To find suitable and sustainable combination processes, techno-economic and life cycle analyses (LCA) are particularly powerful tools (Den et al., 2018, p.17). LCA is, therefore, discussed in more detail in section 2.4.

2.3 Valuable chemicals from lignocellulosic biomass

The pretreatment of LCB opens the door for various commercial industrial value products such as fuels/energy and biochemicals by selectively fractionating them into cellulose, hemicellulose and lignin platforms. The polysaccharide (cellulose and hemicellulose) and lignin platform chemicals can then either be used directly for commercial products or converted into secondary value-added products through appropriate conversion and upgrading processes (Chandel, Garlapati, Singh, Antunes, & da Silva, 2018, p. 373).

2.3.1 Primary products from the polysaccharide platform (cellulose and hemicellulose)

For the use of primary products, the aim is to preserve as much as possible the already highly functional polymers formed by nature. These polymers can be chemically or mechanically modified for specific applications to improve properties and performance (Rødsrud, Frölander, Sjöde, & Lersch, n.d., p.150). Direct products from cellulose typically include pulp, paper, textiles, and nanocellulose (microfibrillated cellulose and bacterial nanocellulose) (Chandel et al., 2018, p.373).

Due to the nanosize of the cellulose, microfibrillated cellulose has interesting new properties (e.g., higher hydrophilicity and reactivity) than conventional cellulose. These properties make them excellent viscosifiers, forming transparent, tear-resistant and oxygen-tight films (Chandel et al., 2018, p.373; Rødsrud et al., n.d., p.150-151). They are also used as an additive in paper and plastics to improve mechanical stability. Bacterial cellulose obtained from LCB has special properties compared to plant cellulose, such as high purity, crystallinity, degree of polymerization, water binding capacity, tensile strength and biocompatibility. It is, therefore, discussed in the medical field for wound dressings and implants. Cellulose of high purity can also be used as a substrate for the production of microbial cellulases. Cellulases have a wide range of industrial applications and, thus, a high economic value (Chandel et al., 2018, p.373).

Hemicellulose can be used as a direct substrate as additives in paper production, cosmetic products, or the production of films, coatings, and hydrogels. The majority of films and coatings made from hemicelluloses are used for packaging and coating purposes in the food industry. The hydrogels produced are used for pharmaceutical applications such as drug carriers (Chandel et al., 2018, p.373; Farhat et al., 2017, p.371).

2.3.2 Secondary products from the polysaccharide platform (cellulose and hemicellulose)

One of the most important secondary platforms of polysaccharides are C5, and C6 sugar compounds, also known as 2G sugars (Chandel et al., 2018, p.373). The enzymatic or hydrolytic saccharification forms the 2G sugars from the polysaccharides (cellulose and hemicellulose). As can be seen in Figure 2, glucose is formed during the depolymerization of cellulose, and in a minor proportion during the depolymerization of hemicellulose. Furthermore, the C5 sugars xylose and arabinose and the C6 sugars mannose, galactose, rhamnose are formed during the depolymerization of hemicellulose (Isikgor & Becer, 2015, p.4501).

Out of these sugar monomers, various value-added compounds can be obtained by biological or chemical processing methods. In their paper, Isikgor & Becer (2015) identified over 15 (excluding Lignin) derivable secondary platforms (see Table 3) from which over 200 value-added compounds can be generated. The 15 secondary platforms include the 12 sugar-derived building block chemicals from the US Department of Energy (DOE) report (Bozell & Petersen, 2010) (Isikgor & Becer, 2015, p.4501).

Table 3.
Derivable secondary chemical platforms from lignocellulosic biorefinery sugars

1,4-Diacid Acids (Succinic Acid, Fumaric Acid, Malic Acid)
2,5-Furandicarboxylic Acid (FDCA)
5-(Hydroxymethyl)furfural (5-HMF)
3-Hydroxypropionic Acid (3-HPA)
Aspartic Acid
Glucaric Acid
Glutamic Acid
Itaconic Acid
Levulinic Acid
3-Hydroxybutyrolacetone
Glycerol
Sorbitol
Lactic Acid
ABE Platform (Acetone, Butanol, Ethanol)
Xylose-Furfural-Arabinitol

Most of these sugars are converted by microbial fermentation into the desired bioproducts, like alcohols, organic acids, alkenes, lipids and other chemicals. A second viable route is through chemical processes, including hydrogenation, dehydrogenation, and oxidation reactions. Examples are the hydrogenation of glucose to sorbitol, the oxidation of glucose to gluconic acid, and the acid dehydrogenation of xylose to furfural (Chandel et al., 2018, p.373; Taylor et al., 2015, p.15).

Besides the sugar platform, cellulose derivatives are also important secondary products. Cellulose derivatives can be produced from cellulose by chemical processes such as esterification or etherification. The most important derivatives include cellulose acetate, carboxymethylcellulose, methylcellulose and hydroxyethylcellulose (Chandel et al., 2018, p.374).

2.3.3 Primary products based on the lignin platform

Unlike cellulose and hemicellulose, lignin has received little attention yet to produce biofuels, biochemicals, and biomaterials (Yamakawa, Qin, & Mussatto, 2018, p.57). One of the reasons is that due to lignin's complex structure, commercial utilization into products is difficult. Besides, it is very energy-rich with a calorific value of 26 MJ/kg (Chandel et al., 2018, p.374). Thus, most of the lignin (~98 %) produced in pulp processes is burned to generate electricity / heat, and only about 2 % is isolated and commercially utilized (Isikgor & Becer, 2015, p.4546). However, in most biorefinery concepts, only about 40 % of the lignin produced is required to meet the plant's energy needs through combustion, resulting in a high amount of unused lignin (Yamakawa et al., 2018, p.57). Moreover, due to its intrinsic aromatic structure, lignin is an important resource for aromatic compounds and has great potential for future bulk and fine chemicals (Isikgor & Becer, 2015, p.4546; Yamakawa et al., 2018, p.57).

As a primary product, lignin is used as an electrolyte material due to its chemical properties and as a sequestering agent, binder, dispersant and emulsifier due to its polymeric structure; to a lesser extent, it is also used as a filler and in adhesives. Another primary application is carbon fibers, which can be produced by extruding filaments from a melt or gel swollen with solvent (Rais & Zibek, 2017, p.475; Yamakawa et al., 2018, p.57).

Lignin can also be used to develop homogeneous colloidal lignin particles. Due to its nano size, colloidal lignin particles has improved properties and a high variety of potential applications, including as a filler in composites (as reinforcement), UV blockers, antibacterial agents, antioxidants/radical scavengers, drug delivery systems, and electrode materials (Beisl, Friedl, & Miltner, 2017).

2.3.4 Secondary products from the lignin platform

Valorization of lignin to aromatics is the main pathway for obtaining secondary products. In this way, aromatic hydrocarbons (e.g., vanillin, dimethylsulfoxide) and BTX (benzene, toluol, and xylene) mixtures can be produced by depolymerization (Yamakawa et al., 2018, p.57). However, efficient depolymerization and valorization of lignin remains a major challenge and is under research (Dahmen, Lewandowski, Zibek, & Weidtmann, 2019, p.113).

When valorizing lignin, it must be taken into account that lignin's natural chemical structure can be altered and degraded during pretreatment. Depending on the pretreatment technology used, this effect is more or less significant. This restricts the conversion and application of lignin into high-value products for some industrial applications (Yamakawa et al., 2018, p.57).

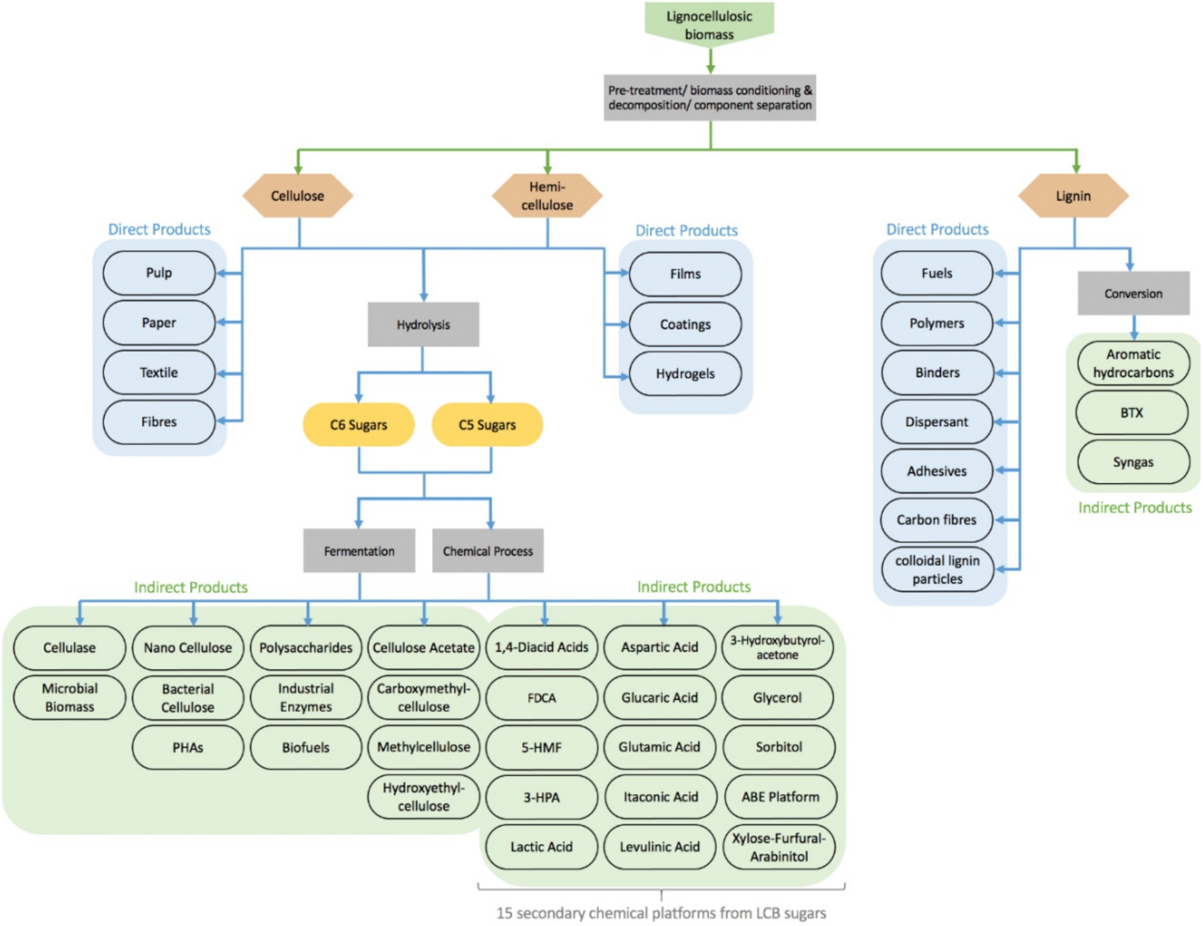

Figure 8. Possible bio products out of the LCB. (adapted from Chandel et al., 2018, p.371)

Figure 8 clearly shows that a large number of commercially useful base and bulk chemicals can be obtained from the polysaccharide platforms (cellulose, hemicellulose) and from the lignin platform. However, the simultaneous use of these polymers depends on their selective fractionation and thus on the chosen pretreatment process. By combining LHW pretreatment (process for hemicellulose hydrolysis) and OS pretreatment (process for lignin hydrolysis), it is possible to dissolve these components in different proportions. This combination allows lignin and hemicellulose to be hydrolyzed in different fractions, achieving a higher overall yield and leaving a cellulose-rich solid stream available for further processing (Serna-Loaiza et al., 2020, p.1-2).

2.4 Life-cycle assessment

Life-cycle assessment (LCA) is an environmental and sustainability management analysis tool standardized according to the ISO 14040 series, which enables the analysis of environmental aspects and impacts of product systems (DIN ISO 14044:2006, p.5; Klöpffer & Grahl, 2009, p.1). The purpose of applying LCA is often to identify opportunities for improving a product's environmental performance, provide information for decision-making in industry, governmental and non-governmental organizations, or as a marketing tool (e.g., implementing an eco-label) (DIN ISO 14044:2006, p.5).

LCA is a holistic methodology that goes beyond the traditional focus and production location and manufacturing processes to address a product's impacts throughout its entire life cycle (cradle to grave approach) (DIN ISO 14044:2006, p.5; Stichnothe, 2017, p.525).

For this purpose, the LCA goes through four stages: Defining the goal and scope of the objective; Inventory Analysis; Impact Assessment; and Interpretation (DIN ISO 14040:2006, p.15). Their sequence and correlations are shown in Figure 9 and discussed in more detail as follows.

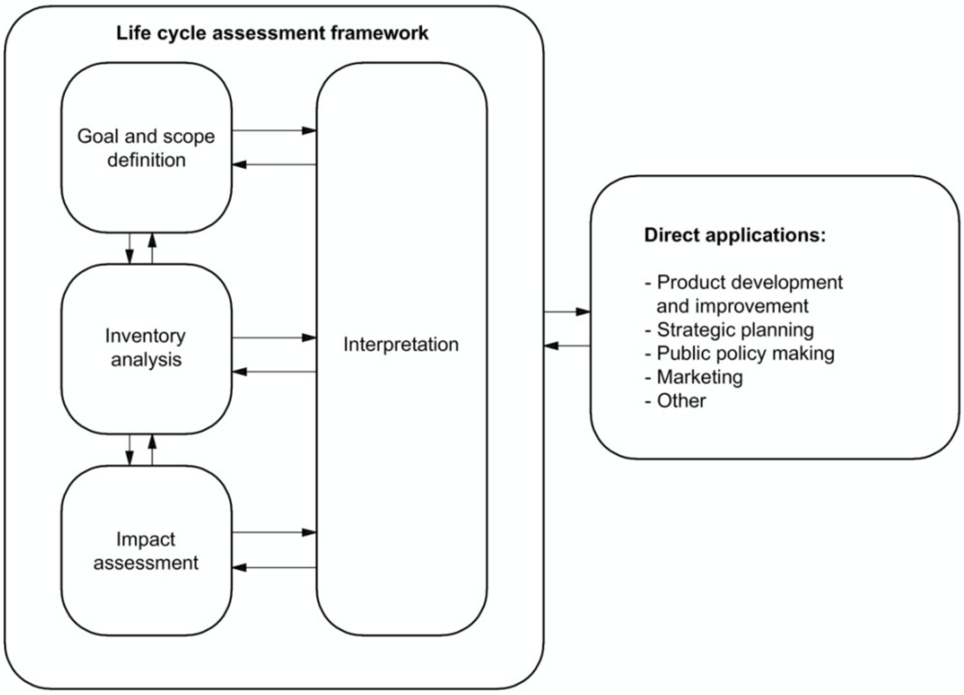

Figure 9. LCA stages. (DIN ISO 14040:2006, p.17)
The arrows' interaction indicates that it is an iterative process; new information and data obtained during the assessment process may require a return to an earlier stage to integrate the latest information

2.4.1 Goal and scope definition

In the first step of a standardized LCA, the goal and the scope of the study are clearly defined. The goal must include the study's motivations and purpose and the intended audience and how the results will be used (DIN ISO 14044:2006, p.15-16; Gnansounou, 2017, p.44).

Based on the defined goals, the scope of the study is then determined. The scope includes several topics, such as the detailed description of the investigated product system (balance sheet system) in the form of a system flow diagram (See Figure 10) with the definition of the system boundaries (technical, geographical and chronological) (Gnansounou, 2017, p. 46).

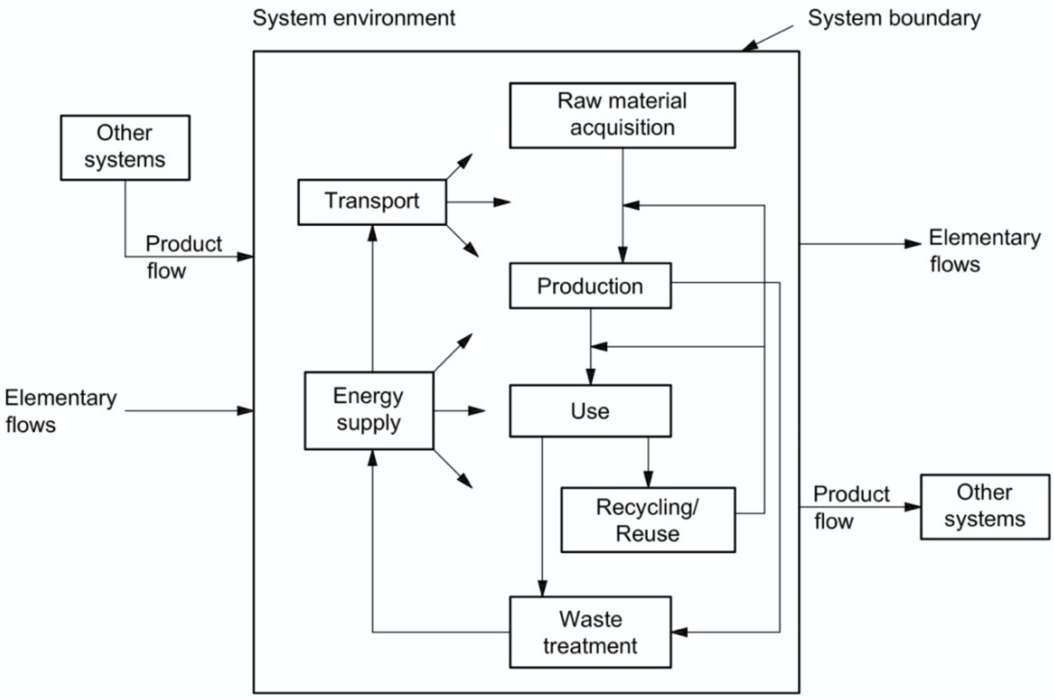

Figure 10. Example of a product system in the form of a system flow diagram. (DIN ISO 14040:2006, p.21)

As shown in Figure10, the product system contains all relevant steps of a product's life cycle, broken down into individual processes, the so-called process modules. The process modules are connected to each other by flows of intermediates and/or residues for treatment, to other product systems by product flows, and to the environment by elementary flows (such as resources and emissions to air, water and soil). Which processes are included or excluded from the system, i.e. in the LCA, is determined by the system boundary (DIN ISO 14040:2006, p.19-20). Therefore, the exclusion is determined by cut-off criteria such as Mass fraction, Energy fraction and Environmental relevance (DIN ISO 14044:2006, p.18-19).

In this step, the function and functional unit (FU) (quantified definition of the function) of the product system are also described. The FU represents a reference value to which the input and output data can be normalized and scaled. In addition, different LCAs can be compared with each other based on the FU (DIN ISO 14044:2006, p.17).

Furthermore, the selection of the impact category as well as data availability and data quality, are taken into account (DIN ISO 14044:2006, p.20). For retrospective LCA (existing product system), the data can usually be obtained on-site or taken from literature or existing databases.

For prospective (forward-looking) LCA, the data must be taken from computer-aided simulations of conceptual designs. According to DIN ISO 14044:2006. p21, these datasets should consider several aspects (such as temporal, geographical, technology coverage, accuracy, completeness, representativeness, consistency, reproducibility, data sources and uncertainty) with respect to their quality (Gnansounou, 2017, p.54).

2.4.2 Inventory analysis

In the first phase (goal and scope), the product system is specified. In the second phase, or Lifecycle Inventory (LCI), the input and output data for each process module are collected, quantified and analyzed at the level of the individual process units or block processes of the product system. The sum of all LCIs of the involved procedures then results in the LCI of the entire product system. The performance of an LCI analysis according to DIN ISO 14044:2006, p.26 comprises the following steps (Gnansounou, 2017, p.54):

i. Preparing for data collection,
ii. Data collection,
iii. Data validation,
iv. Relating data to unit processes,
v. Relating data to the functional unit
vi. Data aggregation

The procedure of LCI is iterative, i.e., several feedback may occur during the process and may lead to redefinitions of the goal and scope and the degree of detail of the product system (Gnansounou, 2017, p.54).

2.4.3 Impact assessment

During the LCI analysis process, a large amount of data is collected, which contain information about the release of different substances that can be harmful to the environment. However, the impact on the environment cannot be answered with this information alone. Since the assessment of the environmental impact is the main reason for the performance of the LCA, it is done in phase three, the Lifecycle Impact Assessment (LCIA). For this purpose, the calculated emissions are grouped to specific impact categories and converted to the specific impact indicator (DIN ISO 14040:2006, p.27; Gnansounou, 2017, p.59).

According to DIN ISO 14040:2006, this phase includes mandatory and optional elements. The binding elements include, after the selection of impact categories (should cover the environmental impacts of the product system being studied) and the characterization models, the assignment (classification) of the LCI data into the categories and their potential impacts quantified using characterization factors (Gnansounou, 2017, p.59).

Various predesigned LCIA methods (ReCiPe, CML, TRACI, EDIP, LIME, IMPACT 2002+, etc.) are available for performing the environmental impact assessment. The ISO standard does not specify which LCIA method should be used, which means that LCIA method's choice will vary depending on the study (Gnansounou, 2017, p.61). Depending on the method, two main approaches are used to classify and characterize environmental impacts: the problem-oriented approach (midpoint) and the harm-oriented approach (endpoint) (Rosenbaum et al., 2018, p.173).

2.4.4 Interpretation

In the end, an interpretation of the results is carried out. The interpretation is closely interrelated with the other three phases. The questions associated with the LCA's goals and scope must be discussed, taking into account the results of the LCI and LCIA. The discussion includes conclusions, limitations, and recommendations and a review of the results for completeness, sensitivity, and consistency (DIN ISO 14044:2006, p.45; Gnansounou, 2017, p.68).

2.5 Fundamentals of modelling

2.5.1 Process simulation ASPEN PLUS®

For prospective (future-oriented) LCAs, where no primary or generic data are available for LCI, the data can be taken from computer-aided process simulations of concepts. Process simulation allows the representation of the chemical or physical transformation processes that take place in a biorefinery in the form of a mathematical model. This model includes calculating the energy and mass balances that follow the principles of thermodynamics and correspond to the chemical reactions taking place (Chaves, López, Zapata, Robayo, & Niño, 2016, p.1).

Process simulation (modeling) aims to describe the processes in a biorefinery using various theoretical models and calculation methods to obtain properties of the process that are as close to reality as possible (Gnansounou, 2017, p.59). This description takes the form of a process flow diagram (PFD).

PFDs are derived from the technological scheme by specifying the required equipment, processes and flows that describe the product system. For this purpose, block modules are used to model different types of equipment. This simulation flowsheet may be different from the real PFD, as real plants or processes may be modeled by several operating blocks; or vice versa, that one operating block in the simulation covers several real plants or processes (Haydary, 2018, p.8).

For the analysis and evaluations of the information contained in the PFD, process simulators such as SPEED UP®, ASPEN PLUS®, DESIGN II®, HYSYM®, ASPEN HYSYS®, CHEMCAD®, und PRO II® are used (Chaves et al., 2016, p.3). As previously mentioned, the analysis of the process is based on a mathematical model that includes linear, nonlinear, and differential-algebraic systems of equations that relate important process variables (e.g., pressure, temperature, compositions, and flow) to equipment configurations (surfaces, geometric configurations, set points, etc.) (Chaves et al., 2016, p.1).

In most simulators, the equation system's solution is performed in sequential-modular mode, where each block/module is solved separately. The output values are then used for the calculation of the next module. The solution sequence is parallel to the material flow of the process. For material cycles, the module input changes so that the module must be re-evaluated (Haydary, 2018, p.9). This process is called a recycling loop, which includes iteration mechanisms (Haydary, 2018, p.10), i.e. the calculations are repeated with new values until the difference between the initial values and the calculated values reaches a certain tolerance (convergence) (Chaves et al., 2016, p.2).

The modular simulators' structure is mainly based on three levels: Flowsheet Topology Level, Unit Operating Model Level, Physical Properties Mode Level (see Figure 11). According to Haydary (2018) the main tasks of each level are the following (Haydary, 2018, p.9):

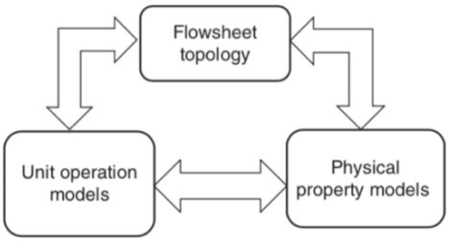

Figure 11. Structure of a modular flowsheet simulator. (Haydary, 2018, p.9)

Flowsheet Topology Level:

- sequencing of unit modules, initialization of the flowsheet,
- identification of the recycle loops and tear streams, and
- convergence of the overall mass and energy balance of the flowsheet.

Unit Operating Model Level:

- solving of each unit (such as heat exchangers, reactors, separators, etc.) using inputs from the flowsheet topology level with a specific calculation procedure for each unit type; and
- feedback of the unit calculation outputs to the flowsheet topology level.

Physical Properties Mode Level:

- calculation of thermodynamic models for phase equilibrium,
- calculation of enthalpy, entropy and other temperature dependent properties of components and flows, and
- it has to be accessed from both the unit operation mode and the flowsheet topology level.

At each of these levels, the systems of equations are solved using the described iterative loops and the interactive solution procedure to gain insights and conclusions about process behavior (Haydary, 2018, p.9).

The simulator used in this work is Aspen Plus®, which is built on the sequential module basis described before. Thus, in Aspen Plus® the product system is represented by simulation or program units (the subroutines or models), by blocks and icons. These are supplied with the appropriate information to solve the mass and energy balances (Chaves et al., 2016, p.7). The process simulation is particularly useful in the case of this work, as it can be used to fill in the missing information in the LCI database.

2.5.2 Life-cycle assessment modeling program

As described in chapter 2.4, a large amount of data is required to prepare an LCA. These are usually taken from databases based on production/experimental data or process simulations. To handle this large amount of data, special tools (LCA software tools) are needed to simplify the LCA modelling and performing. For this purpose, there are several LCA software tools on the market available, such as GaBi, SimaPro, openLCA and Umberto NXT (Silva, Nunes, Moris, Piekarski, & Rodrigues, 2017, p.1). In this work, the software tool GaBi is used to prepare the LCA and is therefore explained in more detail as follows.

In general, a software tool is an interactive instrument that changes its internal state in response to operator input and produces an output. In LCA software tools, the most essential basic functions are: Modeling the life cycles of the product system, calculating and presenting the impact balance. Thereby, the LCA software must be able to sum up or calculate all input and output flows within the defined boundaries of the system according to the defined rules (allocations for co-products, cut-off criteria) and assign them to the impact categories (Lüdemann & Feig, 2014, p.4).

The software GaBi version 10.0.0.71 (Sphera Solution GmbH) is used for the modeling of the LCA. The software includes the company's own GaBi database as well as the EcoInvent and NREL databases. In addition, all LCIA methods recommended by ILCD (International Reference Life Cycle Data System) are available.

In GaBi, the product system's life cycle is plotted on a "plan", thus representing the system with its boundaries. In this plan, the processes, in the form of process modules, are added and connected by flows in arrows. The arrows represent all material and energy flows, i.e., they contain the input and output flows, with their flow width representing the quantity (analogous to the Sankey diagram) (Lüdemann & Feig, 2014, p.10).

The processes are added from the database via the process tree (GaBi DB) or the search function. If the relevant processes are not available in the database, you can also define your own processes. The processes' arrangement is done manually and should be analogous to the PFD (Lüdemann & Feig, 2014, p.10).

For the calculation of the LCI, the FU is defined in a process module indirectly by fixing a reference process. Furthermore, the input and output quantities of the material and energy flows are defined as tracked flows. In this way, a tracked input flow of the subsequent process can be connected in the process chain. Thus, individual parameters can be assigned to each process module (Lüdemann & Feig, 2014, p11).

Once the plan has been fully defined, the LCI and LCIA results can be displayed on the GaBi dashboard. The results are broken down in the GaBi Balance according to the process modules (columns) and flows (rows) used. The results may also be displayed graphically. The user can also edit the results through individual adjustments (such as characterization, normalization and weighting) (Lüdemann & Feig, 2014, p.11).

3 Modelling and life-cycle assessment of the biorefinery scenarios

As described in the introduction in chapter 1.2, this master thesis focuses on the modelling of different pretreatment strategies for the bioconversion of lignocellulosic biomass and analyzing their technical and environmental performance. The specific study case within this thesis is the production of colloidal lignin particles (CLP) from wheat straw (Beisl, Loidolt, Miltner, Harasek, et al., 2018), which has already been developed in a pilot phase. In this process, lignin is extracted from wheat straw with an aqueous ethanol solution and then precipitated directly by a solvent shift reaction. Currently, the process upgrades only the lignin fraction of the feedstock and research is focused on upgrading the lignin and hemicellulose fractions simultaneously to transform the process into a multi-product biorefinery. This implies a combination of pretreatment steps that allows simultaneous upgrading of the individual components of the feedstock, specifically, hemicellulose and lignin. In this context, the combination of OS extraction and LHW extraction was investigated, and three scenarios were proposed based on the pretreatment strategy:

- ***Scenario 1:*** Pretreatment of the wheat straw by OS extraction; referred as *base case scenario*
- ***Scenario 2:*** Pretreatment of wheat straw by OS extraction (as the first step), followed by LHW extraction (as the second step), where the solid residue from the first step is retreated; referred as *OS-LHW scenario*
- ***Scenario 3:*** vice versa to Scenario 2; Pretreatment of wheat straw by LHW extraction, followed by OS extraction; referred as *LHW-OS scenario*

As these are prospective biorefinery concepts, the base data for the scenarios are obtained from laboratory experiments and analyses that have already been carried out on the combinations of Organosolv (OS) and Liquid Hot Water (LHW) extractions for the hydrolysis of the lignin and hemicellulose fractions (Serna-Loaiza et al., 2020). With these experimental data, the concepts/scenarios were created, and a process simulation was carried out. In the following sections, the individual scenarios and the conceptual design are presented in more detail. Each scenario was modelled using the process simulator Aspen Plus® V.10 (36.0.0.249, Aspen Technology Inc.) to calculate the mass and energy balances.

3.1 Process overview and design of the modelled scenarios

3.1.1 Scenario 1: OS (base case scenario)

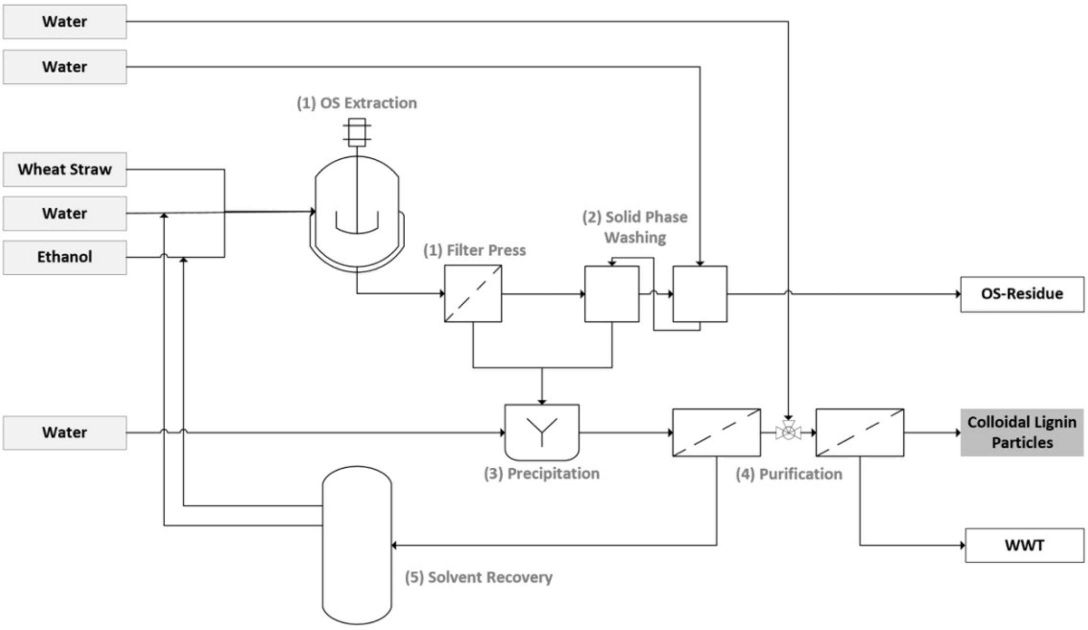

Figure 12. Simplified flow diagram for scenario 1, the base case scenario.

Figure 12 shows the simplified flow diagram developed for scenario 1. The model was divided into five sections (hierarchy levels): (1) OS extraction and solid-liquid phase separation (filter press), (2) solid-phase washing, (3) precipitation, (4) purification (membrane filtration) and (5) solvent recovery. The models developed in the Aspen Plus® Process Simulator are located in Appendix Chapter 7.1. The appendix contains both the overview model (with the hierarchy levels) and the detailed model with the separated processes.

(1) OS-extraction and solid-liquid phase separation

In this process step, wheat straw is treated with a 60 wt% aqueous ethanol mixture and heated to 180 °C. The solids concentration is 8.3 wt.%, which corresponds to a solid-liquid ratio of 1:11 (1 g dry solid per 11 g solvent). Table 4 shows the composition of the wheat straw analyzed in this work. The moisture content of the wheat straw (7.16 wt%) and the ethanol purity (96 wt%) were considered in the calculation of the solvent amount and adjusted appropriately. Table 6 summarizes the reactions and conversions which were considered. For the reactions taking place, the monomeric sugars were grouped to simplify the conversion calculations. Glucan was allocated to the polysaccharide cellulose and the other carbohydrates (arabinan, galactan, xylan and mannan) to the polysaccharide hemicellulose. Furthermore, the notation solid and liquid was used for lignin and ash. The notation solid means that this component is present as a solid in the LCB matrix and the notation liquid means that it is present solubilized in the solvent. The assumptions made are summarized in Table 5.

Table 4.
Lignocellulosic characterization of the Wheat Straw

Component	Arabinan	Galactan	Glucan	Xylan	Mannan	Lignin	Extractives	Ash	Moisture
Weight percentage (%wt)[a]	1,98	0,63	32,89	20,44	0,67	16,16	19,06	1,01	7,16

Note. a Values expressed on a dry weight basis.

Table 5.
Assumptions for component notation in Aspen Plus®

Components in the feedstock	Considered as components in Aspen Plus®	Note
Glucan	Cellulose	
Arabinan (C5-Sugar)	Hemicellulose (C5)	
Xylan (C5-Sugar)	Hemicellulose (C5)	
Galactan (C6-Sugar)	Hemicellulose (C6)	
Mannan (C6-Sugar)	Hemicellulose (C6)	
Lignin	$\text{Lignin}_{\text{(Solid)}}$	Lignin in solid matrix
	$\text{Lignin}_{\text{(Liquid)}}$	Solubilized lignin
Ash	$\text{Ash}_{\text{(Solid)}}$	Ash in solid matrix
	$\text{Ash}_{\text{(Liquid)}}$	Solubilized ash
Extractives	Extractives	

Table 6.
Chemical reactions and fractional conversions during OS-extraction

Reaction	Fractional conversion of component	Fractional conversion
$Cellulose + H_2O \rightarrow Glucose$	Cellulose	$7{,}364 * 10^{-3}$
$Cellulose \rightarrow HMF + 2\,H_2O$	Cellulose	$3{,}173 * 10^{-4}$
$Hemicellulose(C5) + H_2O \rightarrow Arabinose$	Hemicellulose (C5)	$9{,}113 * 10^{-3}$
$Hemicellulose(C5) + H_2O \rightarrow Xylose$	Hemicellulose (C5)	$5{,}233 * 10^{-3}$
$2\,Hemicellulose(C5) + 2\,H_2O \rightarrow 5\,Acetic\ Acid$	Hemicellulose (C5)	$6{,}124 * 10^{-2}$
$Hemicellulose(C5) \rightarrow Furfural + 2\,H_2O$	Hemicellulose (C5)	$5{,}409 * 10^{-4}$
$Hemicellulose(C6) + H_2O \rightarrow Galactose$	Hemicellulose (C6)	$8{,}042 * 10^{-2}$
$Hemicellulose(C6) + H_2O \rightarrow Mannose$	Hemicellulose (C6)	$1{,}931 * 10^{-2}$

$Hemicellulose(C6) + H_2O \rightarrow 3\ Acetic\ Acid$	Hemicellulose (C6)	$6{,}264 * 10^{-2}$
$Lignin_{\text{(Solid)}} \rightarrow Lignin_{\text{(Liquid)}}$	$\text{Lignin}_{\text{(Solid)}}$	$4{,}713 * 10^{-1}$
$Ash_{\text{(Solid)}} \rightarrow Ash_{\text{(Liquid)}}$	$\text{Ash}_{\text{(Solid)}}$	$3{,}230 * 10^{-2}$

For the modelling of the extraction, a stoichiometric reactor block was used, which functions as a black-box model. This black box was used to calculate the reaction products based on the determined conversions (see Table 6). The input streams were defined according to the compositions (characterised wheat straw, calculated solvent amount) and the physical properties of the lignocellulosic components (such as cellulose, hemicellulose, lignin and sugars) were taken from the Aspen Plus® NREL database for biofuel components (Wooley & Putsche, 1996). The thermodynamic model used in the simulation was the NRTL (Non-Random Two-Liquid model). This model was used to describe the behaviour in the liquid phase, and the Redlich-Kwong equation of state was used to describe the vapour phase.

After the extraction, the liquid and solid fractions are separated. At this step, the lignin-rich liquid is separated from the glucan-rich solid by filtration. Table 7 lists the splitting factors of the separation. The glucan-rich solid fraction goes to the solid phase washing step, while the liquid fraction is sent to the precipitation step.

Table 7.
Splitting Factors of solid-liquid filtration

Outlet Stream: Solid Stream					
Substream: MIXED					
Component	Split Fraction	Component	Split Fraction	Component	Split Fraction
$\text{Lignin}_{\text{Liquid}}$	0,0668062	Glucose	0,0668062	Xylose	0,0668062
Arabinose	0,0668062	Mannose	0,0668062	Galactose	0,0668062
Acetic Acid	0,0668062	HMF	0,0668062	Furfural	0,0668062
Extractives	0,827577	Water	0,0668062	Ethanol	0,0668062
$\text{Ash}_{\text{Liquid}}$	0,0662079				
Substream: CISOLID					
Component	Split Fraction	Component	Split Fraction	Component	Split Fraction
Cellulose	0,929273	HEM-C5	0,929273	HEM-C6	0,929273
$\text{Lignin}_{\text{Solid}}$	0,929273	$\text{Ash}_{\text{Solid}}$	0,929273		

Note. Applied stream classes for the simulated sub streams: conventional inert solids (CISOLID) are conventional solids that appear in the solid phase but do not participate in phase equilibrium; in the MIXED sub-stream, all components participate in the phase equilibrium when flash calculations are performed.

As this is a prospective LCA, the extraction and solid-liquid phase separation results are based on experimental results by Serna-Loaiza et al. (2020). In their work, the authors performed the OS extractions under the conditions described above in a stainless-steel high-pressure autoclave (Zirbus, HAD 9/16, Bad Grund, Germany) with a 1 L capacity. The solid and liquid fractions were then separated using a hydraulic press (Hapa, HPH 2.5) at 200 bar and a centrifuge (Sorvall, RC 6+) (see Figure 13).

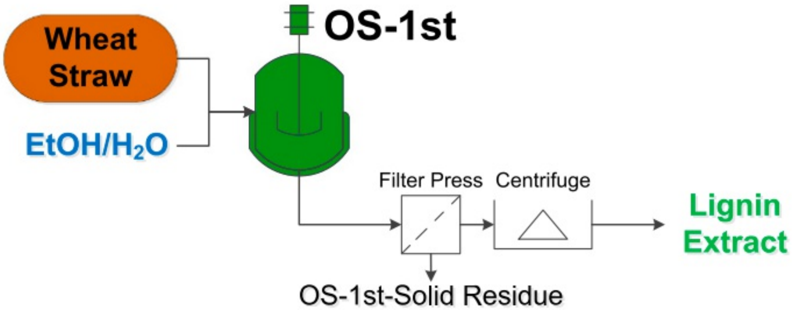

Figure 13. Scheme for the laboratory experiments of the OS-extraction (from Serna-Loaiza et al., 2020)

In addition to determining the wheat straw composition, the mass concentration of sugars, degradation products (acetic acid, HMF and furfural) and lignin of the lignin extract were characterised. With these data, it was possible to calculate the OS solid residue's missing composition assuming that there were no losses and linear scaling to 1 kg raw material. All information on the mass balance calculations carried out in MS-Excel can be found in the appendix, chapter 7.2.

(2) Solid-phase washing

To reduce ethanol losses and contained valuable liquid substances in the solid phase as moisture, these are recovered in a two-stage solid-phase wash. The solid phase is washed with water in counter flow, and then the washing solution is recombined with the liquid fraction from the extraction.

In the process simulation, a replacement wash is modelled for this purpose, whereby the following assumptions are made: (1) the mass of the added water is equal to the mass of the solid phase stream, (2) the moisture content of the solid remains unchanged, i.e., the contained amount of ethanol, dissolved lignin, sugars and degradation products is completely washed out and replaced by water.

(3) Precipitation

Water (antisolvent) is added to the liquid streams combined from extraction and solid-phase washing in the precipitation step to precipitate CLP by a solvent shift process. The amount of water used is twice the volume of the liquid extracts. These precipitation conditions lead to a yield of dissolved CLP of 50 %, based on Beisl's et al. (2018) laboratory experiments. In the process simulation, a black-box model in the form of a stoichiometric reactor block was used for this, analogous to the extraction. Reactions Conversions are shown in Table 8.

Table 8.
Fractional conversions during precipitation

Reaction	Fractional conversion of component	Fractional conversion
$Lignin_{(Liquid)} \rightarrow Lignin_{(Solid)}$	$Lignin_{(Liquid)}$	0,5

(4) Purification (membrane filtration)

In this step, the suspension consisting of the CLP and the ethanol-water mixture is purified by ultrafiltration. In the present process, the ethanol and other dissolved components are removed from the suspension by a two-stage membrane separation from the undissolved components (CLP). The process step simulation was based on data from a previously developed simulation model in IPSEpro by Angela Miltner as part of the research carried out in the Research Group. It was assumed that the CLP and undissolved components are retained to 100 % (retentate) while the majority of the dissolved components (membrane 1: 99.05 % and membrane 2: 99.07 %) pass the membrane (permeate). By adding water, the volume within the first process module is kept constant by replacing the water/ethanol volume separated as permeate with virgin water. The permeate stream from the first membrane unit is fed to solvent recovery, while the diluted permeate stream from the second membrane unit is fed to municipal wastewater treatment. The concentrated CLP in the retentate contains small amounts of residual ethanol and impurities. However, as further treatment of the CLP suspension is not part of the scope of this master thesis, the concentrated suspension is considered as the product.

(5) Solvent recovery

The ethanol must be recovered to operate the biorefinery economically. The process used for this purpose was a rectification column. Since no experimental results were available for this yet, this process step is simulated based on assumptions. However, the simulation provides quite robust results, as the distillation separation of an ethanol-water mixture is an established process. In the process simulator, a RadFrac column with 12 stages, with the following design specifications: (1) the entering water-ethanol mixture is heated to 60 °C in a feed preheater, (2) the ethanol leaving the head is required to have a concentration of 66 wt%, and (3) ethanol recovery is assumed to be 99 %. These design specifications were used by the software to calculate the distillate-to-feed ratio and the reflux ratio and optimized the column in terms of its energy demand and solvent recovery. The distilled ethanol-water mixture is then returned to the extraction process, reducing the amount of virgin ethanol and water required in the process. The liquid residue from the distillation is disposed via municipal wastewater treatment.

3.1.2 Scenario 2: OS-LHW

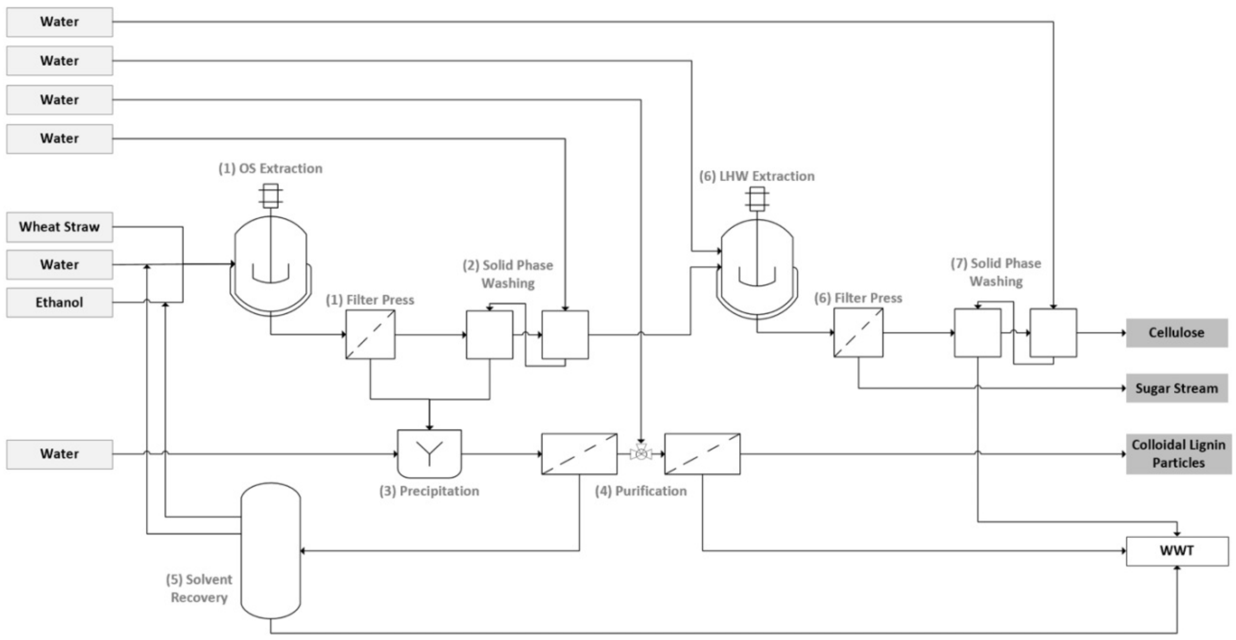

Figure 14. Simplified flow diagram for scenario 2, the OS-LHW scenario.

Key differences to scenario 1:

Figure 14 shows the simplified flow diagram developed for scenario 2. Scenario 1 focuses on the lignin's hydrolysis and its valorization to CLP and considers the other fraction (OS residue) as a residue to be removed and not as a component to be valorized. With a single pretreatment, simultaneous valorization of the fractions is difficult to achieve since the process parameters can only be optimized for one fraction. Therefore, the combination of pre-treatments is suggested to achieve simultaneous valorization of the fractions (lignin, cellulose, hemicellulose) (Serna-Loaiza et al., 2020, p.2).

In this particular case, in scenario 2, analogous to the Base Case Scenario, an OS extraction is carried out at the first stage to dissolve most of the lignin and upgrade it to CLP. However, the OS residue, which is still rich in valuable substances (cellulose and hemicellulose), is not considered as a residue; it is used as a raw material to perform a LHW extraction. As described in the theoretical part, the LHW process is particularly well suited for hemicellulose hydrolysis. Therefore, the extraction yields a sugar-rich liquid stream and leaves a purer cellulose-rich solid (compared to the baseline scenario). These two streams can therefore be considered as additional intermediates. Like the CLP-rich suspension, the sugar-rich liquid stream and the cellulose-rich solid have to be further processed into final products in a secondary refining process, which is, however, outside the scope of the Master thesis.

The combination of pretreatments requires further process steps. To the five stages (hierarchy levels) of the base case scenario, two additional stages (hierarchy levels) are added: (6) LHW extraction and solid-liquid phase separation (filter press), (7) solid-phase washing. The simulation models developed for this purpose (with the hierarchy levels, the detailed model with the separated processes) can be found in the appendix, chapter 7.1.2. In the following, only the two further stages are described in more detail, as the first five are analogous to the base case scenario.

(6) LHW-extraction and solid-liquid phase separation

The feedstock for LHW extraction is the solid residue from OS extraction. In this previous OS extraction, most of the lignin and only a small part of the hemicellulose is dissolved from the wheat straw. As described in scenario 1, the liquid and solid fractions are separated after extraction. The lignin-rich liquid fraction is sent to the precipitation step, where a CLP-rich suspension is formed, which is considered an intermediate product after the subsequent purification. The solid residue is washed in a two-stage solid-phase wash to recover liquid valuable substances and ethanol. The washed solid (OS residue) is then used as a feedstock in the LHW extraction. The previous OS extraction reduces the OS residue's recalcitrance; therefore, the hemicellulose in the solid matrix is more accessible. For this reason, the sugar yield can also increase during LHW extraction (Serna-Loaiza et al., 2020, p.2).

In the process step of LHW extraction, water is added to the washed solid residue at 180 °C, whereby mainly hemicellulose is hydrolyzed, and only a few degradation products (such as furfural, HMF and acetic acid) are formed. The solid-liquid ratio is 1:11 (1 g dry solid per 11 g solvent), analogous to the OS extraction, corresponding to a solid's concentration of 8.3 wt%. The moisture content of the residue was taken into account when calculating the amount of solvent required. For modelling the extraction, a stoichiometric reactor block was used in analogy to the OS extraction to calculate the reaction products formed at the prevailing temperature and pressure values. Table 9 summarizes the reactions and conversions considered.

Table 9.
Chemical reactions and fractional conversions during LHW-extraction

Reaction	Fractional conversion of component	Fractional conversion
$Cellulose + H_2O \rightarrow Glucose$	Cellulose	$2{,}465 * 10^{-2}$
$Cellulose \rightarrow HMF + 2\ H_2O$	Cellulose	$7{,}787 * 10^{-4}$
$Hemicellulose(C5) + H_2O \rightarrow Arabinose$	Hemicellulose (C5)	$3{,}326 * 10^{-2}$
$Hemicellulose(C5) + H_2O \rightarrow Xylose$	Hemicellulose (C5)	$2{,}956 * 10^{-1}$
$2\ Hemicellulose(C5) + 2\ H_2O \rightarrow 5\ Acetic\ Acid$	Hemicellulose (C5)	$2{,}290 * 10^{-2}$
$Hemicellulose(C5) \rightarrow Furfural + 2\ H_2O$	Hemicellulose (C5)	$2{,}024 * 10^{-2}$
$Hemicellulose(C6) + H_2O \rightarrow Galactose$	Hemicellulose (C6)	$3{,}711 * 10^{-1}$
$Hemicellulose(C6) + H_2O \rightarrow Mannose$	Hemicellulose (C6)	$1{,}274 * 10^{-1}$
$Hemicellulose(C6) + H_2O \rightarrow 3\ Acetic\ Acid$	Hemicellulose (C6)	$2{,}343 * 10^{-2}$
$Lignin_{(Solid)} \rightarrow Lignin_{(Liquid)}$	$Lignin_{(Solid)}$	$2{,}823 * 10^{-1}$
$Ash_{(Solid)} \rightarrow Ash_{(Liquid)}$	$Ash_{(Solid)}$	$8{,}828 * 10^{-1}$

The data for the simulation of the extraction and the solid-liquid phase separation is also based on the experimental results of Serna-Loaiza et al. (2020) (see Figure 15). By determining the wheat straw composition and the lignin extract's composition, the missing composition of the OS residue could be calculated by a mass balance calculation in MS-Excel. Analogously, the composition of the solid residue of the LHW extraction was calculated using the sugar concentration in the sugar extract. In this mass balance calculation, linear scaling (scaling factor = $feedstock(dry)_{1kg}$ / $feedstock(dry)_{laboratory\ scale}$) was also performed to a starting feedstock of 1 kg wheat straw.

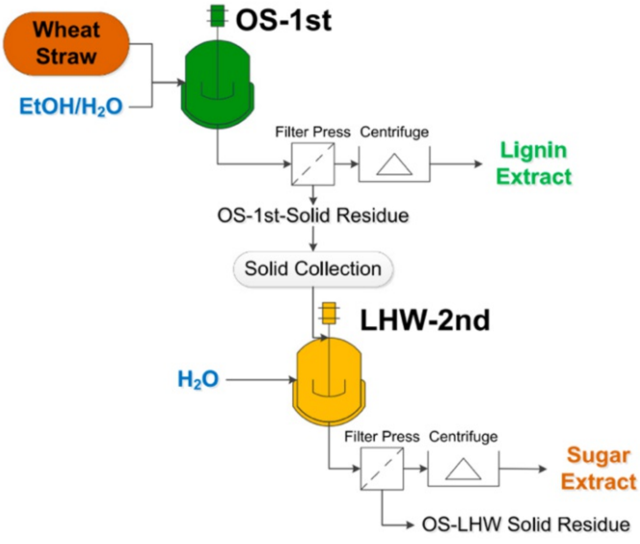

Figure 15. Scheme for the laboratory experiments of the OS-extraction (Serna-Loaiza et al., 2020)

3.1.3 Scenario 3: LHW-OS

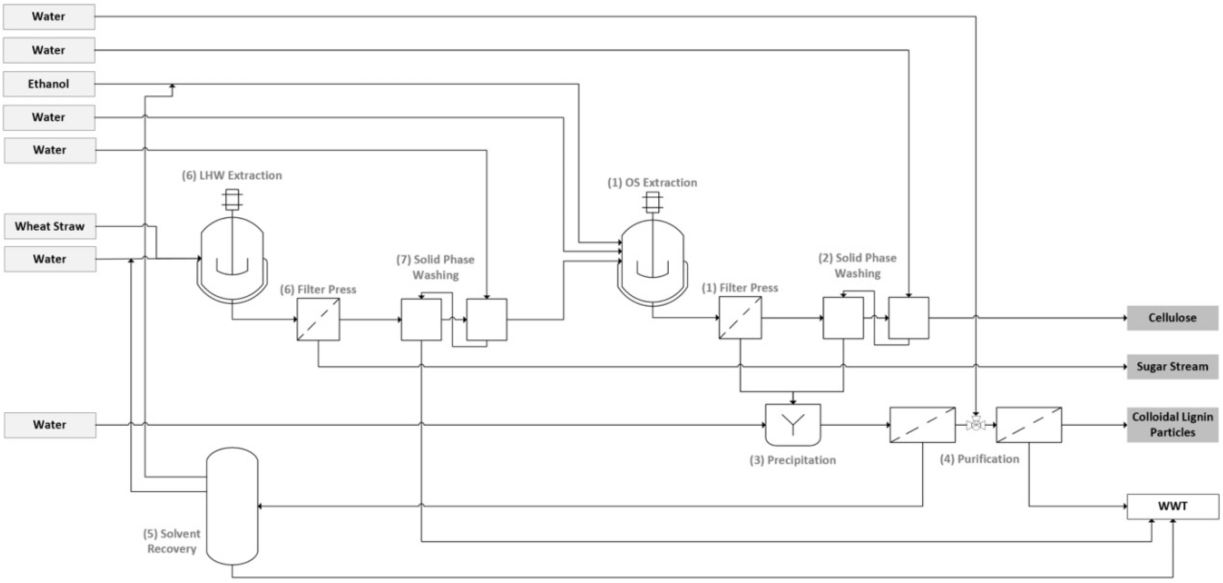

Figure 16. Simplified flow diagram for scenario 3, the LHW-OS scenario

Figure 16 shows the simplified flow diagram developed for scenario 3. This scenario is exactly the opposite of scenario 2. The wheat straw is pretreated by LHW extraction followed by OS extraction. In this particular case, LHW extraction first removes most of the hemicellulose and only a small part of the lignin. The result is a solid whose matrix is more accessible for subsequent lignin hydrolysis in OS extraction. The basis for the calculation and simulation is again the experimental data from Serna-Loaiza et al. (2020). For the simulation itself, the same approach was used as for scenario 2. The conversion rates for the LHW and OS extraction as well as the separation factors for the solid-liquid phase separation (filter press) and the data for the rectification column can be found in the appendix.

3.2 LCA

This thesis aims to determine both the technical performance (composition of the intermediates and the resulting downstream processing potential) of the three scenarios and, more importantly, assess their environmental impacts. Thus, the process simulation will be combined with the subsequent LCA to support the sustainable development of an LCB biorefinery. Based on the overall picture obtained (technical performance and environmental impact), critical issues will be identified to determine the most appropriate scenario for further process development. LCA was chosen because it is one of the most effective methods to evaluate and compare different scenarios from an environmental perspective. The LCA is performed according to the ISO 14040 and 14044 standards (DIN ISO 14040:2006; DIN ISO 14044:2006,) and is explained in more detail as follows.

3.2.1 Goal and scope definition

3.2.1.1 Goal of the study

The original goal of this master thesis was the LCA of a multi-product biorefinery. In order to perform the ecological evaluation of the multi-product biorefinery, the first step should be to create a basic model with available literature data in the LCA software GaBi. This model should represent several product lines that would be possible with an LCB using a suitable pretreatment process. Through the cradle-to-grave approach, important key parameters should be identified.

This goal was defined in very general terms because, as described in the theoretical part, there is a great variety of LCB raw materials and pretreatment processes. Different intermediate and final products can be produced depending on the composition of the LCB and the chosen pretreatment process. Due to this outstanding variability, it is not easy to draw up a meaningful life cycle assessment. Therefore, the LCB biomass was limited to wheat straw and the pretreatment process to OS-Extraction in the first consideration.

In the next step, a comprehensive literature search was conducted using the keywords "Life Cycle Assessment_-Wheat Straw Organosolv; "Life Cycle Assessment_-Lignocellulosic Biomass; "Life Cycle Assessment_-Biorefinery. The literature search showed that there are not enough LCA studies on the combination (wheat straw and OS) to develop a basic model with different product lines.

Therefore, the focus of this master thesis is on modelling different process pathways of the primary refining of a multi-product LCB refinery. This is a crucial task for process development. The specific study case within this thesis is the process development of pretreatment strategies of a wheat straw LCB multi-product biorefinery. In which the fractions (cellulose, hemicellulose, lignin) are simultaneously upgraded by pretreatment combinations (OS and LHW). The basis for the study are previous findings and results from practical laboratory experiments and already conducted laboratory analyses on the combinations of OS and LHW extractions for the hydrolysis of the fractions lignin and hemicellulose (Serna-Loaiza et al., 2020). In this context, it is of particular interest to determine which pretreatment combination has a better technical and ecological performance and what is the influence of implementing an additional pretreatment technology.

The aim of this LCA is a comparative techno-environmental assessment of three different scenarios to evaluate the technical performance (composition of the intermediate products and the resulting further processing potential) as well as their environmental impact. Based on the overall picture obtained (technical performance and environmental impact), critical points are to be identified to be able to determine the most efficient and environmentally friendly scenario for further process and product development.

3.2.1.2 Scope of the study

The scope and system boundary of the LCA study was considered as a cradle-to-gate approach taking into account the impacts of the primary refining activities from wheat straw to the intermediate platforms of CLP suspension, sugar stream and cellulose-rich solid phase. The product systems of the respective scenarios are shown schematically in Figures 17, 18 and 19 which represent the technical system boundary of the LCA study.

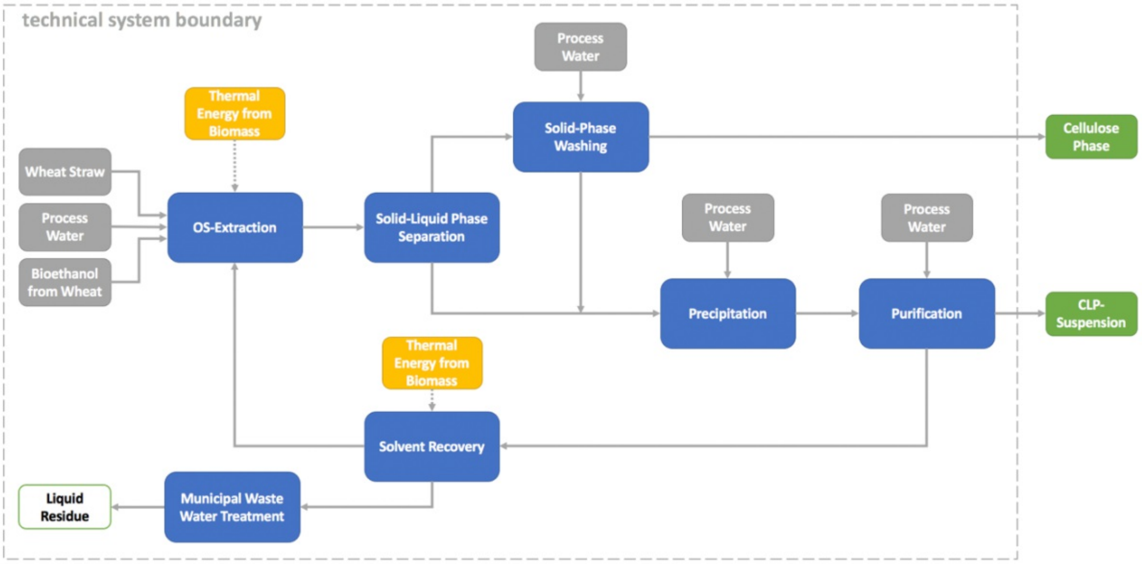

Figure 17. Product system of scenario 1(OS-Base Case) representing the technical system boundary

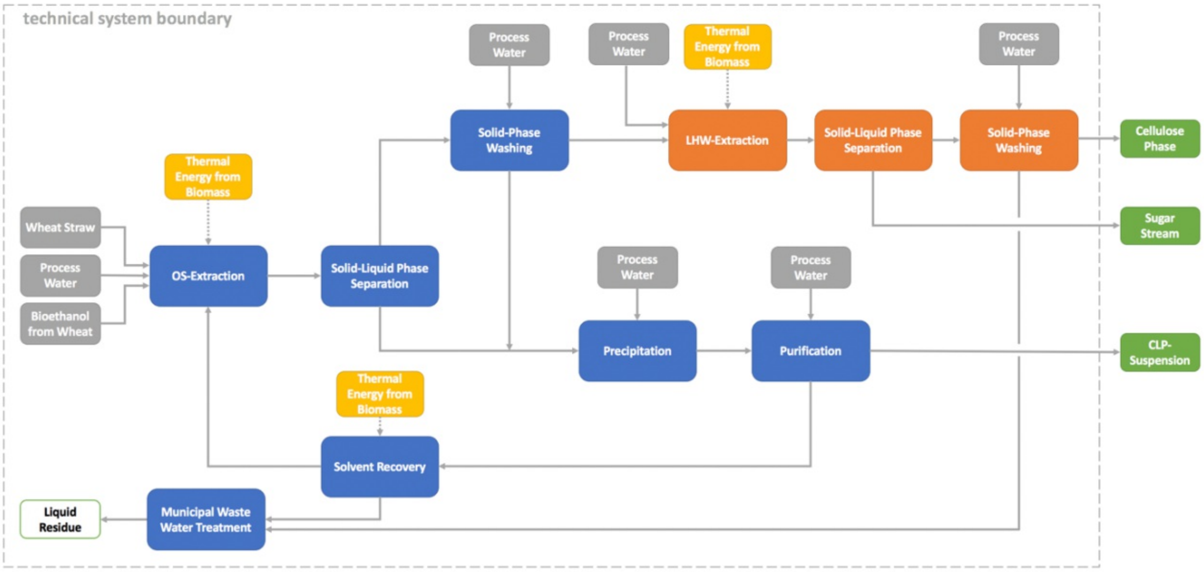

Figure 18. Product system of scenario 2 (OS-LHW) representing the technical system boundary

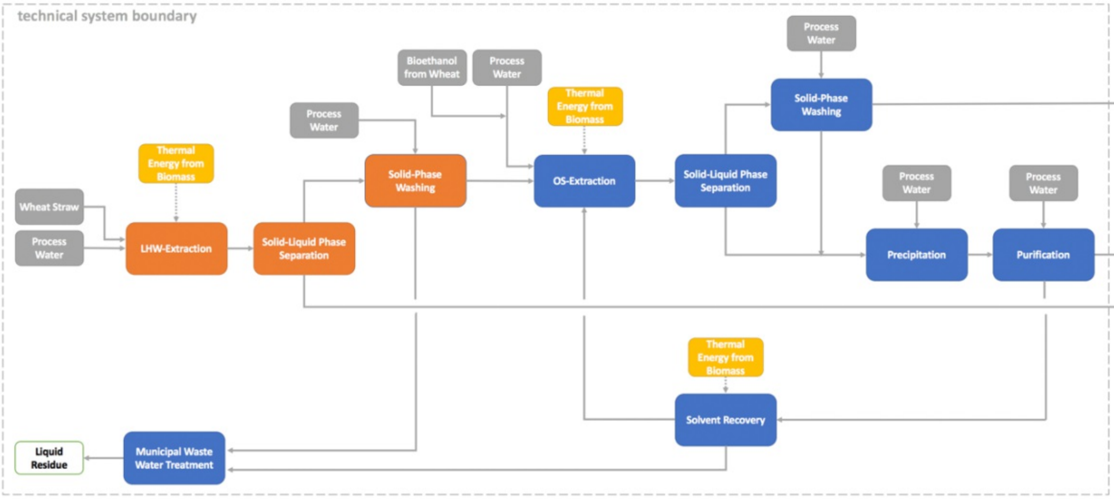

Figure 19. Product system of scenario 3 (LHW-OS) representing the technical system boundary

The technical system boundary separates the production process from its environment, i.e. from the environment (ecosphere) and also from parts of the production process that are not considered (Klöpffer & Grahl, 2009, p.32-33). The technical system boundary includes the process units for the supply of wheat straw, ethanol, process water and the thermal energy required in the production process. On the output side, the liquid residue from solvent recovery and the permeate from the second membrane stage were included in the scope after having been sent to a municipal wastewater treatment plant. Outside the technical system boundary are the intermediate products (CLP suspension, sugar stream and cellulose-rich solid phase), as these have to be processed into end products in subsequent secondary refining process steps. Due to the lack of primary data for secondary refining, the inclusion of these steps at this stage would have led to many assumptions and would not have enabled a meaningful assessment according to the goal of this study. Therefore, the intermediate products are considered as raw materials for secondary refining so that no emissions to the environment need to be assessed. The inclusion of secondary refining should be done at a later stage of the process development (when the necessary information is available).

Further assumptions that differ from the implementation of primary refining in a real industrial environment are the following. No transport activities of feedstock (wheat straw, process water, thermal energy) and material handling in the process were considered. The infrastructure, construction, installation, or decommissioning processes were also not considered, as their impacts are very small due to the expected operating time/lifetime (Bello, Méndez-Trelles, Rodil, Feijoo, & Moreira, 2020, p.5). Due to missing life cycle inventory data, the membrane production and due to missing long-term tests and lifetimes of the membranes, the membrane cleaning of the process step purification is also not considered. In the process module solid-liquid phase separation, the same assumptions were made, and the use of auxiliary materials or mechanical power was not taken into account, meaning only the mass balance was considered. In a later phase of process development, these aspects should also be included. Another deviation is the moisture content of the wheat straw. In the process simulation, the solvent compositions were related to the wheat straw's actual moisture content of 7,16 % (Table 4). In contrast, in the GaBi simulator, there is a background module of wheat straw with 12% moisture. On the output side of the liquid residue from solvent recovery and the permeate from the second membrane stage, only the components water and ethanol were considered. The other contained liquid components and possible solid residues were not considered due to their low contribution to the total mass fraction.

The geographical system boundary was referred to the region of Austria if these data sets were available in the GaBi database. If this was not the case, the next step was to refer to the German or, in a further instance, to the EU-28 average data. In this particular study, the background data for wheat straw production in the field and bioethanol production from wheat in the plant are referred to the region of Germany. The background data for the production of process water, the municipal wastewater treatment plant and its wastewater discharge into the rivers are referred to the EU-28 average data. The background data for thermal energy from biomass, on the other hand, are taken from the region Austria.

3.2.1.3 Functional unit and allocation procedure

The functional unit (FU) is the reference quantity to which the input and output data are normalized, i.e., which best reflects the purpose of the product system under investigation. In this particular case, the FU is set to 1 kg of wheat straw, which is used in the primary refinery-step of the LCB biorefinery as feedstock for the selective fractionation of the CLP suspension, the sugar stream and the cellulose-rich solid phase. The composition of the wheat straw used has already been listed in Chapter 3.1 in Table 4.

By choosing the FU on the raw material wheat straw, an intermediate product allocation (CLP suspension, sugar stream and cellulose-rich solid phase) is not necessary. All effects of the process modules are related to 1 kg wheat straw and thus allocated equally to all intermediate products. In this stage of the development, it is impossible to distinguish which intermediate is responsible for which share of the emissions. However, it is not necessary for the initial estimates of the total environmental effects of the different scenarios.

Moreover, an allocation according to the current state of the art (up to primary refinery) would be affected by significant uncertainties. A mass allocation is not possible due to the high and varying dilution of the streams. As these are intermediate products that have to be further processed into end products in secondary refining, it is difficult to find a representative price, and makes an economic allocation not appropriate.

3.2.2 Life-cycle inventory analysis (LCI)

The data required for the life cycle inventory were taken from four different sources (experimental data, MS Excel simulation, Aspen Plus® V.10 process simulation, GaBi V.10.0.0.71 - LCA simulation). As described in detail in Chapter 3.1, the experimental data at laboratory-scale conducted by Serna-Loaiza et al. (2020) is the basis for the life cycle inventory. With this information, the first step was to scale up the three scenarios to an input quantity of 1 kg of raw material (wheat straw) in a Microsoft Excel Model. In the next step, these results were used to simulate the scenarios with the software Aspen Plus. The detailed balances of the individual scenarios resulting from the simulation form the final gross inventories for the LCI phase of the LCA. The gross inventories (mass and energy flows) for each scenario can be found in the Appendix under point 7.4. These data are normalized to the FU 1 kg wheat straw. In the fourth step, these data were implemented in the LCA software GaBi. In the GaBi LCA model, the background data from the GaBi technical database were linked to the process steps of the raw material and input deliveries for wheat straw, process water, bioethanol, thermal energy, and downstream process steps for wastewater treatment. Table 10 shows the corresponding database record names and Globally Unique Identifier numbers (GUIDE) for the individual utilities.

The process modules containing the GaBi background data are explained in more detail as follows. The process modules from the Aspen Plus simulation programme are described in detail in Chapter 3.1. Figure 20 illustrates the data origin of the LCA model using Scenario 1 as an example.

Table 10.
An explicit description of the data sets used from the GaBi database

Utility	Dataset name in GaBi	GUID
Wheat Straw	Winter wheat straw, at field (12% H_2O content) (economic allocation)	EBF20867-F028-4CC6-BCCE-61D777397282
Bioethanol	Bioethanol from wheat, at plant	642F1725-F082-44D4-8494-DD118EB6D298
Thermal Energy	Thermal energy from biomass (solid)	BBBEA4B6-7A30-4B83-ADD1-765D27B72EBB
Process Water	Process water	DB009015-338F-11DD-BD11-0800200C9A66
Waste water treatment	Municipal waste water treatment (sludge 50% agricultural/50% incineration, for regionalization)	E5DD49EB-E23F-4C95-85BD-11EB1651068A

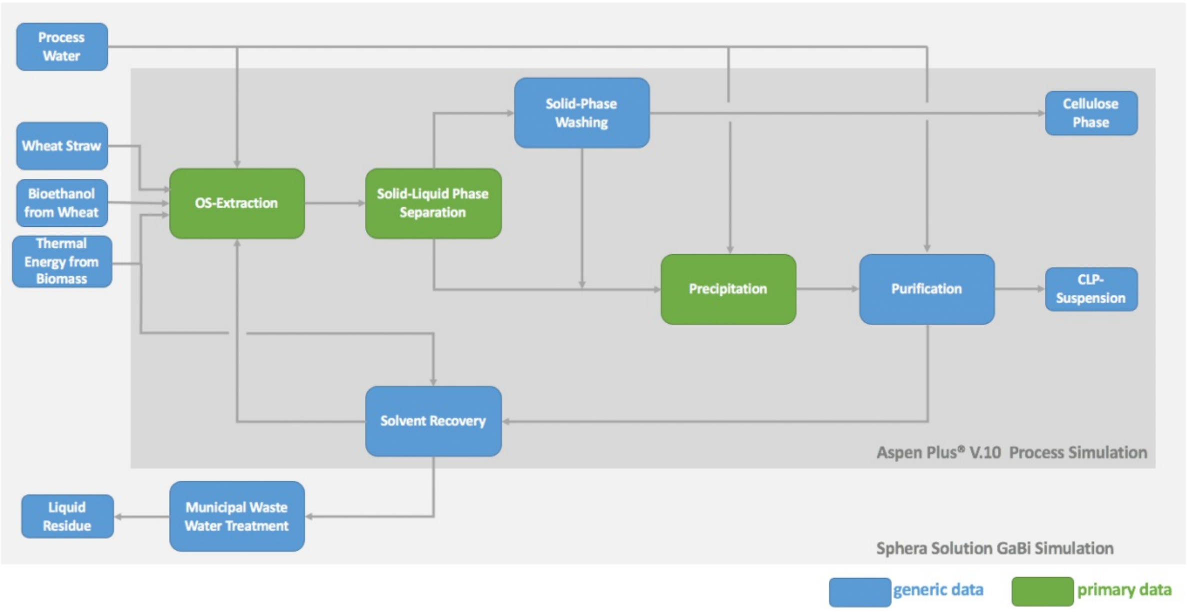

Figure 20. Illustration of the data origin of the LCA models using the example of scenario 1.

3.2.2.1 Process modules from the GaBi background data

Wheat Straw

The GaBi dataset with the name winter wheat straw, at field (12 % H_2O content), economic allocation was used for the process module wheat straw. Figure 21 shows the process in the form of a flowchart. The cultivation of winter wheat on cropland of 5 ha was modelled. The modelled module covers all relevant process steps/technologies (use of fertilizers, pesticides, and agricultural equipment (e.g., for harvesting)) along the supply chain of the presented cradle-to-gate balance. Seeding occurs in the early fall of the previous year and requires 1.5 -8.5 t

MM (wet mass) grain/ha, 70% starch content. Wheat straw (annual grass up to 1.2 m tall) and winter wheat are harvested after full maturity. The allocation between wheat grain and wheat straw was based on market value (Sphera Solution GmbH, 2018).

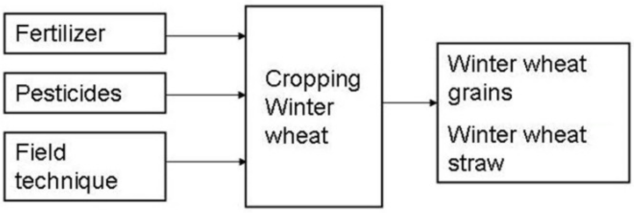

Figure 21. Flow diagram of the modeled process module winter wheat straw. (from Sphera Solution GmbH, 2018)

Process water

The process module for the pretreatment of process water is called in GaBi process water. Figure 22 shows the modelled process in the form of a flow diagram, where groundwater is treated with ion exchangers. During this process, the cations (metal ions) and anions (acid residue) from the water are exchanged for protons and hydroxide ions from the salt solution, to fully demineralize the water. For the process, all operating materials such as hydrochloric acid and caustic soda, the ion exchange plant's operation, and the wastewater, which is not suitable for use due to impurities, are taken into account (Sphera Solution GmbH, 2018).

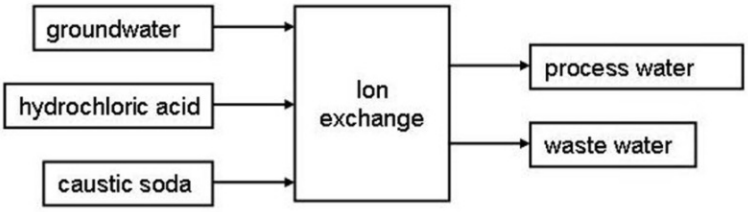

Figure 22. Flow diagram of the modeled process module process water. (from Sphera Solution GmbH, 2018)

Bioethanol

The process module for the provision of ethanol used in GaBi is named bioethanol from wheat, at plant. Figure 23 shows the process in the form of a flow chart. The modeled module covers all relevant process steps/technologies along the supply chain of the presented cradle-to-gate balance.

The process module includes three main process steps: 1) transport route from field to intermediate storage (4 km) and subsequent conditioning of wheat (screening and drying water content from 16 % to <14 %); 2) transport to ethanol production site (40 km); 3) ethanol processing: saccharification process according to the Hohenheim dispersion mashing process:

3.1) Grinding by hammer mill; 3.2) Addition of liquefaction enzyme (e.g., Termamyl) in storage tank; 3.3) Dispersing machine: separation of seeds and addition of water; 3.4) liquefaction tank: heating of mash; 3.5) Heat exchanger: tempering of the mash to 52 -54 °C; 3.6) Bioreactor / Digester: addition of saccharification enzymes and yeast; 3.7) Distillation: extraction of alcohol from the fermented mash; 3.8) Rectification: increase of purity from 82 – 87 vol.% after distillation to 99.8 Vol-%; 3.9) Dehydration: addition of an entrainer – cyclohexane; 3.10) Distillation sieve: separation of thin stillage and solid stillage; 3.11.) Thin stillage reservoir: preparation to DDS (Distiller`s Dried Grain & Solubles); 3.12) stillage concentration; 3.13.) Production of enzymes: very energy consuming (9.9 t steam per t enzyme and 7 MWh electricity per t enzyme) (Sphera Solution GmbH, 2018).

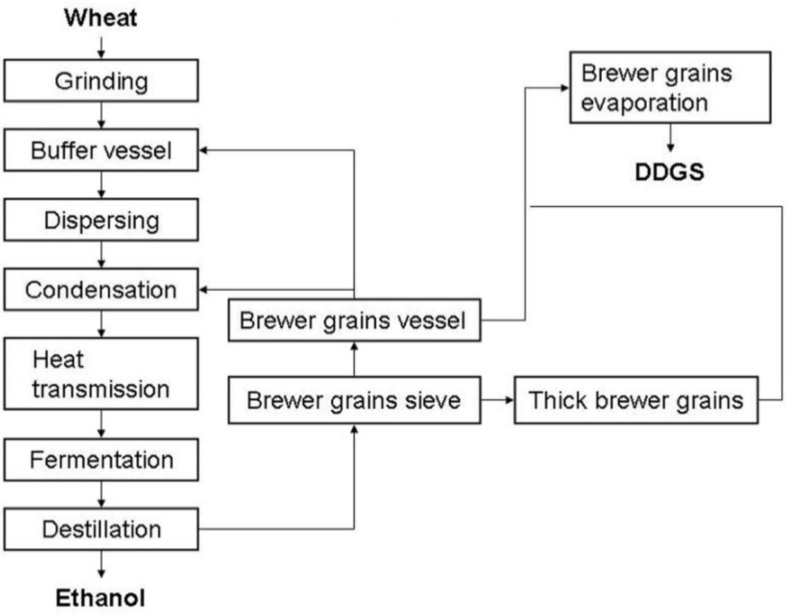

Figure 23. Flow diagram of the modeled process module bioethanol. (from Sphera Solution GmbH, 2018)

Thermal energy

The process module used has the name thermal energy from biomass (solid) in GaBi. Figure 24 shows the process in a flow diagram. The modelled data set includes all relevant process steps and technologies along the value chain of a technology mix concerning combustion and flue gas cleaning in Austria. The entire biomass supply chain was modelled, i.e., from the generation, preparation, and transport of the fuels to the heating plants. For the generation of thermal energy, a detailed biomass-specific power plant model is simulated. The power plant model combines measured emission data (e.g., NO_x) with calculated emission values (e.g., heavy metals) and takes into account the national and region-specific technology standards of the heating plants with respect to efficiency, combustion technology, flue gas desulfurization, NO_x removal, and dust removal. The combustion residues (e.g., gypsum, slag or fly ash) are considered as secondary raw material for reuse (e.g., in construction measures) (Sphera Solution GmbH, 2018).

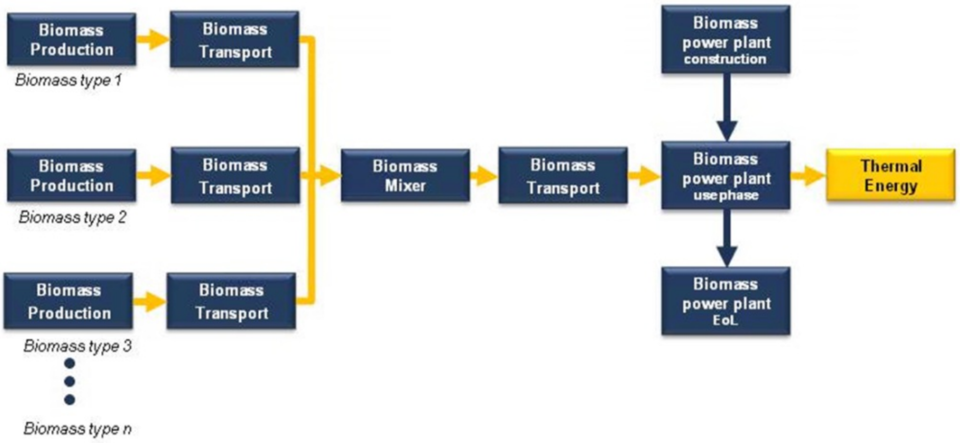

Figure 24. Flow diagram of the modeled process module thermal energy. (from Sphera Solution GmbH, 2018)

3.2.3 Life-cycle impact assessment (LCIA) and selected impact indicators

In the LCIA, the results of the LCI (input and output data) are “translated” into a limited number of environmental impact values and assigned (classified) to the corresponding impact categories. This process is conducted with the help of so-called characterization factors, which indicate the environmental impact per unit of the stressor (e.g., per kg of resource consumed or emission released). Two methods are available for deriving characterization factors: at the midpoint or endpoint level. Characterization factors at the midpoint level consider environmental impacts up to the directly describable or measurable effects resulting from the environmental impact mechanisms (cause-effect chain). Endpoint-level characterization factors correspond to a damaging approach triggered by midpoint categories (Huijbregts et al., 2016, p.13).

Several characterization models are available for the quantification of the respective impact categories. The different models and the fact that ISO 14044 does not specify a binding list of impact categories make it difficult to select the models to be used in the study (Gnansounou, 2017, p.61). To investigate the environmental impacts of the three different biorefinery pretreatment scenarios, the hierarchical midpoint method ReCiPe 2016 v.1.1 was selected because it is the most up-to-date and comprehensive method to the author's state of knowledge.

ReCiPe was developed in the Netherlands by LCA researchers to harmonize the choice of characterization models. It is a combined (updated) method of the Eco-Indicator 99 and the CML 2001 method. It combines the advantages of the two approaches that the category indicators are considered at both the mid and endpoint levels (Gnansounou, 2017, p.62). The midpoint-level was chosen because its characterization has more connection to environmental flows and has relatively low uncertainties (Huijbregts et al., 2016, p.13).

The LCIA was performed using GaBi software (v.10.0.0.71, Sphera Solution GmbH). Table 11 shows the 18 ReCiPe impact categories and their mid-level indicators. The major environmental impacts of the three pretreatment scenarios mainly result from feedstock preparation (wheat straw, bioethanol, process water) and auxiliary supply (thermal energy) and ethanol emission from the liquid residue and water consumption. Table 11 presents the 18 ReCiPe impact categories; from this, four main impacts (highlighted in green) were selected for the evaluation of the scenarios and are discussed in more detail in the results.

Table 11.
ReCiPe 2016 midpoint categories and related impact indicators.

Impact category	Indicator	Unit	CFm	Abbr.	Unit
Climate change	**Infra-red radiative forcing increase**	**W*yr/m^2**	**Global warming potential**	**GWP**	**kg CO_2 to air**
Ozone depletion	Stratospheric ozone decrease	ppt*yr	Ozone depletion potential	ODP	kg CFC-11 to air
Ionizing radiation	Absorbed dose increase	man*Sv	Ionizing radiation potential	IRP	kBq Co-60 to air
Fine particulate matter formation	PM2.5 population intake increase	kg	Particulate matter formation potential	PMFP	kg PM2.5 to air
Photochemical oxidant formation: ecosystem quality	Tropospheric ozone increase (AOT40)	ppb.yr	Photochemical oxidant formation potential: ecosystems	EOFP	kg NOx to air
Photochemical oxidant formation: human health	Tropospheric ozone population intake increase (M6M)	kg	Photochemical oxidant formation potential: humans	HOFP	kg NOx to air
Terrestrial acidification	Proton increase in natural soils	yr*m^2*mol/l	Terrestrial acidification potential	TAP	kg SO_2 to air
Freshwater eutrophication	**Phosphorus increase in fresh water**	**yr*m^3**	**Freshwater eutrophication potential**	**FEP**	**kg P to fresh water**
Marine eutrophication	Dissolved inorganic nitrogen increase in marine water	yr.kgO_2/kgN	Marine eutrophication potential	MEP	kg N to marine water
Human toxicity: cancer	Risk increase of cancer disease incidence	-	Human toxicity potential	HTPc	kg 1,4- DCB to urban air

Human toxicity: noncancer	**Risk increase of non-cancer disease incidence**	**-**	**Human toxicity potential**	**HTPnc**	**kg 1,4- DCB to urban air**
Terrestrial ecotoxicity	Hazard- weighted increase in natural soils	$yr*m^2$	Terrestrial ecotoxicity potential	TETP	kg 1,4- DCB to industrial soil
Freshwater ecotoxicity	Hazard- weighted increase in fresh waters	$yr*m^3$	Freshwater ecotoxicity potential	FETP	kg 1,4- DCB to fresh water
Marine ecotoxicity	Hazard- weighted increase in marine water	$yr*m^3$	Marine ecotoxicity potential	METP	kg 1,4- DCB to marine water
Land use	**Occupation and time-integrated transformation**	**$yr*m^2$**	**Agricultural land occupation potential**	**LOP**	**m^2*yr annual crop land**
Water use	Increase of water consumed	m^3	Water consumption potential	WCP	m^3 water consumed
Mineral resource scarcity	Ore grade decrease	kg	Surplus ore potential	SOP	kg Cu
Fossil resource scarcity	Upper heating value	MJ	Fossil fuel potential	FFP	kg oil

Note. From (Huijbregts et al., 2016, p.23-24); CFm: midpoint characterization factor

Global warming potential (including biogenic carbon as well as excluding biogenic carbon), freshwater eutrophication potential, and agricultural land potential were selected because renewable resources are used to provide both feedstock (wheat straw) and auxiliary substances (thermal energy and bioethanol). Human toxicity potential is another important impact indicator to determine harm to human health. For these reasons, the four impact categories were chosen to be examined in more detail.

Although a significant amount of water is used in the three biorefinery pretreatment scenarios, the water use potential is not explicitly discussed, because these are analogous to the water demand results of the process simulation, and the water demand is therefore discussed in detail in the process simulation results.

4 RESULTS AND DISCUSSION

4.1 Balance results from the process simulation

In this chapter, the results of the mass and energy balances of the Aspen process simulation are presented. The balance results of the process simulation include all process steps from the first extraction stage to the intermediate products. The water and energy demand that occurs before the first extraction stage and the groundwater required for process water treatment are not considered. This means that only the net water and energy consumption required in the process is considered – a so-called gate-to-gate approach.

4.1.1 Process water demand

The net process water demand of the three scenarios, determined using the Aspen Plus software, is summarized in Diagrams 1 and 2. In diagram 2, the results of the process water demand for each sub-process as well as for the total amount of the three scenarios (OS, OS-LHW, LHW-OS) are shown comparatively in a bar chart in relation to the functional unit 1 kg wheat straw. In addition, the diagram shows the corresponding numerical values. Diagram 1 compares the three scenarios in terms of the total amount of process water required relative to each other.

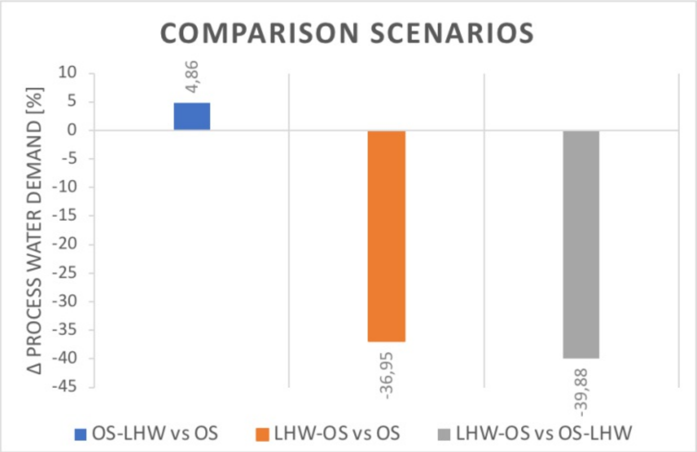

Diagram 1. Comparison of the total amount of process water of the three scenarios with each other.

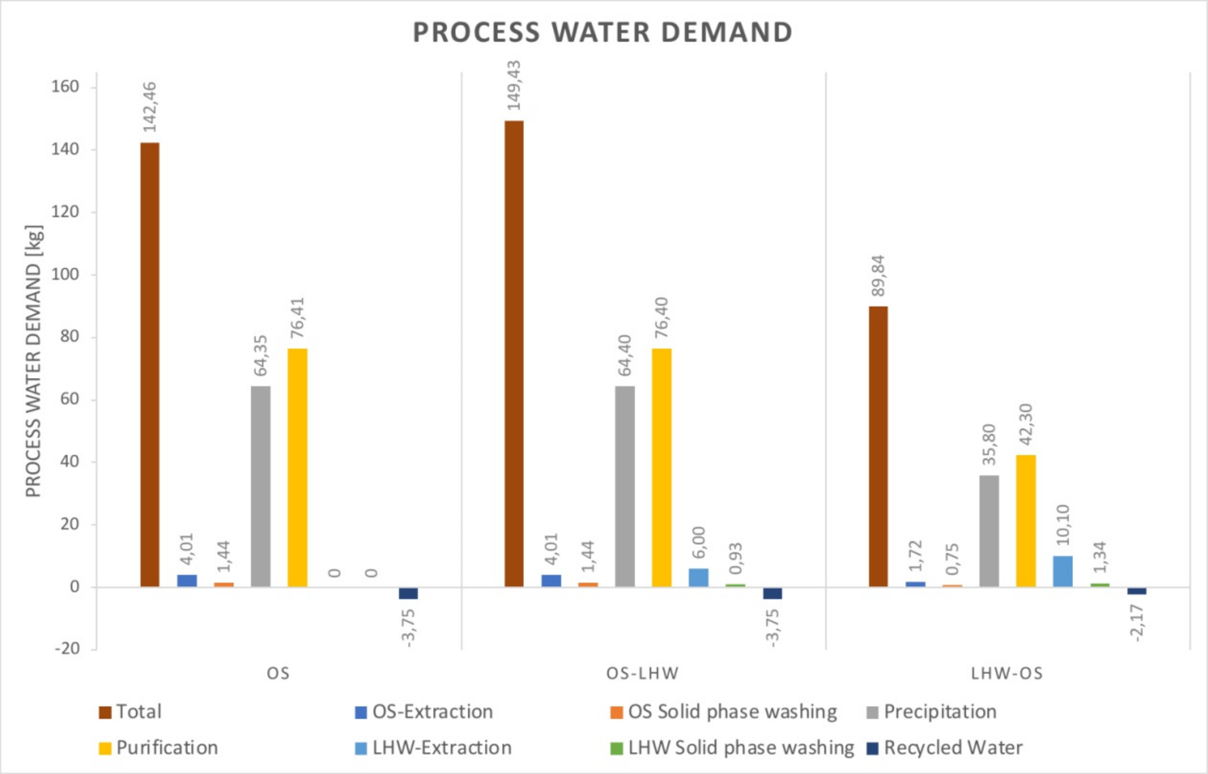

Diagram 2. Process water demand for each sub-process.

From the two diagrams, it can be seen that overall, the scenario LHW-OS with a total process water requirement of approximately 90 kg requires about 37 % less than scenario 1 (OS) and about 40 % less than scenario 2 (OS-LHW). This is due to the fact that scenario 3 (LHW-OS) requires less process water, especially for the precipitation and purification process steps.

In scenario 3 (LHW-OS), the pre-LHW extraction dissolves a large part of the hemicellulose and extractives, only a small amount of the lignin and hardly any cellulose (see Diagram 3, where the compositions of the feedstocks for the OS extraction are given). The dissolved components are then removed during solid-phase separation and subsequent solid-phase washing (displacement washing = replacement by water). The dissolved components reduce the amount of solid mass for the subsequent OS extraction so that less solvent (solid-liquid ratio equals 1:11) is required. In addition, due to the previous LHW extraction and displacement washing, the water content of the solid is higher, which also reduces the amount of solvent. Due to the reduced solvent requirement, the dissolved components are present in higher concentrations after the subsequent solid-liquid separation (after the OS Extraction). This reduces the total amount of combined liquid streams (from extraction and solid-phase washing), which implies that correspondingly less water is needed as an antisolvent to precipitate the CLP particles. This aspect that the solution is more concentrated due to the pre-LHW extraction impacts subsequent process steps such as purification (less water is needed after the 1st membrane stage) and solvent recovery. Accordingly, less energy is consumed during solvent recovery.

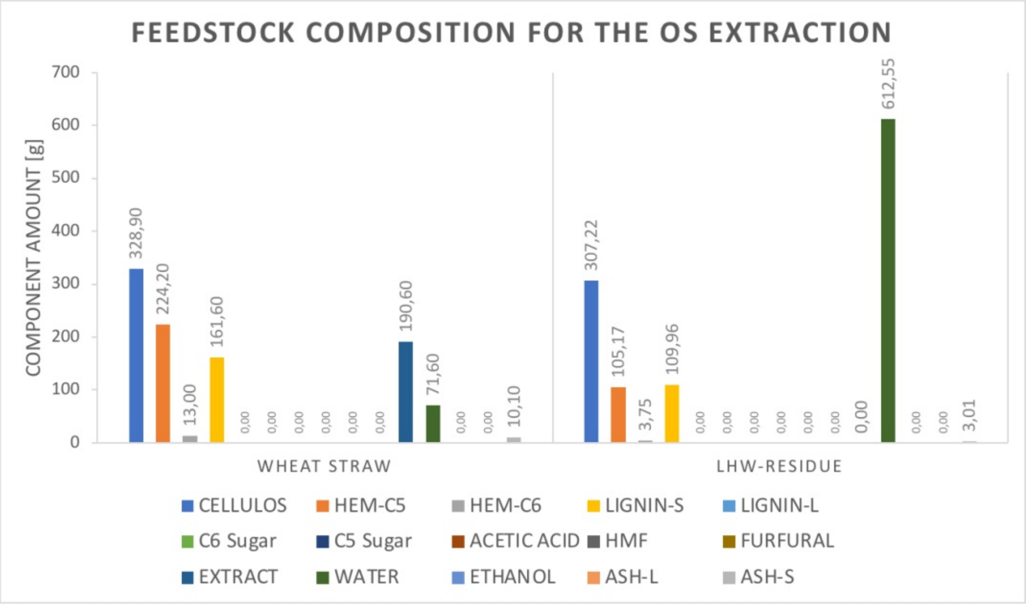

Diagram 3. Illustration of the composition of the Wheat Straw and LHW solid residue.

For the other process steps (OS and LHW-solid phase washing), the deviations are only marginal. Furthermore, it can be seen from the diagrams that scenario 2 (OS-LHW) requires approx. 5% more process water than scenario 1 (OS). This additional demand results from the two extra process steps (LHW extraction and LHW solid-phase washing) since all other process steps have the same demand.

Diagram 4 shows the process water leaving the product system, i.e., the process water losses. It can be seen that a significant proportion leaves the system via the liquid residue from the rectification and the permeate from the second membrane stage through the WWT system. The wash water from the LHW solid-phase washing step accounts for only a small portion here. The same applies to the removed water portions of the intermediate products (cellulose phase, CLP suspension and sugar stream).

For further process development, there is still enormous potential in the water management system. Through an intelligent process water management system, which takes into account the water losses (especially from rectification and 2nd membrane), this stream could be reused as process water in the system. The wastewater can be reused, especially in the water-intensive processes of precipitation and purification. Through this optimization, the process water demand can be reduced enormously. However, it must be examined to what extent the water quality and the wastewater components affect the process performance and whether additional water treatment processes may be required.

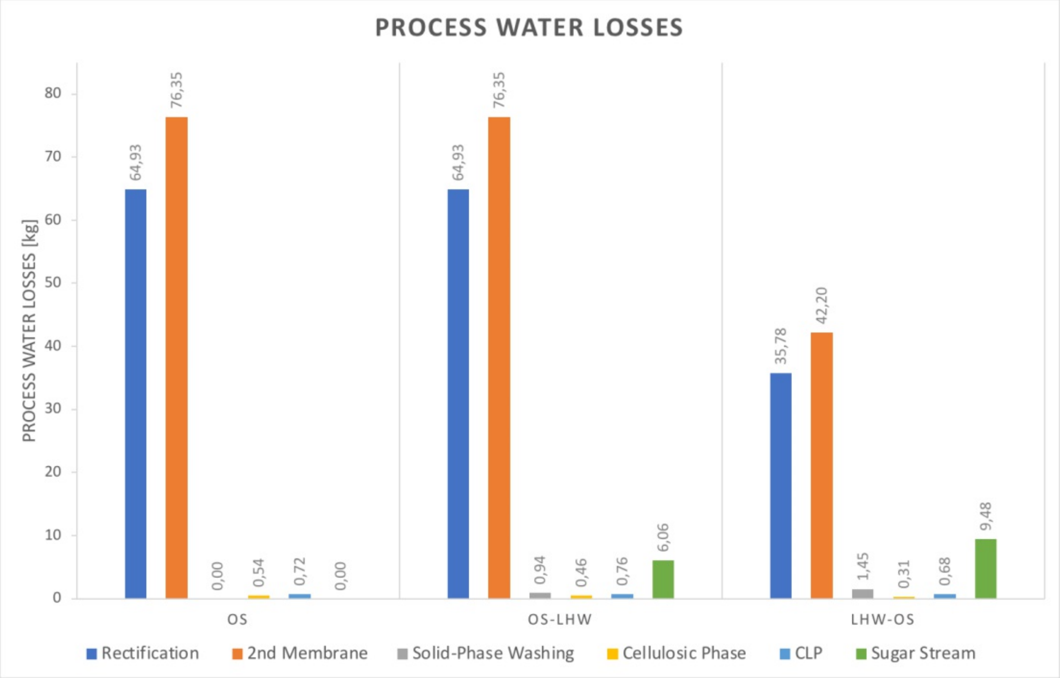

Diagram 4. Illustration of the process water leaving the system via the process stages and intermediate products.

4.1.2 Ethanol demand

Diagram 5 illustrates the amount of ethanol required for the OS extraction for the three scenarios. In addition, it shows the total required amount of ethanol broken down into amount of recovered ethanol (which is recycled by solvent recovery) and amount of virgin ethanol to be added. It can be seen that Scenario 1 (OS) and Scenario 2 (OS-LHW) have the same ethanol demand and solvent recovery rate. Since OS extraction is the first pretreatment step in both scenarios, the same feedstock (1 kg wheat straw) is treated. This results in the same solvent makeup (solid to liquid ratio of 1:11 with a 60 wt% aqueous ethanol mixture). In Scenario 3 (LHW-OS), significantly less ethanol is required to achieve the desired solvent composition due to the concentration effects and different feedstock composition (LHW residue versus wheat straw). The cause of these effects has already been described in detail in the previous section (Chapter 4.1.1 process water demand). In addition, the recovery rate is higher in comparison since a more concentrated solution is already fed into the solvent recovery (rectification).

Diagrams 6 and 7 illustrate the three scenarios in terms of total ethanol required and the amount of ethanol to be added (virgin ethanol) relative to each other.

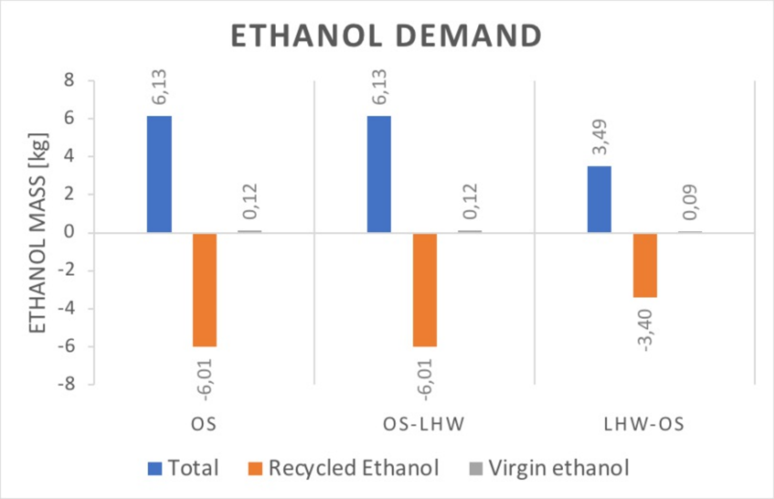

Diagram 5. Ethanol demand of the three scenarios broken down into recycled ethanol (from solvent recovery) and demand for virgin ethanol.

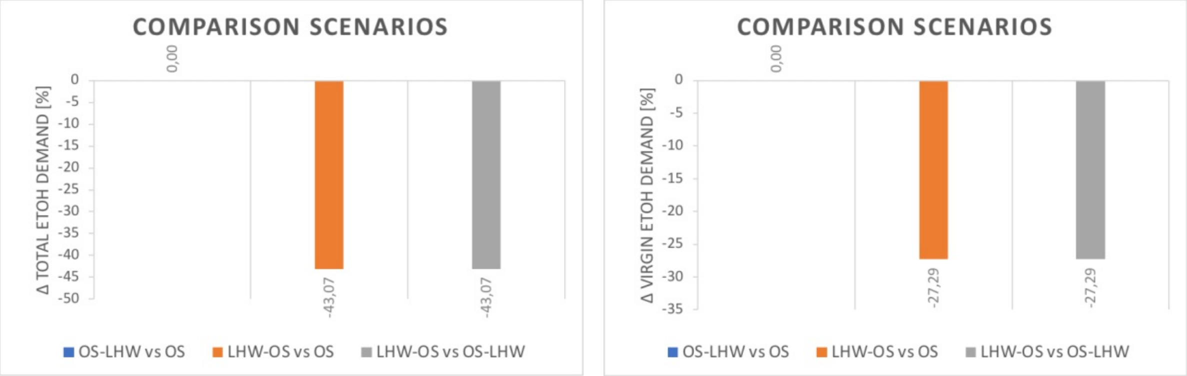

Diagram 6. Comparison of the total ethanol demand of the three scenarios.

Diagram 7. Comparison of the virgin ethanol demand of the three scenarios.

4.1.3 Thermal energy demand

Diagram 8 compares the results of the thermal energy demand of the three scenarios. The total energy demand is further split into the process modules extractions (OS extraction and LHW extraction) and solvent recovery (feed preheating and rectification). Since no energy demand was simulated for the other process modules and the energy demand for media transport was not considered, a further splitting is not appropriate. Diagram 9 shows the three scenarios relative to each other in terms of total energy demand.

Scenario 2 (OS-LHW) requires about 11 % more energy than scenario 1 (OS). This is due to the additional extraction step (OS residual is treated further by LHW extraction), as all other process modules have the same energy demand (see diagram 8). Scenario 3 (LHW-OS) requires about 28 % less energy than scenario 1 (OS) and about 35 % less than scenario 2 (OS-LHW). This is due to the concentrated solutions after LHW extraction, discussed in the previous sections. The concentrated solution implies that a lower volumetric flow rate enters to the solvent recovery system. Thus, less energy is required for the heating (feed preheating) and purification (rectification). These are the most significant energy differences, as the two extraction steps (regardless of order) have similar aggregated energy demands.

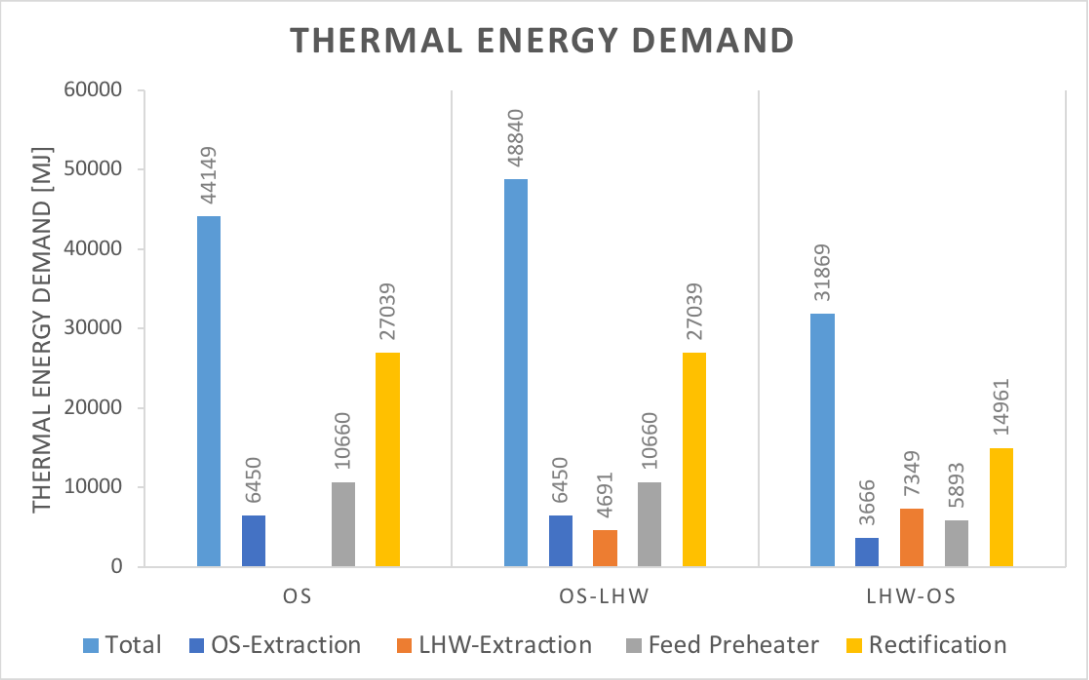

Diagram 8. Thermal energy demand for each process module.

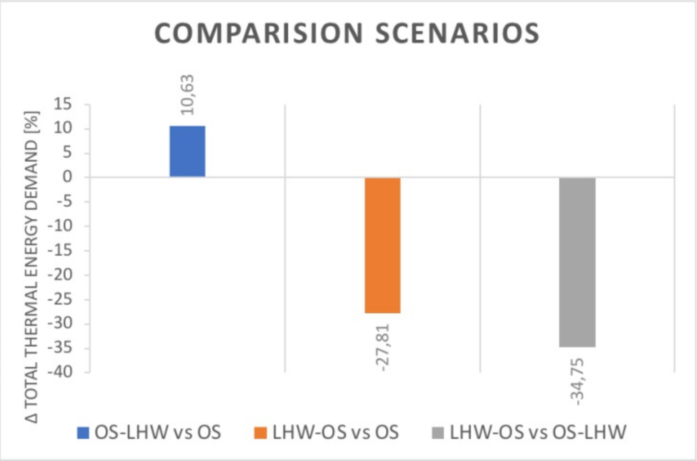

Diagram 9. Comparison of the total amount of thermal energy of the three scenarios with each other.

4.1.4 Composition of the intermediates

Within the scope of this master thesis, not only the ecological performance of the three pretreatment strategies is to be determined, but also their technical performance. Therefore, in this section, the technical quality of the intermediates of the respective scenarios is examined. For this purpose, the composition of the intermediate products is presented in the form of a bar chart (Diagrams 10 to 14; corresponding data see appendix 7.4.4), and their potential for further processing (secondary refining) is determined. Since the individual fractions still have a high-water content, the composition of the intermediates excluding the water content is also shown to illustrate better the proportions of the value components.

4.1.4.1 CLP suspension

Diagram 10 shows that despite purification (two-stage membrane filtration), the CLP are highly diluted in water (~95 % water content). In addition, a small amount of residual ethanol and traces of dissolved sugars and degradation products (HMF, furfural, acetic acid and extracts) are present. However, these components are all below 0.017g (0.002 %wt) and are therefore not illustrated in the diagram. Diagram 11 shows the composition without water, from which it can be seen that both scenarios 1 and 2 (OS and OS-LHW) produce the same amount of CLP with 38 g CLP. This is because in both scenarios the OS extraction was performed under the same conditions with the same feedstock (wheat straw). In contrast, scenario 3 (LHW-OS) produces about 36 g of CLP. The difference of 2 g is because the upstream LHW extraction already dissolves out some of the lignin, leaving less lignin in the matrix of the LHW residual (lignin content in the wheat straw 161.60 g versus a lignin content of 109.96 g in the LHW residual). This situation is shown graphically in Diagram 3 Chapter 4.1.1 (Illustration of the Composition of the Wheat Straw and LHW Solid Residue). This means that 2 g less CLP can be produced in absolute quantities, but relative to feedstock composition, a higher yield is obtained with Scenario 3 (LHW-OS). Scenarios 1 and 2 (OS and OS-LHW) achieve a yield of 23.6 %, while Scenario 3 (LHW-OS) achieves a yield of 32.4 % (yield = (amount of lignin(solid) in the feedstock/amount of CLP)*100%). This is because the pre-extraction of LHW makes the lignin in the LHW residual material more accessible.

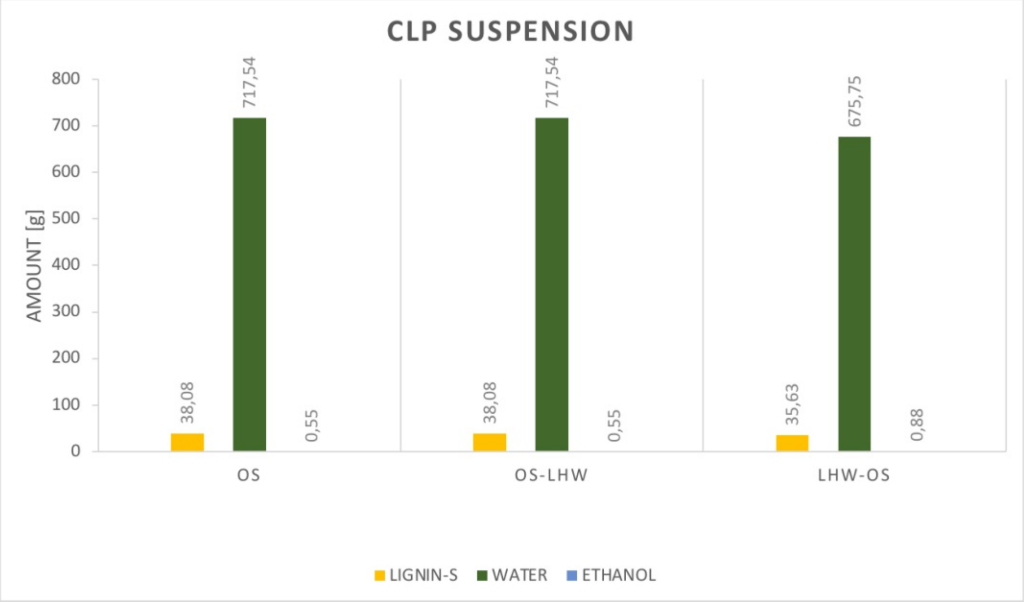

Diagram 10. Illustration of the composition of the CLP suspension (inclusive water content).

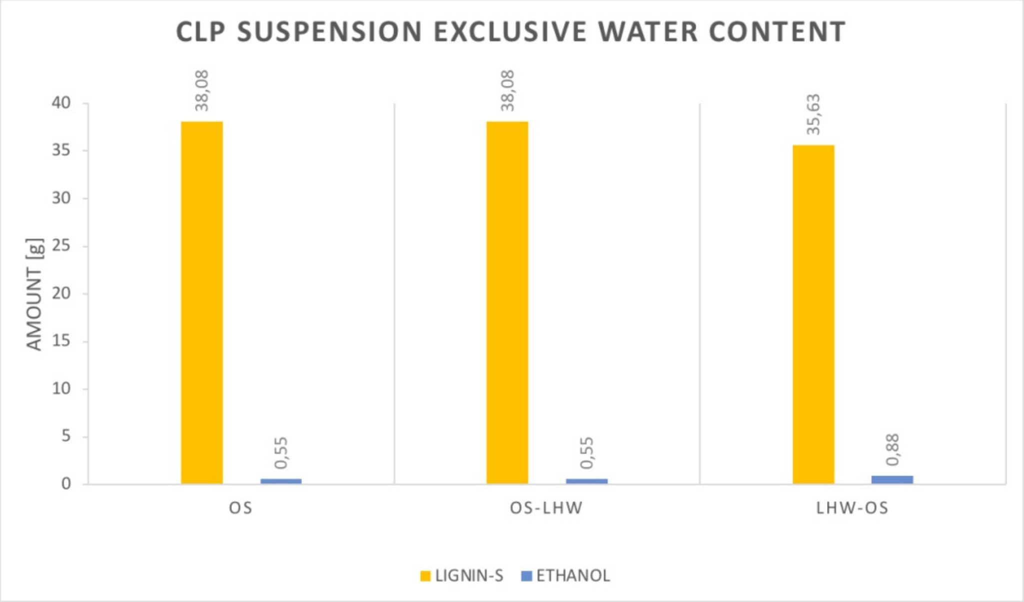

Diagram 11. Illustration of the composition of the CLP suspension (exclusive water content).

4.1.4.2 Cellulose phase

Diagram 12 shows the composition of the cellulose-rich solids of the three scenarios. It can be seen that the cellulose content differs only slightly in all three scenarios (OS: ~303 g; OS-LHW: ~282 g; LHW-OS: 294 g). However, the solids of the three scenarios contain different amounts of minor by-components. For example, the cellulose-rich solids in Scenario 1 (OS) and Scenario 2 (OS-LHW) still contain significant amounts of water, hemicellulose, and lignin. The proportion of other components is higher in Scenario 1 than in Scenario 2 because the additional extraction stage dissolves these components. Scenario 3 (LHW-OS) provides the "purest" cellulose-rich solid. Thus, it also has a higher potential for further applications since, for example, a certain quality is required for paper or fiber production.

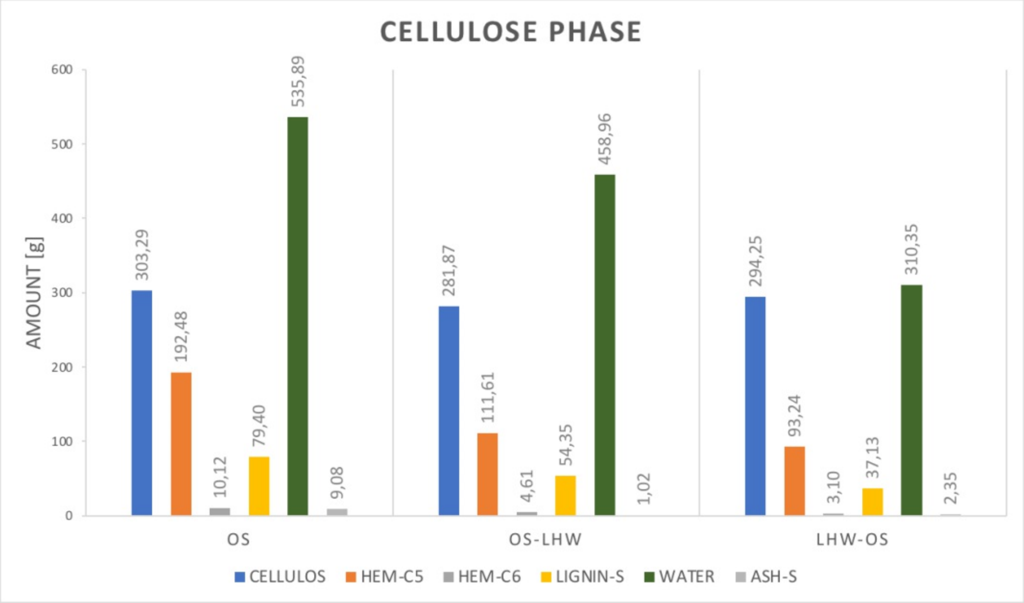

Diagram 12. Illustration of the composition of the cellulose phase.

4.1.4.3 Sugar stream

The sugar stream is obtained after LHW extraction and subsequent solid-liquid separation (separated liquid stream). Diagram 13 shows the composition of the sugar stream of the three scenarios in the form of a bar chart. Since the sugar stream is highly diluted by the LHW treatment (high water content), Diagram 14 shows the composition of the components without the water content to illustrate better the proportions of the valuable components. In scenario 1 (OS), no sugar stream is obtained; therefore, no values are indicated.

From diagram 13 it can be seen that in scenario 3 (LHW-OS), the water content is significantly higher than in scenario 2 (OS-LHW). This is again due to the concentration effects caused by the two extraction stages. In scenario 2 (OS-LHW), the LHW extraction is performed in the second stage, using an already pretreated OS residue as feedstock. This OS residue has a lower dry mass than the wheat straw due to the pre-OS extraction, which requires less solvent (solid to liquid ratio 1:11). Because of the reduced addition of solvent, the hydrolyzed and dissolved sugars are more concentrated.

Diagram 14 shows that the sugar concentrations (C5 and C6 sugars) are higher in scenario 3 (LHW-OS) than in scenario 2 (OS-LHW) because the feedstock wheat straw contains more hemicellulose for their hydrolysis than the solid after performing OS. However, LHW extraction as the first step also produces more degradation products (HMF, furfural and acetic acid), due to the same effect previously discussed. These can be troublesome for practical application or for further processing in secondary refinery and limit the application field. A detailed analysis of the quality and composition of the individual fractions can be found at Serna-Loaiza et al. (2020).

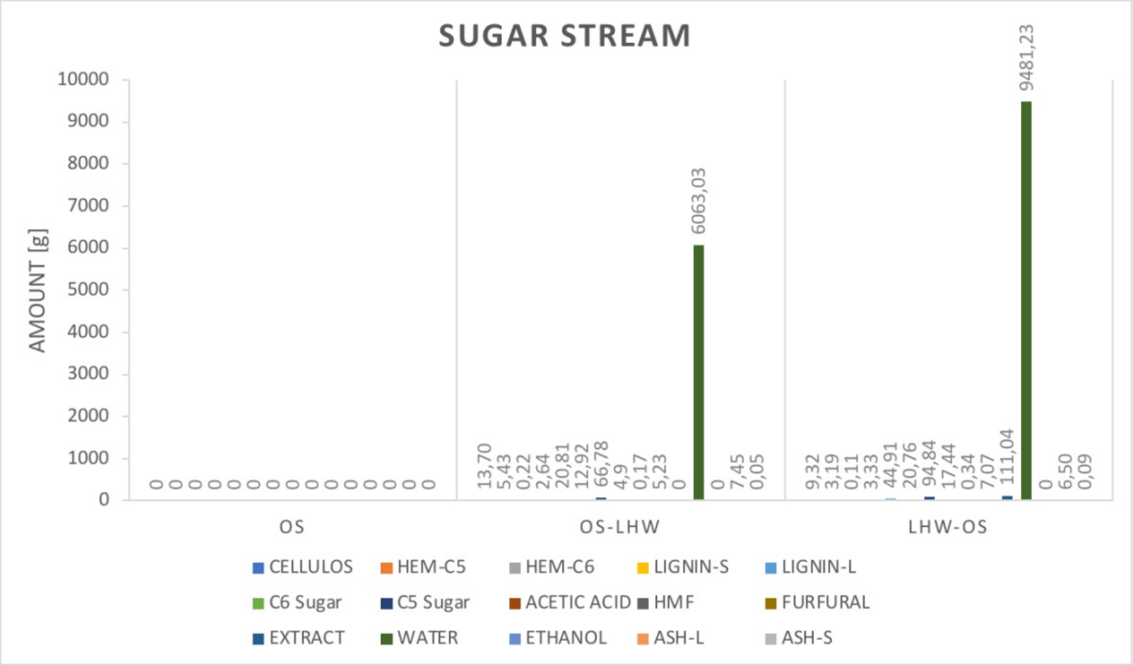

Diagram 13. Illustration of the composition of the sugar stream (inclusive water content).

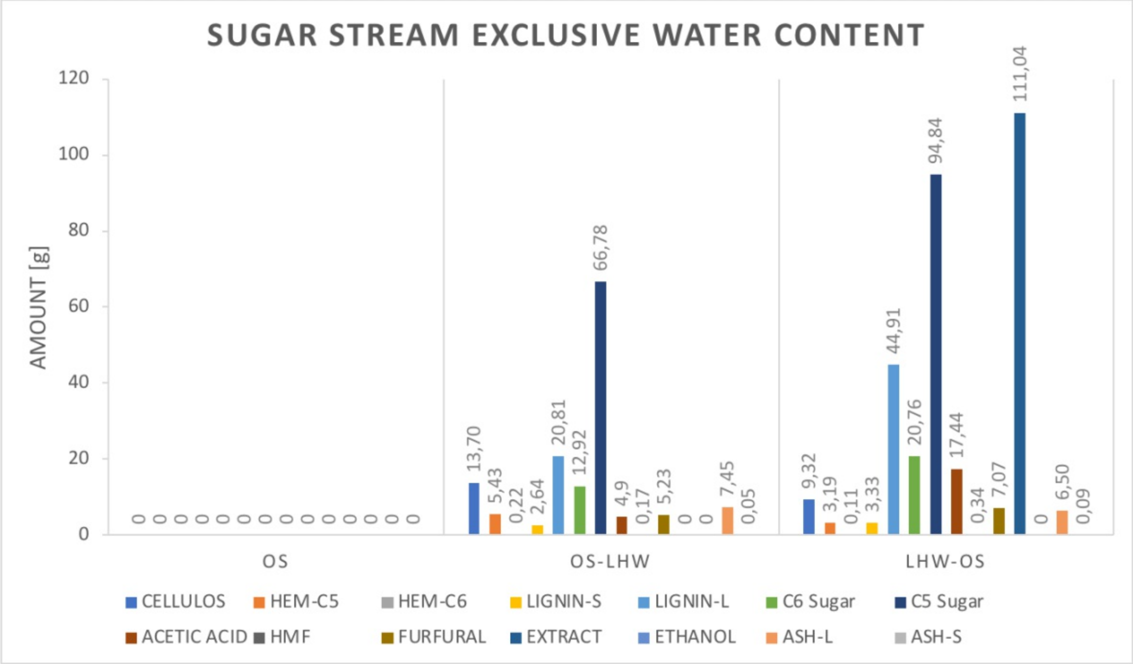

Diagram 14. Illustration of the composition of the sugar stream (exclusive water content).

4.2 LCA results of the LCB biomass pretreatment scenarios

A key part of this work is to obtain insights into the environmental impacts of the individual pretreatment scenarios to determine not only the technical but also the ecological performance. The midpoint environmental indicators and impact categories from the "ReCiPe" assessment method (chapter 3.2.1.5) are applied to determine the potential ecological impacts. In this thesis, there is no straight listing of all results of the 18 different environmental indicators. The four ecological indicators considered to be particularly relevant in Chapter 3.2.1.5 are discussed as follows. The results of the other impact indicators can be found in the appendix under Chapter 7.6.

4.2.1 Climate change

To characterize climate change impacts, ReCiPe uses the global warming potential (GWP) characterization factor. GWP is a comparative measure that quantifies the infrared radiative increase of greenhouse gas (GHG) integrated over time (100 years for the Hierarchist approach), expressed in kg CO_2-eq. When a GHG (kg) is emitted into the atmosphere, the concentration of GHGs (ppb) in the atmosphere increases. The consequence of the increased concentration is that the radiative forcing (W/m^2) is also increased. The radiative forcing is a parameter of how the Earth's energy balance and the atmosphere are changed. Thus, it reflects the balance between the incident solar radiation and the infrared radiation emitted by the Earth. If this balance is unbalanced (due to anthropogenically emitted greenhouse gases), the climate has a "forcing" to change temperature, resulting in an increase in global mean temperature (°C). The increase in global mean temperature then results in impacts (damage) to human health and the ecosystem (land and freshwater) (Huijbregts et al., 2016, p. 27-28).

The following equation shows the calculation of the average characterization factor of any GHG (x) and any time horizon (TH) where the absolute global warming potential (AGWP) is the amount of radiative forcing integrated over time caused by the emission of 1 kg GHG (Huijbregts et al., 2016, p.28).

$$GWP_{\mathrm{x,TH}} \frac{AGWP_{\mathrm{x,TH}}}{AGWP_{\mathrm{CO2,TH}}}$$

The calculation of GWP can be performed both with and without biogenic carbon. Biogenic carbon is the CO_2 that biomass captures from the atmosphere during the growth (CO_2 in the atmosphere -> CO_2 uptake/H_2O/sunlight/surface-> plant growth -> harvested biomass -> use of biomass as fuel or material -> CO_2 combustion/decomposition -> CO_2 uptake in the atmosphere->...). If biogenic carbon is included in the calculation, the sequestered CO_2 amount must also be considered (Sequestered CO_2 amount is subtracted from emissions). If biogenic carbon is excluded, CO_2 captured by biomass is omitted from the calculation (Baitz et al., 2016, p. 53-61).

Since the conceptual design of the three biorefineries uses biomass for both feedstock and auxiliary supply (thermal energy and bioethanol), the climate change is shown both with (Diagram 17 and 18) and without the inclusion of biogenic carbon (Diagram 15 and 16). In the following diagrams, the total GWP of the process is divided into five subcategories: thermal energy, process water, bioethanol, wheat straw, and wastewater treatment (WWT). The subcategory “thermal energy” sums up the process modules: OS extraction, LHW extraction, feed preheating, and rectification. The subcategory “process water” sums up the process modules: OS extraction, LHW extraction, precipitation, purification (membrane) and solid phase washing. In Diagram 15 and 17, the three scenarios are once again shown relative to each other in terms of total GWP.

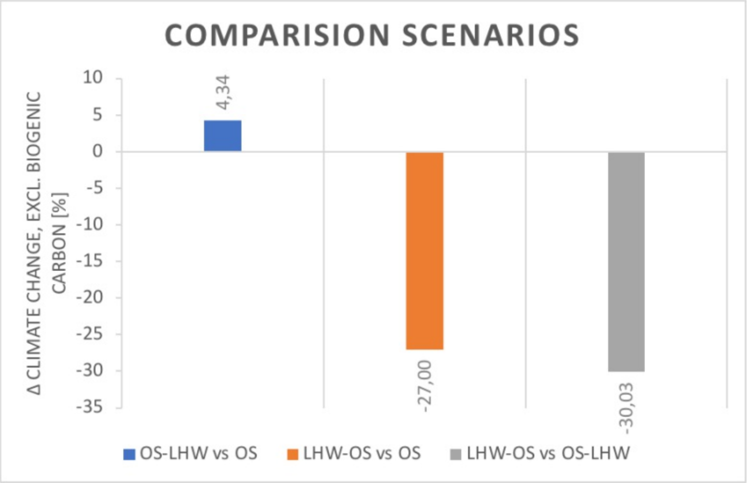

Diagram 15. Comparison of the total amount of climate change (excl. biogenic carbon) of the three scenarios compared with each other.

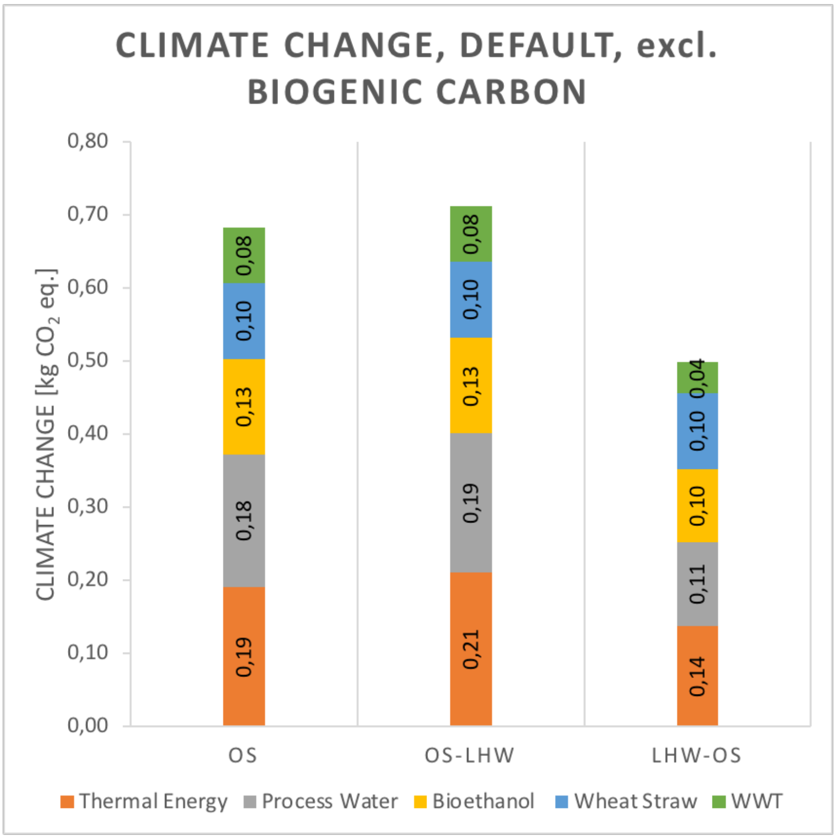

Diagram 16. Climate change (excl. biogenic carbon) indicator for the different subcategories expressed in kg of CO_2 equivalents.

Diagram 15 shows that scenario 3 (LHW-OS) with 0.50 kg CO_2 eq. contributes ~20% less to the impact category climate change than scenario 1 (OS) with 0.68 kg CO_2 eq. Compared to scenario 2 (OS-LHW) with 0.71 kg CO_2 eq. it even contributes ~26% less. Broken down in Diagram 16, it can be seen that the supply of thermal energy and process water are the largest GWP contributors, followed by bioethanol production, biomass cultivation (wheat straw) and WWT.

Since the same amount of feedstock (1 kg wheat straw) was used for the three scenarios, the GWPs corresponding to the production of wheat straw are the same. The increased GWP of scenario 2 (OS-LHW) compared to scenario 1 (OS) is due to the two additional process steps (LHW extraction + solid-liquid separation and solid-phase washing), resulting in a difference in thermal energy demand as well as in the required process water. The significantly better performance of scenario 3 (LHW-OS) results from the pre-LHW extraction, where the wheat straw is treated, and a large part of the hemicellulose is dissolved. This makes the LHW residue more accessible and has a lower dry matter content, therefore, less solvent (reduced ethanol and water requirements) is needed for subsequent extraction, resulting in a more concentrated solution (reduced water requirements for precipitation and lower energy requirements for solvent recovery). This leads to less CO_2 emissions for the supply of process water, bioethanol and thermal energy.

If biogenic carbon is taken into account, the GWP for the three scenarios is even negative. In addition, the same trend as without biogenic carbon can be observed. Scenario 3 (LHW-OS) performs better with -1.06 kg CO_2 eq. than scenario 1 (OS) with -0.88 kg CO_2 eq. and even better than scenario 2 (OS-LHW) with -0.84 kg CO_2 eq. Furthermore, it can be seen that the most significant amount of CO_2 is sequestered in the cultivation of wheat straw. Moreover, the consideration of biogenic carbon changes the contributions of the process modules thermal energy, bioethanol and process water. The production process of bioethanol, for example, has a negative GWP because the sequestered biogenic CO_2 in wheat leads to a credit. For the provision of thermal energy and process water, the consideration of biogenic carbon reflects an opposite trend (instead of a credit, a debit occurs) since biomass combustion in the biomass power plant and process water treatment releases sequestered biogenic CO_2 back into the environment in the form of emissions.

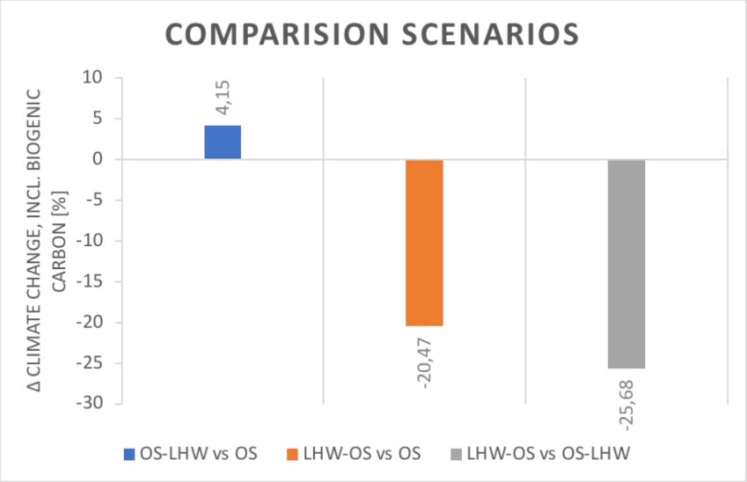

Diagram 17. Comparison of the total amount of climate change (incl. biogenic carbon) of the three scenarios with each other.

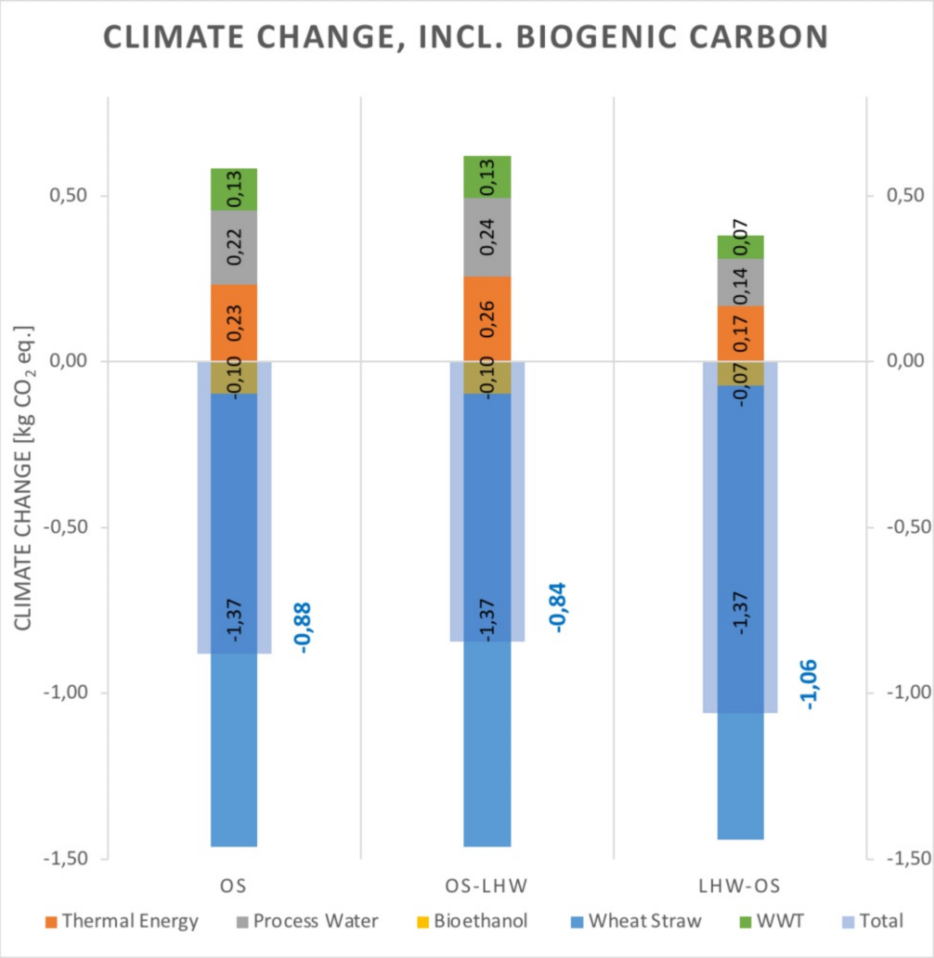

Diagram 18. Climate change (incl. biogenic carbon) indicator for the different subcategories.

4.2.2 Freshwater eutrophication

Increased inputs of nutrients cause eutrophication of freshwater into the soil or freshwater components. The increased input leads to an increase in the concentration of nutrients (phosphorus and nitrogen) in freshwater and results in numerous environmental impacts. The oversupply causes increased growth of cyanobacteria and algae (autotrophic organisms) and an increase in fish and invertebrates (heterotrophic species). The increased growth of these species ultimately leads to a change in the species spectrum. The freshwater eutrophication potential (FEP) is used as a characterization factor, where the individual components are expressed in kg P on freshwater equivalents (Huijbregts et al., 2016, p. 65-66).

Diagram 19 shows the FEP of the three scenarios, again divided into the five subcategories: thermal energy, process water, bioethanol, wheat straw and WWT. Diagram 20 shows the three scenarios relative to each other in relation to the total FEP. Diagram 20 shows the same trend as for GWP. Scenario 3 (LHW-OS) performs ~31 % better than scenario 1 (OS) with

$1.94*10^{-4}$ kg P eq. and ~33 % better than scenario 2 (OS-LHW) $2.00*10^{-4}$ kg P eq. with $1.34*10^{-4}$ kg P eq. The main reasons are again the concentration effects due to the pre-LHW extraction. Diagram 19 also shows that WWT has the largest contribution to FEP, as the wastewater is discharged directly into the rivers after wastewater treatment. This is followed by thermal energy treatment, which is mainly caused by incineration residues and waste gases. Wheat straw has the same proportion in all three scenarios (FU 1 kg wheat straw), mainly caused by fertilization on the field.

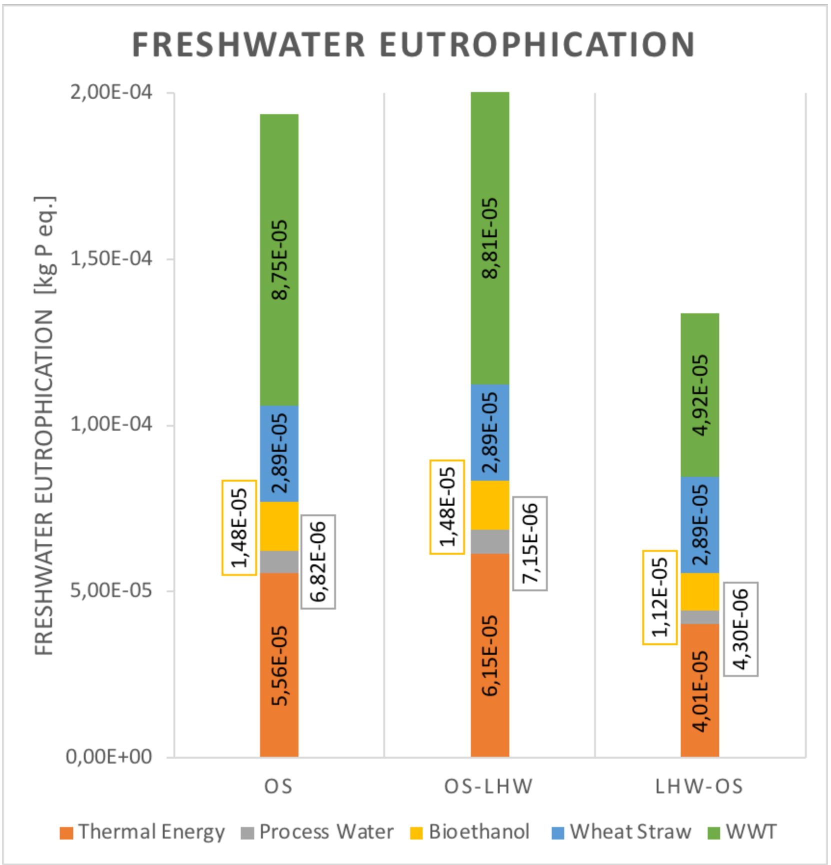

Diagram 19. Freshwater eutrophication indicator for the different subcategories.

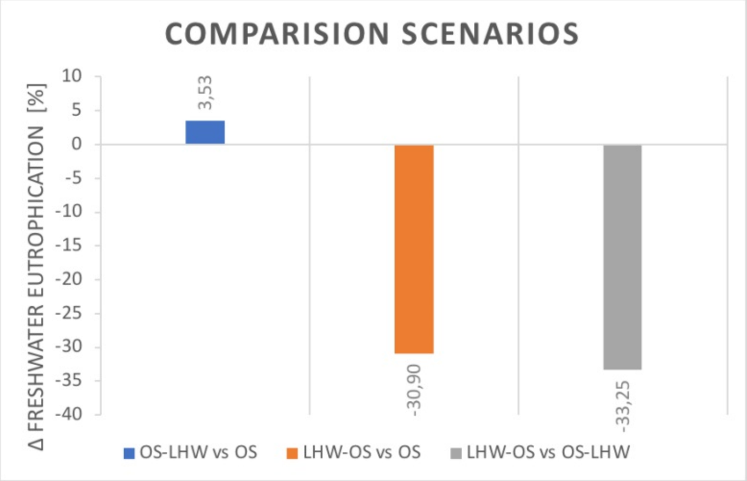

Diagram 20. Comparison of the total amount of freshwater eutrophication of the three scenarios with each other.

4.2.3 Human toxicity

Human toxicity as an impact category includes environmental persistence (fate), accumulation in the human food chain (exposure) and toxicity (effect) of substances on human health. The cause-effect pathway begins with the emission of the substances into the environment, which leads to an increase in the chemical concentration of the substances in the environment. With the increased concentration in the environment, humans' uptake of hazardous substances also increases, which finally leads to an increase in cases of illness and damage to health. The characterization model are derived from toxicity data from humans and laboratory animals, and the fate and exposure factors are simulated using "evaluative" multimedia models. To make the results comparable, the fate and effects of chemical emissions are related to the reference substance 1,4-dichlorobenzene equivalents (1,4DCB-eq). ReCiPe uses the global multimedia Fate, Exposure and Effects Model USES-LCA 2.0 as a basis for calculation. In this model, the human-toxicological effect factors are derived for both carcinogenic (HTPc) and non-carcinogenic effects (HTPnc) (Huijbregts et al., 2016, p. 73-80).

Since mainly non-carcinogenic substances are used in the present process scenarios, this impact category is explained in more detail below, whereby the human toxicological impact category for carcinogens can be found in the appendix (Chapter 7.6). Diagram 21 shows the HTPnc of the three scenarios, again divided into the five subcategories: thermal energy, process water, bioethanol, wheat straw and WWT. Diagram 22 shows the three scenarios again relative to each other in terms of total HTPnc.

Diagram 21 shows the same trend as the previous impact categories. Scenario 3 (LHW-OS) with $9.06*10^{-2}$ kg 1.4-DB eq. has a ~33 % lower hazard potential than scenario 1 (OS) with

$1.36*10^{-1}$ kg 1.4-DB eq. and ~36 % less than scenario 2 (OS-LHW) $1.41*10^{-1}$ kg 1.4-DB eq. The main reasons are again the concentration effects due to the pre-LHW extraction. As a result, less wastewater is treated in the WWT, and thus, less wastewater is released into the environment. In addition, fewer emissions and combustion residues are released in the biomass power plant due to the lower energy demand. Diagram 21 shows that these two process units (WWT and thermal energy) account for the most significant amount of HTPnc. Wheat straw supply again has the same share in all three scenarios (FU 1 kg wheat straw) caused by fertilization in the field. Scenario 3 also differs in the process units (bioethanol and process water supply) due to the effects mentioned, but the differences are not as significant.

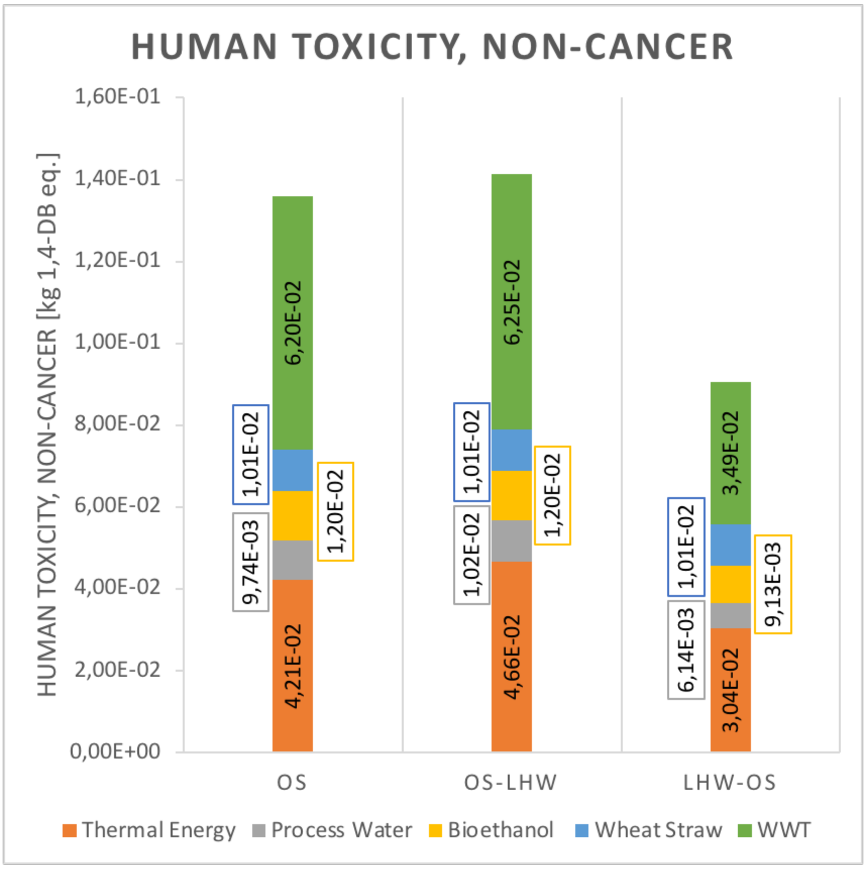

Diagram 21. Human toxicity non-carcinogenic potential indicator for the different subcategories.

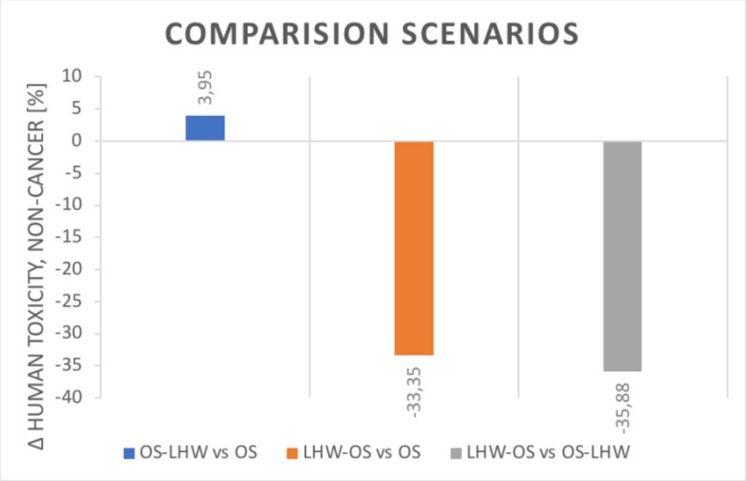

Diagram 22. Comparison of the total amount of human toxicity non-carcinogenic potential of the three scenarios with each other

4.2.4 Land use

The land use characterization factor, expressed in m^2 annual crop equivalents per year, refers to the relative species loss due to local land use, which includes the process of land conversion, land occupation and land relaxation (see Figure 25). The impact pathway includes the effects of land use on terrestrial species, firstly through land-use change (which affects the original habitat and thus the natural species composition) and secondly through actual land use (which restricts the habitat of some species) (Huijbregts et al., 2016, p. 89-93).

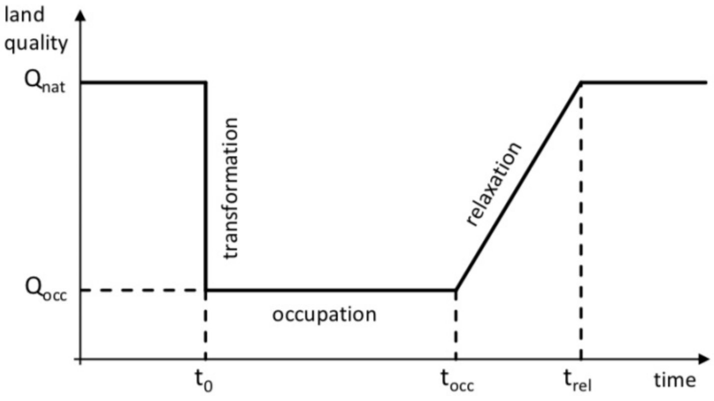

Figure 25. Illustration of the three phases of land use and their impact on land quality. (Huijbregts et al., 2016, p. 90)

As shown in Figure 25, in the process of land use, the land is first prepared for its new function (transformation phase), i.e., by, e.g.: removal of the original vegetation. In the second phase (use phase), the land is used. The potential species loss caused by the two phases is expressed in annual crop equivalents. The occupation phase is followed by the recovery phase, in which the exploited land returns to a “semi-normal” state, always leaving some negative species diversity (Huijbregts et al., 2016, p. 89-93).

Diagram 23 shows the LOP (land occupation potential) of the three scenarios, again divided into the five subcategories: thermal energy, process water, bioethanol, wheat straw and WWT. Diagram 24 shows the three scenarios relative to each other in relation to the total LOP.

Diagram 24 reflects the same trend as before. Scenario 3 (LHW-OS) performs ~23 % better than scenario 1 (OS) with 1.89 annual crop equivalents and ~29 % better than scenario 2 (OS-LHW) 2.65 annual crop equivalents with 2.46 annual crop equivalents. One major reason for this is that less energy is needed in the process due to the concentration effects of the pre-LHW extraction, and therefore less biomass has to be burnt to produce it. Thermal energy accounts for the largest share of land use, as $6.67*10^{-19}$ m^2*yr of land is required to produce 1 MJ. Scenarios 1 to 3 require 44149 MJ, 48840 MJ and 31869 MJ, respectively. In comparison, bioethanol production of 1 kg requires more land, $9.02*10^{-18}$ m^2*yr, but only 0.12 kg of bioethanol is required for scenarios 1 and 2 and 0.9 kg for scenario 3. 1 kg of wheat straw requires $1.62*10^{-18}$ m^2*yr of land to be supplied (GaBi background data). Taking into account the three phases (transformation phase, occupation phase, recovery phase), the values shown in diagram 23 are obtained expressed in annual crop eq per year.

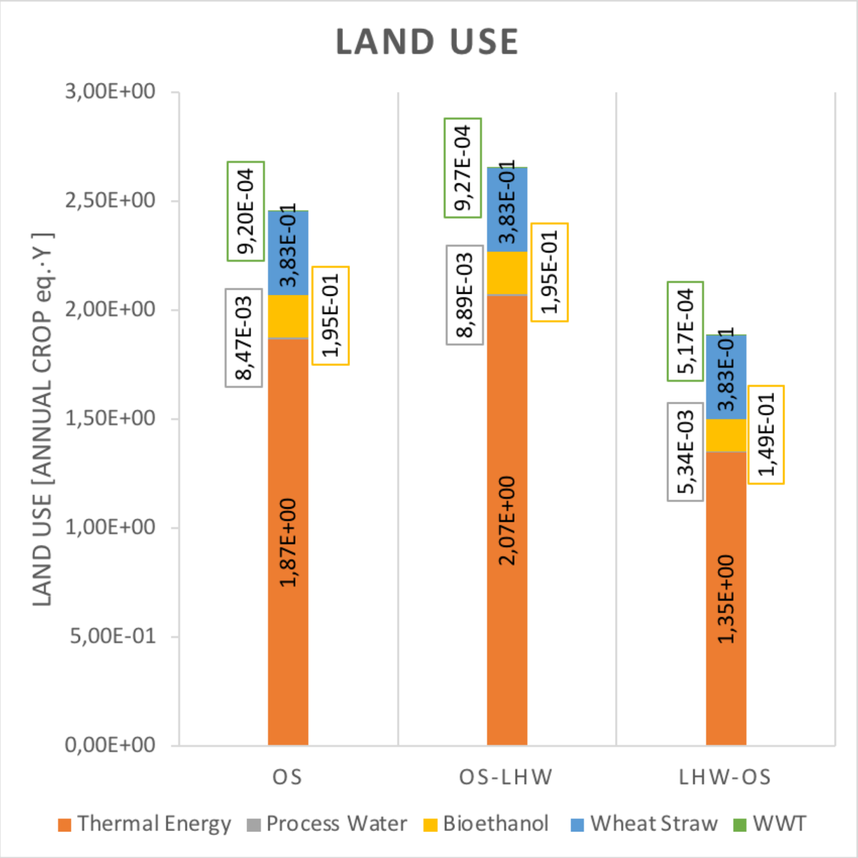

Diagram 23. Land use indicator for the different subcategories.

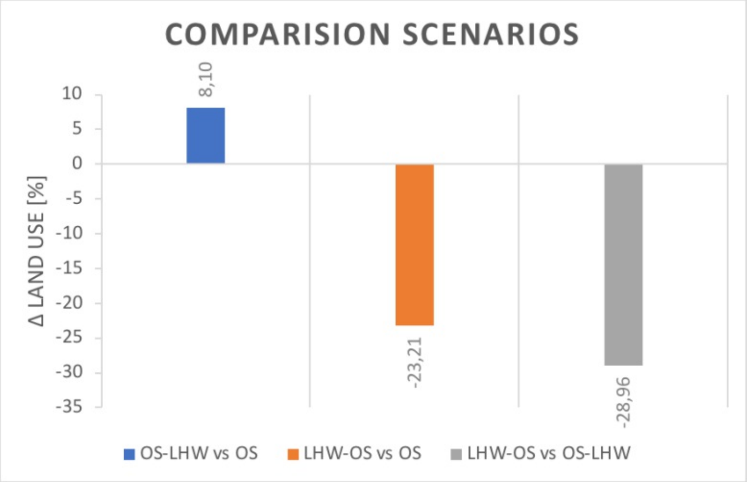

Diagram 24. Comparison of the total amount of land use potential of the three scenarios with each other.

4.3 Summary & Discussion of the Results

In this master thesis, three pre-treatment strategies for the bioconversion of LCB were investigated and compared concerning their technical-ecological performance. In the investigation process, a large amount of data was generated from the process life cycle inventory (through process simulation) and the impact assessment (through LCA). Based on these data and within the framework of the analysis performed, it was shown that the choice of pre-treatment strategy has a significant influence with regard to the sustainable development of LCB biorefineries. The results and findings of the investigations are explained in more detail as part of the answer to the research question.

***RQ:** How do the ecological hot spots, the environmental impact, the composition of the individual fractions and the potential for further processing into valuable products change when:*

- *the solid residues of the OS extraction are further treated with an LHW extraction?*

The results from the life cycle inventory of the two pretreatment scenarios (OS, OS-LHW) are based on a gate-to-gate approach, i.e., all process steps from the first extraction stage to the point where the intermediate products are obtained (CLP, cellulose-rich solid, sugar stream) were considered. Within the scope of this assessment, the mass balance of process water, ethanol and energy demand was determined. The life cycle inventory results show that in scenario 2 (OS-LHW) ~5 % more process water and ~11 % more thermal energy are required than scenario 1 (OS). This extra demand results from the two additional process steps (LHW extraction and LHW solid-phase washing). Apart from that, the process steps and conditions are identical. This is also reflected in the results of the environmental impact assessment according to the ReCiPe method. For the environmental impact assessment, however, a cradle-to-gate approach was taken into account, i.e., the effects of the treatment of the process water, the thermal energy and the cultivation and harvesting of the wheat straw were also taken into account. Due to the additional process step, scenario 2 (OS-LHW) has a ~4 % higher potential than scenario 1 (OS) for climate change (calculated with and without credits for biogenic carbon), freshwater eutrophication and human toxicity; and a ~8 % higher potential for land use.

From the aspect of intermediate product quality, the results of the process simulation show that in scenario 2 (OS-LHW), due to the subsequent LHW extraction, the solids stream is „purer" (less residues such as hemicellulose and lignin) and contains less water (OS: ~536 g, OS-LHW: ~459 g), with almost the same cellulose content (OS: ~303 g, OS-LHW: ~282 g). Thus, the solid from Scenario 2 (OS-LHW) has a higher potential for further applications, as, e.g., in paper or fiber production, where a certain quality is required. The further LHW extraction also results in a liquid stream that is rich in C5 sugars. This additional intermediate stream can be converted into various value products through different secondary refining steps (see Figure 8, Chapter 2.3). The yield and quality of the colloidal lignin particles (CLP) suspension are identical in both scenarios.

As a conclusion, it can be stated that the additional LHW extraction step produces a higher-value cellulose-rich solid and another intermediate product (sugar-rich liquid stream). However, the further treatment of the solid residue of the OS extraction with an LHW extraction increases the auxiliary demand (process water, thermal energy), which increases the environmental impact. From an ecological point of view, the additional extraction step does not pay off. From a technical point of view, an economic evaluation must be carried out to decide whether the additional effort and the resulting additional environmental impact are justified. However, this is not yet possible at this stage of development, as no trustworthy prices can yet be determined for the intermediate products. This is only possible once the path of further secondary refining has been determined.

RQ: *How do the ecological hot spots, the environmental impact, the composition of the individual fractions and the potential for further processing into valuable products change when:*

- *the technological treatment strategy arrangement is changed (OS-LHW / LHW-OS)?*

The life cycle inventory data from the process simulation and the life cycle inventory were again used to answer this question. The life cycle inventory results show a trend opposite to the one observed for the previous research question. Despite the additional process steps (LHW extraction), Scenario 3 (LHW-OS) requires ~37 % less process water and ~28 % lower thermal energy demand compared to Scenario 1 (OS). In addition, ~28 % less virgin ethanol is required for OS extraction. As a result of the lower input requirement, Scenario 3 (LHW-OS) has ~27 % lower contribution to the climate change potential (without biogenic carbon) and ~20 % (with biogenic carbon), ~31 % lower freshwater eutrophication, ~33 % lower human toxicity, and ~23 % lower land use potential than the base case. This trend is due to the concentration effects from the pre-LHW extraction.

From the aspect of intermediate product quality, the results of the process simulation show that in scenario 3 (LHW-OS), due to the pre-LHW extraction, the solids stream is once again significantly "purer". It contains fewer residues such as hemicellulose and lignin and less water (OS: ~536 g, LHW-OS: ~310 g), with almost the same cellulose content (OS: ~303 g, LHW-

OS: ~294 g). Thus, the solid from scenario 3 (LHW-OS) has the highest potential of the three scenarios for further applications. Compared to scenario 2 (OS-LHW), the obtained sugar stream is richer in C5 sugars due to the pre-LHW extraction (OS-LHW: ~67 g, LHW-OS ~95 g). However, the sugar stream also contains dissolved extractives and is significantly more diluted. For further processing in secondary refining steps (e.g., direct fermentation), this should not have a limiting effect. The upstream LHW extraction also makes the lignocellulosic matrix more accessible, which increases the CLP yield by ~8.8 %. However, since the LHW extraction also dissolves a small part of the lignin, ~2 g less CLP is produced in absolute quantities (OS-LHW: 38 g, LHW-OS: 36 g).

As a conclusion of the investigations, it can be stated that compared to the other two scenarios (OS, OS-LHW), the LHW-OS arrangement is the preferable scenario from an ecological point of view due to the lower demand for auxiliary substances (process water, ethanol, thermal energy) and thus have a lower environmental impact of the process (in all considered impact categories). In addition, higher-value intermediate product streams (cellulose phase and sugar stream) are obtained, and a ~8.8 % higher CLP yield is achieved. Therefore, this scenario is also preferable from a technical point of view.

This section of the results should also address the limitations of the LCA. As this is a prospective LCA, not all data for a complete LCA are yet available. For example, in the process step of purification, the production of the membranes, their lifetime and the cleaning requirement could not be taken into account, as the data from the necessary laboratory tests are not available yet. The electrical energy demand for the necessary purification was also not considered due to a lack of data. Furthermore, the electrical energy demand for the process steps (solid-liquid separation, solid-phase purification) and the entire fluid handling (pumps, dynamic head) was not taken into account. However, compared to the extraction steps and solvent recovery, these can be considered as subsidiary consumptions, respectively, they will not change the trend of the results.

Furthermore, the energy consumption of the processes has not yet been optimized due to the early phase of process development. Through systematic optimization using a pinch analysis, the energy consumption of the three pretreatment strategies for the bioconversion of LCB can be minimized. Within the analysis, the process conditions and energy supply systems and heat transfer networks for heat recovery are coordinated with each other so that the minimum thermodynamic energy requirement is obtained in the end. In addition, there is still enormous potential in water management. By intelligently managing the process water, the need for additional fresh process water can be reduced significantly by reusing the water losses (especially from rectification and 2nd membrane). The recycled water can then be reused, especially in the water-intensive processes of precipitation and purification. However, it must be checked in advance to what extent the water quality and the components of the wastewater affect the process performance and whether additional water treatment processes may be necessary.

Since this is a comparative LCA to determine the "most sustainable" pretreatment strategy for the bioconversion of LCB from the three scenarios, a meaningful result can be obtained even without taking these data into account. However, it should be noted that the concentration effects of the pre-LHW extraction in scenario 3 (LHW-OS), taking into account the additional electrical energy demand, would shift the result even more significantly in the direction of scenario 3.

5 CONCLUSIONS

The focus of the EU economy is on sustainable, resource-efficient concepts such as circular-bioeconomy, where biomass (in this specific case, lignocellulosic biomass (LCB)) is converted into a wide range of valuable products in biorefineries. However, the use of biomass does not necessarily implicate a sustainable process. Biomass recalcitrance makes it difficult to separate selectively LCB into the intermediate fraction's cellulose, hemicellulose and lignin. However, to fulfil the CBE concept, selective extraction is a prerequisite to valorize all biomass constituents. A combination of different pretreatments shows potential in this regard, yet when considering the process itself, the addition of another process step increases usually energy- and resource-consumption, which requires a well-designed overall concept. In this context, a systematic and holistic approach for the development of pretreatment strategies for the conversion of lignocellulosic biomass was carried out in this work (see Figure 26). The technical and environmental evaluation allowed the determination of the potential ecological impacts and the identification of the "most sustainable" pretreatment configuration for the intermediate refining of wheat straw into hemicellulosic sugars, lignin and pulp at this stage of research.

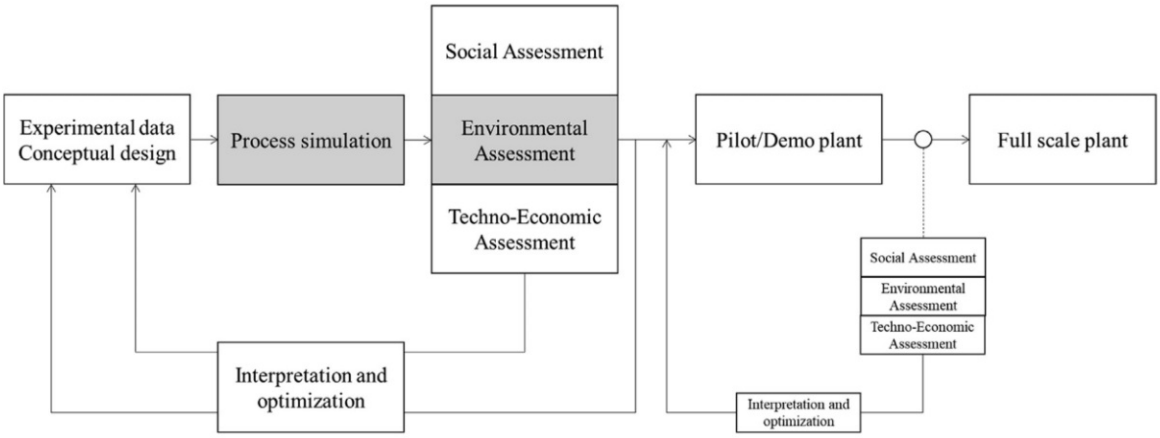

Figure 26. Framework for the design of a new biorefinery concept. (from Bello et al., 2020, p. 2)
The phases explored in this master's thesis are highlighted in grey

A major advantage of a technical and environmental impact assessment at this early stage of process development is that these findings can then be taken into account in the further process design and optimization of the concept (even before the design and construction of a pilot plant), where one has even more degrees of freedom for development. However, a disadvantage of the early phase is the limited data quality resulting from the uncertainty of the laboratory tests and possible changes during upscaling. It is also important to note that the findings obtained in this work were limited to a cradle-to-gate approach, and under this context, it served to answer the question which pretreatment configuration has better performance. Nevertheless, the observed trends and hot spots may change when secondary refinement of the produced intermediates to final products with respective end-of-life is carried out.

Nevertheless, the findings of the technical assessment and the environmental assessment results give a clear recommendation for a certain process strategy that is the development of the LHW-OS scenario.

The technical assessment showed that the pretreatment strategy LHW-OS requires less process water (37-40%) and less thermal energy (28-35%) compared to the other two pretreatment strategies (OS & OS-LHW). In addition, ~28% less fresh ethanol is required. LHW-OS scenario showed also a better environmental performance, with ~27 % lower climate change potential (without biogenic carbon), ~20 % lower climate change potential (with biogenic carbon), ~31 % lower freshwater eutrophication and ~33 % lower human toxicity, and ~23 % lower land use potential, when compared to the other studied configuration (OS-LHW).

Changing the process from a standalone process (OS) to an intermediate biorefinery (LHW-OS) producing three different block platforms showed both better technical and environmental performance, i.e. more efficient feedstock use with higher quality of intermediate products and lower environmental impact for the studied impact categories. In this case, another process step leads to higher efficiency with lower environmental impact.

Even so, thermal energy demand and process water treatment were identified as hotspots of environmental emissions. For the climate change impact category, thermal energy demand is responsible for 28 % of equivalent CO_2 emissions (excluding biogenic carbon), and process water treatment is responsible for 23 % of equivalent CO_2 emissions (excluding biogenic carbon). Thermal energy generation is also primarily responsible (72 %) for land-use change since biomass is used, 30 % of freshwater acidification, and 34 % human toxicity, non-cancer. In terms of freshwater eutrophication, leakage of non-recycled substances (e.g. ethanol in solvent recovery) into freshwater during wastewater treatment was identified as a hotspot (responsible for 37 % of this impact category).

From these points of view, it becomes clear that not only a closed solvent loop, but also a closed process water loop is a key issue to be addressed in further design steps of this proposed biorefinery. Systematic optimization using pinch analysis can significantly reduce both the process water demand and energy consumption related to thermal energy demand.

As a final remark, lifecycle assessment is a powerful tool to evaluate the environmental performance of biorefineries and processes in general from the design stage. However, it should be emphasized the importance of evaluating multiple impact indicators, not only those related to climate change and global warming potential, but having a wider perspective covering different possible impacts of a process. This provides a more holistic insight on the performance and hotspots of the evaluated system.

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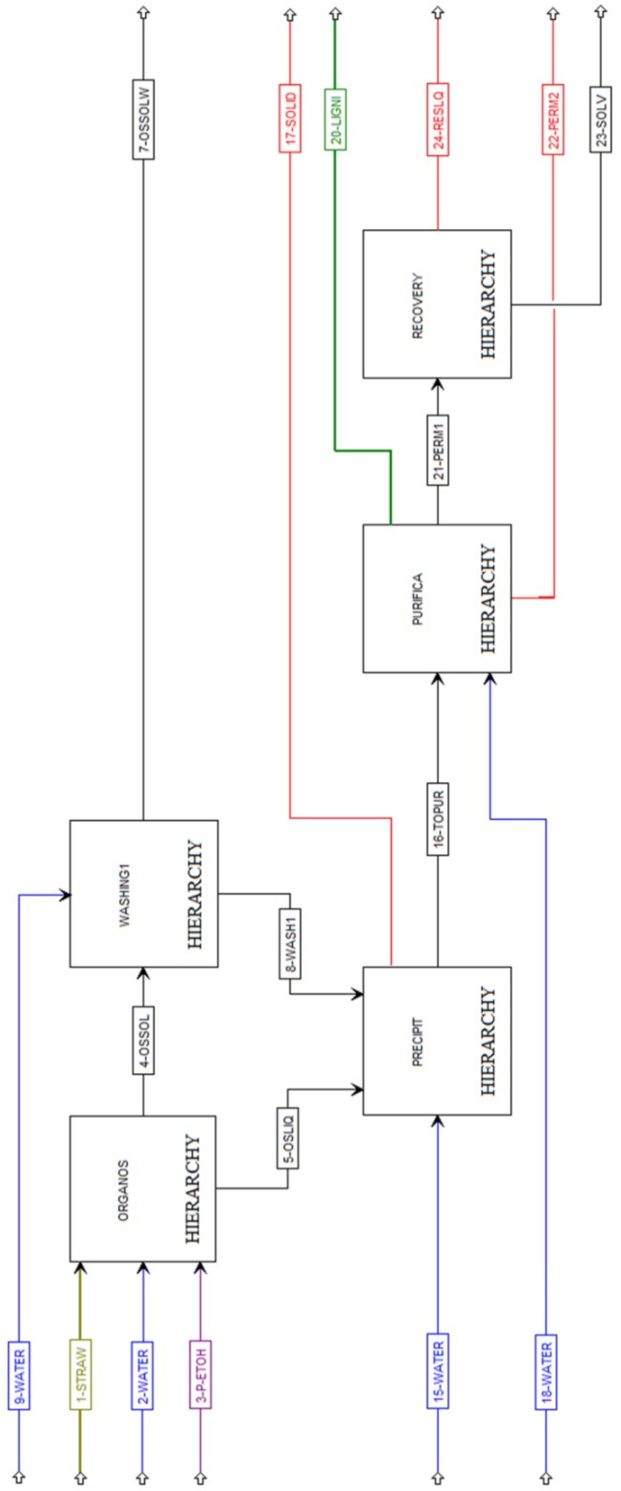
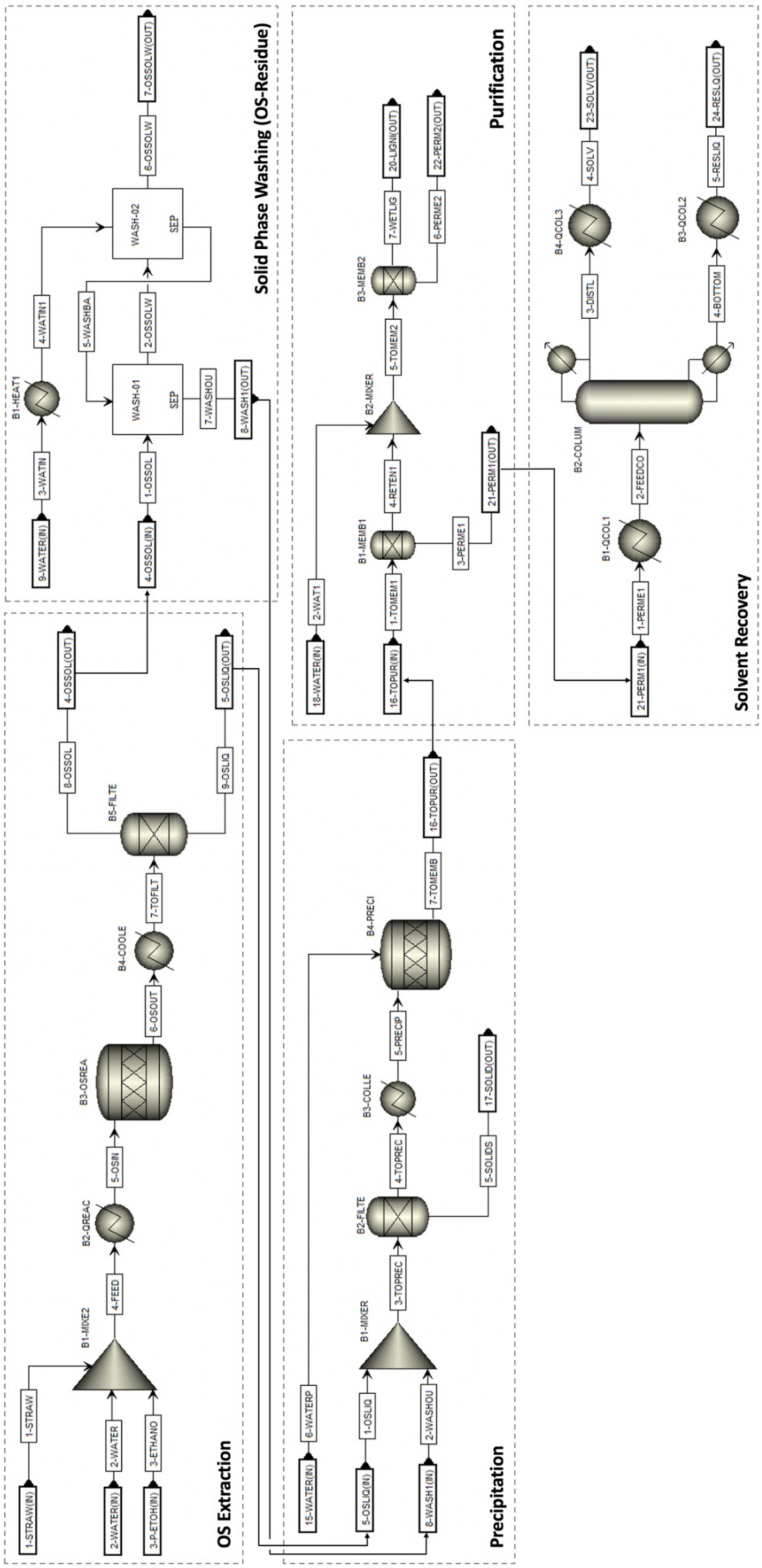
7 APPENDIX

7.1 Aspen Plus® Process Simulation Models

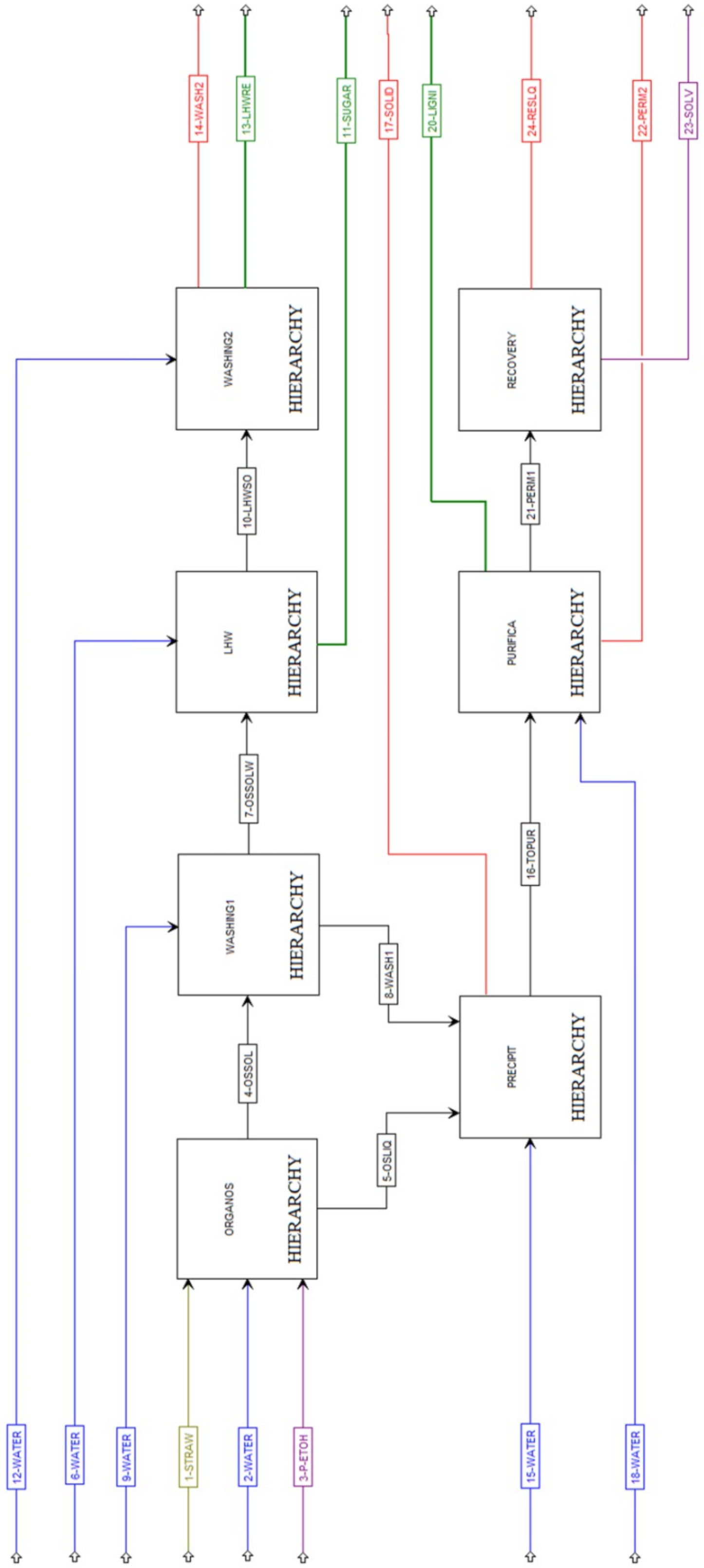
7.1.1 Scenario 1: OS (Base Case Scenario)

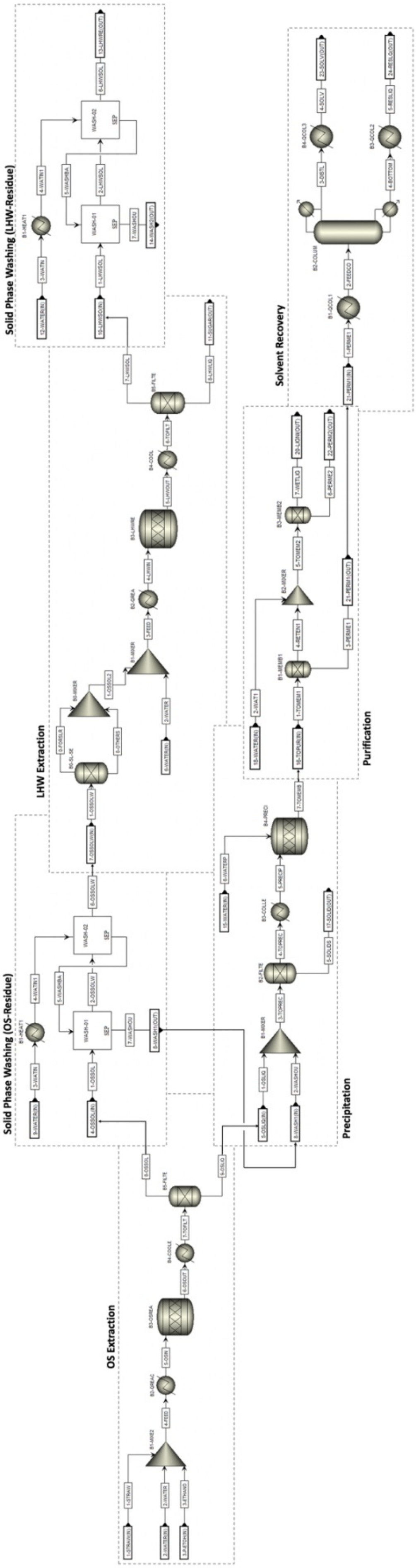


APPENDIX

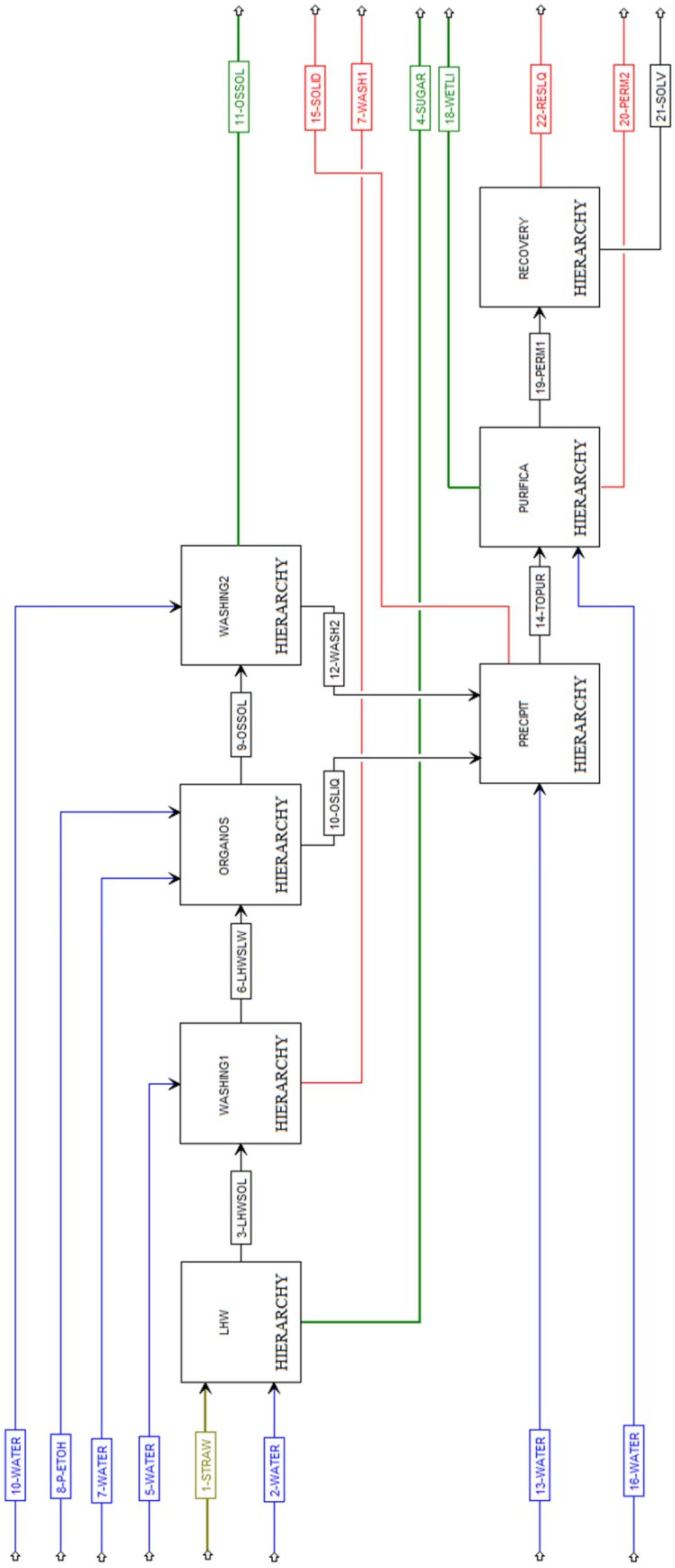

OS Extraction
1-STRAW(IN)
1-STRAW
2-WATER(IN)
2-WATER
3-P-ETOH(IN)
3-ETHANO
B1-MIXE2
4-FEED
B2-QREAC
5-OSIN
B3-OSREA
6-OSOUT
B4-COOLE
7-TOFILT
B5-FILTE
8-OSSOL
4-OSSOL(OUT)
9-OSLIQ
5-OSLIQ(OUT)
Solid Phase Washing (OS-Residue)
4-OSSOL(IN)
1-OSSOL
WASH-01
SEP
9-WATER(IN)
3-WATIN
B1-HEAT1
4-WATIN1
5-WASHBA
2-OSSOLW
WASH-02
SEP
6-OSSOLW
7-OSSOLW(OUT)
7-WASHOU
8-WASH1(OUT)
Precipitation
15-WATER(IN)
6-WATERP
5-OSLIQ(IN)
1-OSLIQ
8-WASH1(IN)
2-WASHOU
B1-MIXER
3-TOPREC
B2-FILTE
5-SOLIDS
17-SOLID(OUT)
4-TOPREC
B3-COLLE
5-PRECIP
B4-PRECI
7-TOMEMB
16-TOPUR(OUT)
Purification
18-WATER(IN)
2-WAT1
16-TOPUR(IN)
1-TOMEM1
B1-MEMB1
3-PERME1
21-PERM1(OUT)
4-RETEN1
B2-MIXER
5-TOMEM2
B3-MEMB2
7-WETLIG
20-LIGN(OUT)
6-PERME2
22-PERM2(OUT)
Solvent Recovery
21-PERM1(IN)
1-PERME1
B1-QCOL1
2-FEEDCO
B2-COLUM
3-DISTL
B4-QCOL3
4-SOLV
23-SOLV(OUT)
4-BOTTOM
B3-QCOL2
5-RESLIQ
24-RESLQ(OUT)

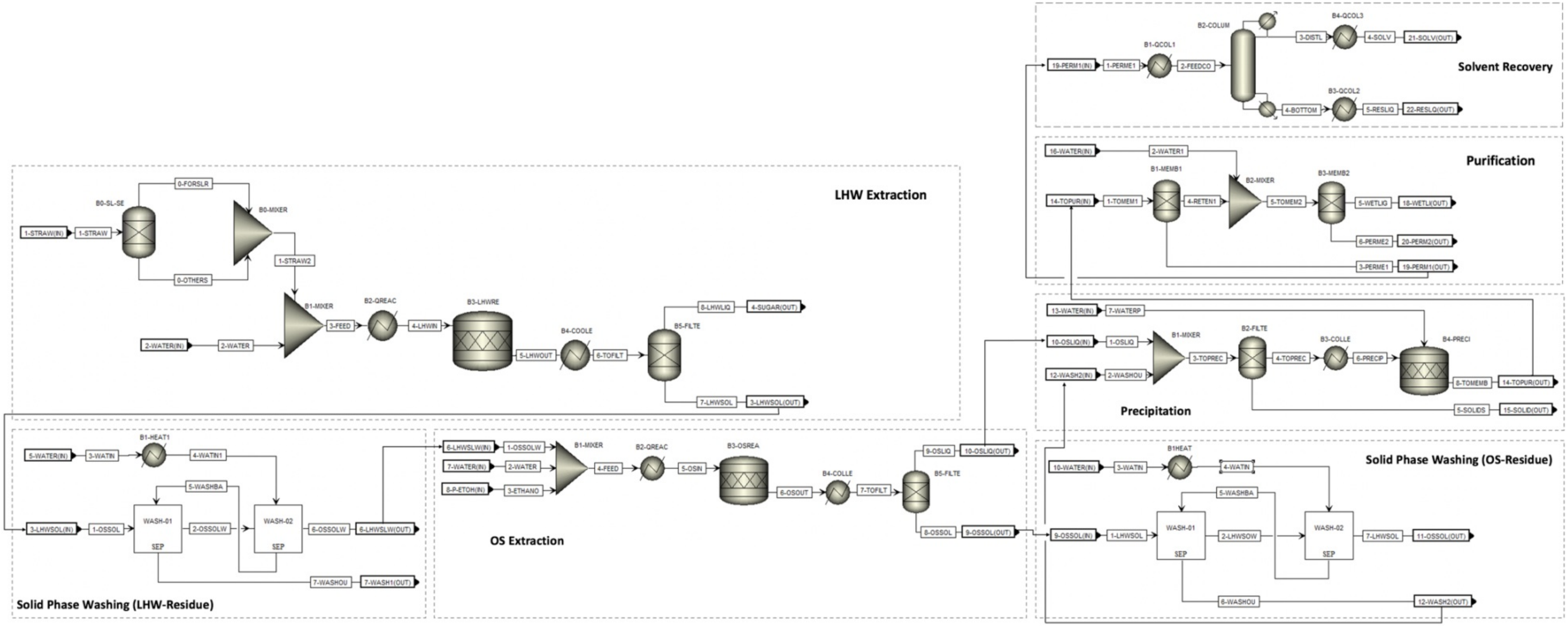
7.1.2 Scenario 2: OS-LHW



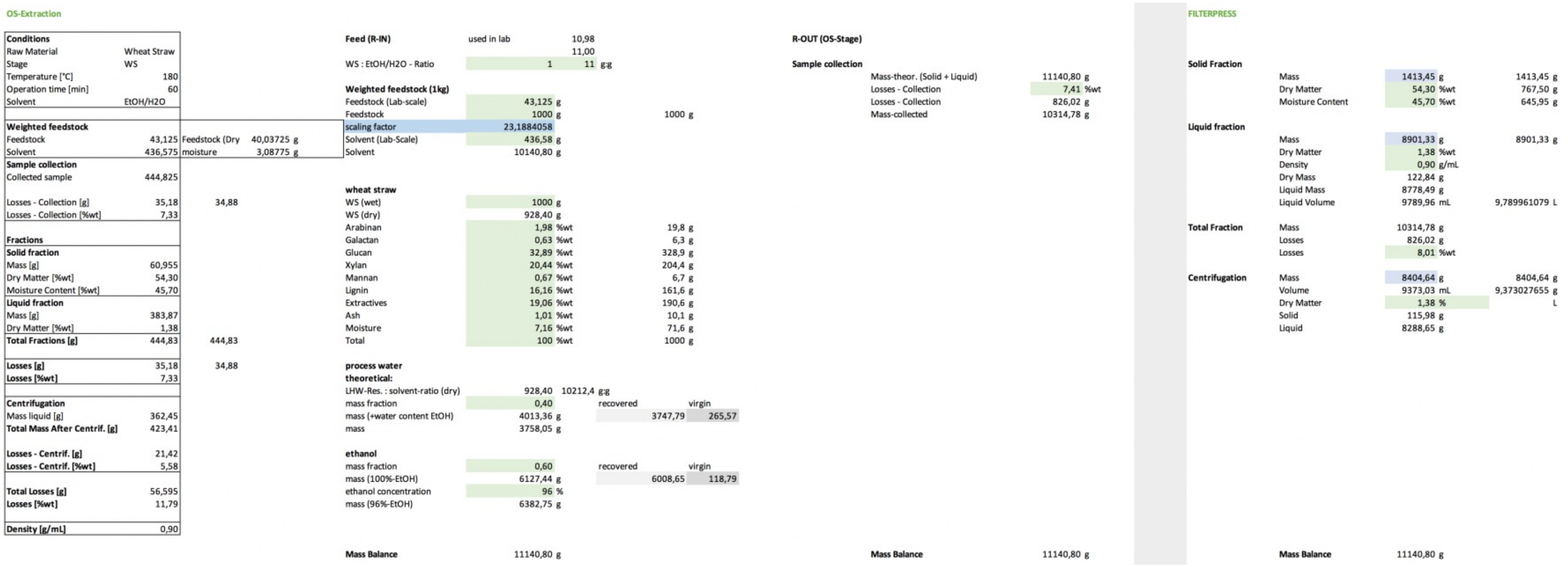

Solid Phase Washing (LHW-Residue)
LHW Extraction
Solvent Recovery
Purification
Solid Phase Washing (OS-Residue)
Precipitation
OS Extraction

7.1.3 Scenario 3: LHW-OS




Solvent Recovery
19-PERM1(IN)
1-PERME1
B1-QCOL1
2-FEEDCO
B2-COLUM
3-DISTL
B4-QCOL3
4-SOLV
21-SOLV(OUT)
4-BOTTOM
B3-QCOL2
5-RESLIQ
22-RESLQ(OUT)
Purification
16-WATER(IN)
2-WATER1
14-TOPUR(IN)
1-TOMEM1
B1-MEMB1
4-RETEN1
B2-MIXER
5-TOMEM2
B3-MEMB2
5-WETLIQ
18-WETLI(OUT)
6-PERME2
20-PERM2(OUT)
3-PERME1
19-PERM1(OUT)
LHW Extraction
1-STRAW(IN)
1-STRAW
B0-SL-SE
0-FORSLR
0-OTHERS
B0-MIXER
1-STRAW2
B1-MIXER
2-WATER(IN)
2-WATER
3-FEED
B2-QREAC
4-LHWIN
B3-LHWRE
5-LHWOUT
B4-COOLE
6-TOFILT
B5-FILTE
8-LHWLIQ
4-SUGAR(OUT)
7-LHWSOL
3-LHWSOL(OUT)
Precipitation
13-WATER(IN)
7-WATERP
10-OSLIQ(IN)
1-OSLIQ
12-WASH2(IN)
2-WASHOU
B1-MIXER
3-TOPREC
B2-FILTE
4-TOPREC
B3-COLLE
6-PRECIP
B4-PRECI
8-TOMEMB
14-TOPUR(OUT)
5-SOLIDS
15-SOLID(OUT)
Solid Phase Washing (LHW-Residue)
5-WATER(IN)
3-WATIN
B1-HEAT1
4-WATIN1
5-WASHBA
3-LHWSOL(IN)
1-OSSOL
WASH-01
SEP
2-OSSOLW
WASH-02
SEP
6-OSSOLW
6-LHWSLW(OUT)
7-WASHOU
7-WASH1(OUT)
OS Extraction
6-LHWSLW(IN)
1-OSSOLW
7-WATER(IN)
2-WATER
8-P-ETOH(IN)
3-ETHANO
B1-MIXER
4-FEED
B2-QREAC
5-OSIN
B3-OSREA
6-OSOUT
B4-COLLE
7-TOFILT
B5-FILTE
9-OSLIQ
10-OSLIQ(OUT)
8-OSSOL
9-OSSOL(OUT)
Solid Phase Washing (OS-Residue)
10-WATER(IN)
3-WATIN
B1HEAT
4-WATIN
5-WASHBA
9-OSSOL(IN)
1-LHWSOL
WASH-01
SEP
2-LHWSOW
WASH-02
SEP
7-LHWSOL
11-OSSOL(OUT)
6-WASHOU
12-WASH2(OUT)

7.2 MS-Excel Model



OS-Extraction

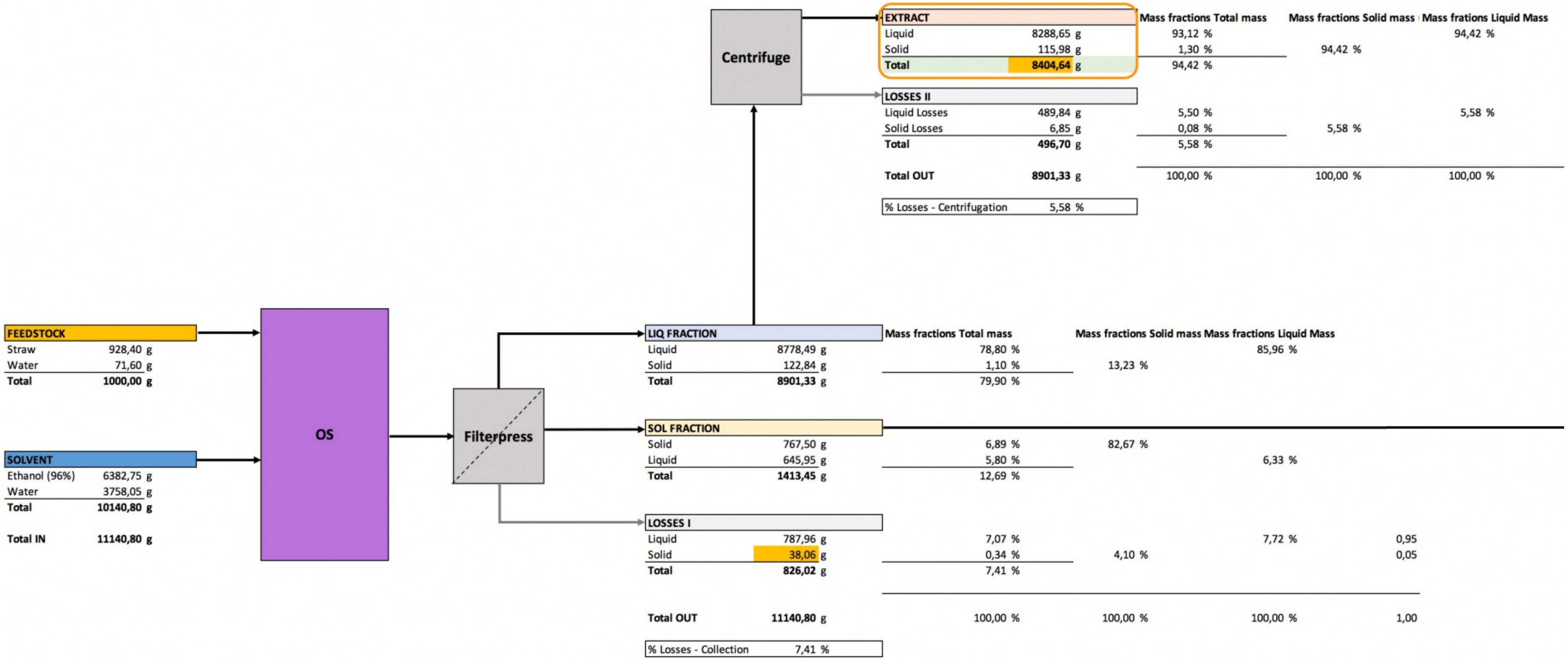
Conditions				
Raw Material	Wheat Straw			
Stage	WS			
Temperature [°C]	180			
Operation time [min]	60			
Solvent	EtOH/H2O			
Weighted feedstock				
Feedstock	43,125	Feedstock (Dry	40,03725	g
Solvent	436,575	moisture	3,08775	g
Sample collection				
Collected sample	444,825			
Losses - Collection [g]	35,18	34,88		
Losses - Collection [%wt]	7,33			
Fractions				
Solid fraction				
Mass [g]	60,955			
Dry Matter [%wt]	54,30			
Moisture Content [%wt]	45,70			
Liquid fraction				
Mass [g]	383,87			
Dry Matter [%wt]	1,38			
Total Fractions [g]	444,83	444,83		
Losses [g]	35,18	34,88		
Losses [%wt]	7,33			
Centrifugation				
Mass liquid [g]	362,45			
Total Mass After Centrif. [g]	423,41			
Losses - Centrif. [g]	21,42			
Losses - Centrif. [%wt]	5,58			
Total Losses [g]	56,595			
Losses [%wt]	11,79			
Density [g/mL]	0,90			

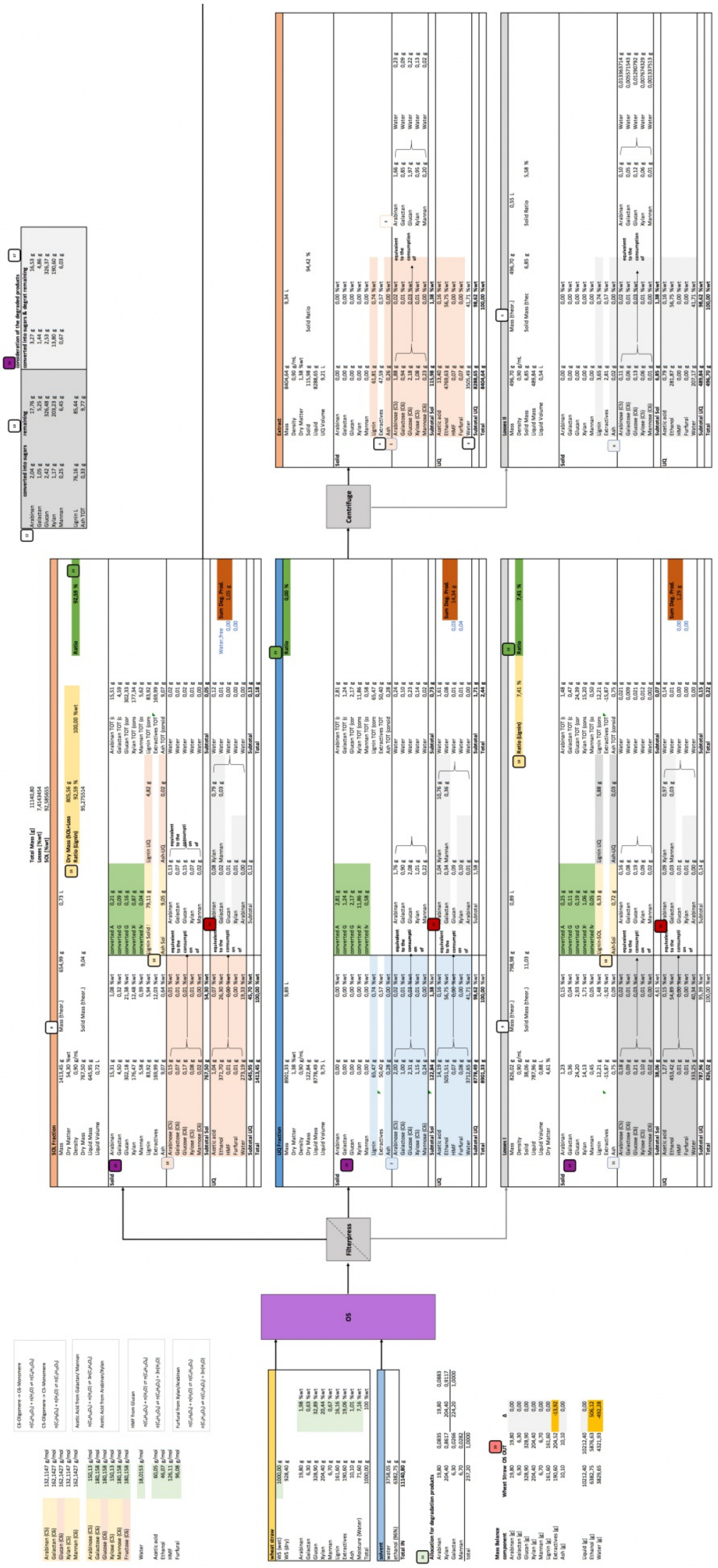
Feed (R-IN)	used in lab	10,98			
		11,00			
WS : EtOH/H2O - Ratio	1	11 g:g			
Weighted feedstock (1kg)					
Feedstock (Lab-scale)	43,125	g			
Feedstock	1000	g		1000 g	
scaling factor	23,1884058				
Solvent (Lab-Scale)	436,58	g			
Solvent	10140,80	g			
wheat straw					
WS (wet)	1000	g			
WS (dry)	928,40	g			
Arabinan	1,98	%wt		19,8 g	
Galactan	0,63	%wt		6,3 g	
Glucan	32,89	%wt		328,9 g	
Xylan	20,44	%wt		204,4 g	
Mannan	0,67	%wt		6,7 g	
Lignin	16,16	%wt		161,6 g	
Extractives	19,06	%wt		190,6 g	
Ash	1,01	%wt		10,1 g	
Moisture	7,16	%wt		71,6 g	
Total	100	%wt		1000 g	
process water					
theoretical:					
LHW-Res. : solvent-ratio (dry)	928,40	10212,4 g:g			
mass fraction	0,40		recovered		virgin
mass (+water content EtOH)	4013,36	g		3747,79	265,57
mass	3758,05	g			
ethanol					
mass fraction	0,60		recovered		virgin
mass (100%-EtOH)	6127,44	g		6008,65	118,79
ethanol concentration	96	%			
mass (96%-EtOH)	6382,75	g			
Mass Balance	11140,80	g			

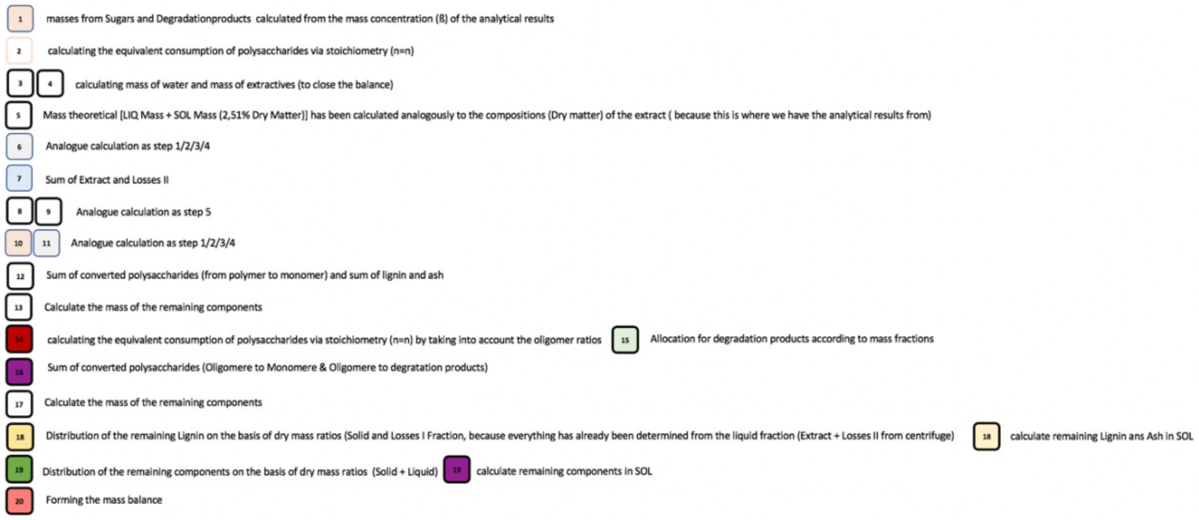
R-OUT (OS-Stage)			
Sample collection			
	Mass-theor. (Solid + Liquid)	11140,80	g
	Losses - Collection	7,41	%wt
	Losses - Collection	826,02	g
	Mass-collected	10314,78	g
	Mass Balance	11140,80	g

FILTERPRESS

Solid Fraction	Mass	1413,45	g	1413,45	g
	Dry Matter	54,30	%wt	767,50	g
	Moisture Content	45,70	%wt	645,95	g
Liquid fraction	Mass	8901,33	g	8901,33	g
	Dry Matter	1,38	%wt		
	Density	0,90	g/mL		
	Dry Mass	122,84	g		
	Liquid Mass	8778,49	g		
	Liquid Volume	9789,96	mL	9,789961079	L
Total Fraction	Mass	10314,78	g		
	Losses	826,02	g		
	Losses	8,01	%wt		
Centrifugation	Mass	8404,64	g	8404,64	g
	Volume	9373,03	mL	9,373027655	g
	Dry Matter	1,38	%		L
	Solid	115,98	g		
	Liquid	8288,65	g		
	Mass Balance	11140,80	g		


FEEDSTOCK
Straw 928,40 g
Water 71,60 g
Total 1000,00 g
SOLVENT
Ethanol (96%) 6382,75 g
Water 3758,05 g
Total 10140,80 g
Total IN 11140,80 g
OS
Filterpress
Centrifuge
EXTRACT
Liquid 8288,65 g
Solid 115,98 g
Total 8404,64 g
Mass fractions Total mass
93,12 %
1,30 %
94,42 %
Mass fractions Solid mass
94,42 %
Mass frations Liquid Mass
94,42 %
LOSSES II
Liquid Losses 489,84 g
Solid Losses 6,85 g
Total 496,70 g
5,50 %
0,08 %
5,58 %
5,58 %
5,58 %
Total OUT 8901,33 g
100,00 %
100,00 %
100,00 %
% Losses - Centrifugation 5,58 %
LIQ FRACTION
Liquid 8778,49 g
Solid 122,84 g
Total 8901,33 g
Mass fractions Total mass
78,80 %
1,10 %
79,90 %
Mass fractions Solid mass
13,23 %
Mass fractions Liquid Mass
85,96 %
SOL FRACTION
Solid 767,50 g
Liquid 645,95 g
Total 1413,45 g
6,89 %
5,80 %
12,69 %
82,67 %
6,33 %
LOSSES I
Liquid 787,96 g
Solid 38,06 g
Total 826,02 g
7,07 %
0,34 %
7,41 %
4,10 %
7,72 %
0,95
0,05
Total OUT 11140,80 g
100,00 %
100,00 %
100,00 %
1,00
% Losses - Collection 7,41 %





1 masses from Sugars and Degradationproducts calculated from the mass concentration (ß) of the analytical results

2 calculating the equivalent consumption of polysaccharides via stoichiometry (n=n)

3 4 calculating mass of water and mass of extractives (to close the balance)

5 Mass theoretical [LIQ Mass + SOL Mass (2,51% Dry Matter)] has been calculated analogously to the compositions (Dry matter) of the extract (because this is where we have the analytical results from)

6 Analogue calculation as step 1/2/3/4

7 Sum of Extract and Losses II

8 9 Analogue calculation as step 5

10 11 Analogue calculation as step 1/2/3/4

12 Sum of converted polysaccharides (from polymer to monomer) and sum of lignin and ash

13 Calculate the mass of the remaining components

14 calculating the equivalent consumption of polysaccharides via stoichiometry (n=n) by taking into account the oligomer ratios 15 Allocation for degradation products according to mass fractions

16 Sum of converted polysaccharides (Oligomere to Monomere & Oligomere to degratation products)

17 Calculate the mass of the remaining components

18 Distribution of the remaining Lignin on the basis of dry mass ratios (Solid and Losses I Fraction, because everything has already been determined from the liquid fraction (Extract + Losses II from centrifuge) 18 calculate remaining Lignin ans Ash in SOL

19 Distribution of the remaining components on the basis of dry mass ratios (Solid + Liquid) 19 calculate remaining components in SOL

20 Forming the mass balance

7.3 Process Simulation Data for Scenario 3

Chemical reactions and fractional conversions during LHW-extraction

Reaction	Fractional conversion of component	Fractional conversion
$Cellulose + H_2O \rightarrow Glucose$	Cellulose	$3{,}616 * 10^{-2}$
$Cellulose \rightarrow HMF + 2\ H_2O$	Cellulose	$1{,}437 * 10^{-3}$
$Hemicellulose(C5) + H_2O \rightarrow Arabinose$	Hemicellulose (C5)	$3{,}646 * 10^{-2}$
$Hemicellulose(C5) + H_2O \rightarrow Xylose$	Hemicellulose (C5)	$3{,}640 * 10^{-1}$
$2\ Hemicellulose(C5) + 2\ H_2O \rightarrow 5\ Acetic\ Acid$	Hemicellulose (C5)	$6{,}961 * 10^{-2}$
$Hemicellulose(C5) \rightarrow Furfural + 2\ H_2O$	Hemicellulose (C5)	$4{,}663 * 10^{-2}$
$Hemicellulose(C6) + H_2O \rightarrow Galactose$	Hemicellulose (C6)	$4{,}135 * 10^{-1}$
$Hemicellulose(C6) + H_2O \rightarrow Mannose$	Hemicellulose (C6)	$2{,}178 * 10^{-1}$
$Hemicellulose(C6) + H_2O \rightarrow 3\ Acetic\ Acid$	Hemicellulose (C6)	$7{,}120 * 10^{-2}$
$Lignin_{(Solid)} \rightarrow Lignin_{(Liquid)}$	Lignin$_{(Solid)}$	$2{,}989 * 10^{-1}$
$Ash_{(Solid)} \rightarrow Ash_{(Liquid)}$	Ash$_{(Solid)}$	$6{,}926 * 10^{-1}$

Chemical reactions and fractional conversions during OS-extraction

Reaction	Fractional conversion of component	Fractional conversion
$Cellulose + H_2O \rightarrow Glucose$	Cellulose	$1{,}664 * 10^{-3}$
$Cellulose \rightarrow HMF + 2\ H_2O$	Cellulose	$2{,}414 * 10^{-4}$
$Hemicellulose(C5) + H_2O \rightarrow Arabinose$	Hemicellulose (C5)	$6{,}121 * 10^{-3}$

$Hemicellulose(C5) + H_2O \rightarrow Xylose$	Hemicellulose (C5)	$6{,}035 * 10^{-2}$
$2\ Hemicellulose(C5) + 2\ H_2O \rightarrow 5\ Acetic\ Acid$	Hemicellulose (C5)	$4{,}404 * 10^{-3}$
$Hemicellulose(C5) \rightarrow Furfural + 2\ H_2O$	Hemicellulose (C5)	$5{,}252 * 10^{-3}$
$Hemicellulose(C6) + H_2O \rightarrow Galactose$	Hemicellulose (C6)	$8{,}475 * 10^{-2}$
$Hemicellulose(C6) + H_2O \rightarrow Mannose$	Hemicellulose (C6)	$5{,}128 * 10^{-2}$
$Hemicellulose(C6) + H_2O \rightarrow 3\ Acetic\ Acid$	Hemicellulose (C6)	$4{,}505 * 10^{-3}$
$Lignin_{(Solid)} \rightarrow Lignin_{(Liquid)}$	$\mathrm{Lignin}_{(Solid)}$	$6{,}481 * 10^{-1}$
$Ash_{(Solid)} \rightarrow Ash_{(Liquid)}$	$\mathrm{Ash}_{(Solid)}$	$1{,}842 * 10^{-1}$

Splitting Factors of solid-liquid filtration after LHW-extraction

Outlet Stream: Solid Stream					
Substream: MIXED					
Component	Split Fraction	Component	Split Fraction	Component	Split Fraction
$\mathrm{Lignin}_{\mathrm{Liquid}}$	0,0704096	Glucose	0,0704096	Xylose	0,0704096
Arabinose	0,0704096	Mannose	0,0704096	Galactose	0,0704096
Acetic Acid	0,0704096	HMF	0,0704096	Furfural	0,0704096
Extractives	0,417412	Water	0,0703445	Ethanol	-
$\mathrm{Ash}_{\mathrm{Liquid}}$	0,0704096				
Substream: CISOLID					
Component	Split Fraction	Component	Split Fraction	Component	Split Fraction
Cellulose	0,97057	HEM-C5	0,97057	HEM-C6	0,97057
$\mathrm{Lignin}_{\mathrm{Solid}}$	0,97057	$\mathrm{Ash}_{\mathrm{Solid}}$	0,97057		

Note. Applied stream classes for the simulated sub streams: conventional inert solids (CISOLID) are conventional solids that appear in the solid phase but do not participate in phase equilibrium; in the MIXED sub-stream, all components participate in the phase equilibrium when flash calculations are performed.

Splitting Factors of solid-liquid filtration after OS-extraction

Outlet Stream: Solid Stream					
Substream: MIXED					
Component	Split Fraction	Component	Split Fraction	Component	Split Fraction
$\mathrm{Lignin}_{\mathrm{Liquid}}$	0,0535992	Glucose	0,0535992	Xylose	0,0535992
Arabinose	0,0535992	Mannose	0,0535992	Galactose	0,0535992
Acetic Acid	0,0535992	HMF	0,0535992	Furfural	0,0535992
Extractives	0,827577	Water	0,0535992	Ethanol	0,0535992
$\mathrm{Ash}_{\mathrm{Liquid}}$	0,0535992				
Substream: CISOLID					

Component	Split Fraction	Component	Split Fraction	Component	Split Fraction
Cellulose	0,959601	HEM-C5	0,959601	HEM-C6	0,959601
Lignin$_{Solid}$	0,959601	Ash$_{Solid}$	0,959601		

Note. Applied stream classes for the simulated sub streams: conventional inert solids (CISOLID) are conventional solids that appear in the solid phase but do not participate in phase equilibrium; in the MIXED sub-stream, all components participate in the phase equilibrium when flash calculations are performed.

7.4 Life Cycle Inventories

7.4.1 Scenario 1: OS (Base Case Scenario)

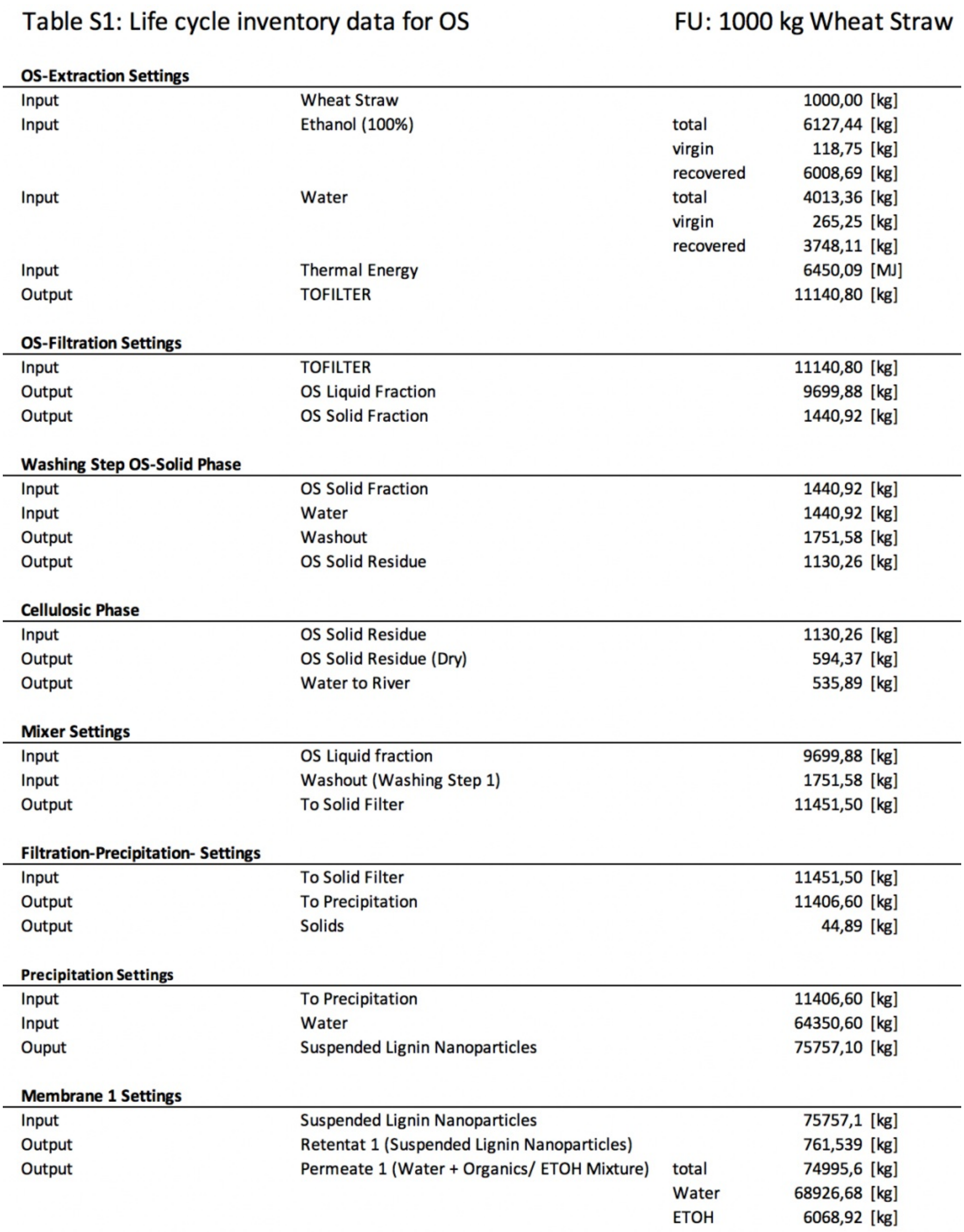


Table S1: Life cycle inventory data for OS FU: 1000 kg Wheat Straw

OS-Extraction Settings				
Input	Wheat Straw		1000,00	[kg]
Input	Ethanol (100%)	total	6127,44	[kg]
		virgin	118,75	[kg]
		recovered	6008,69	[kg]
Input	Water	total	4013,36	[kg]
		virgin	265,25	[kg]
		recovered	3748,11	[kg]
Input	Thermal Energy		6450,09	[MJ]
Output	TOFILTER		11140,80	[kg]
OS-Filtration Settings				
Input	TOFILTER		11140,80	[kg]
Output	OS Liquid Fraction		9699,88	[kg]
Output	OS Solid Fraction		1440,92	[kg]
Washing Step OS-Solid Phase				
Input	OS Solid Fraction		1440,92	[kg]
Input	Water		1440,92	[kg]
Output	Washout		1751,58	[kg]
Output	OS Solid Residue		1130,26	[kg]
Cellulosic Phase				
Input	OS Solid Residue		1130,26	[kg]
Output	OS Solid Residue (Dry)		594,37	[kg]
Output	Water to River		535,89	[kg]
Mixer Settings				
Input	OS Liquid fraction		9699,88	[kg]
Input	Washout (Washing Step 1)		1751,58	[kg]
Output	To Solid Filter		11451,50	[kg]
Filtration-Precipitation- Settings				
Input	To Solid Filter		11451,50	[kg]
Output	To Precipitation		11406,60	[kg]
Output	Solids		44,89	[kg]
Precipitation Settings				
Input	To Precipitation		11406,60	[kg]
Input	Water		64350,60	[kg]
Ouput	Suspended Lignin Nanoparticles		75757,10	[kg]
Membrane 1 Settings				
Input	Suspended Lignin Nanoparticles		75757,1	[kg]
Output	Retentat 1 (Suspended Lignin Nanoparticles)		761,539	[kg]
Output	Permeate 1 (Water + Organics/ ETOH Mixture)	total	74995,6	[kg]
		Water	68926,68	[kg]
		ETOH	6068,92	[kg]

Mixer Settings

Input	Suspended Lignin Nanoparticles		761,54	[kg]
Input	Water		76410,06	[kg]
Output	Suspended Lignin Nanoparticles		77171,60	[kg]

Membrane 2 Settings

Input	Suspended Lignin Nanoparticles		77171,60	[kg]
Output	**Retentat 2 (Suspended Lignin Nanoparticles)**		**756,54**	**[kg]**
Output	Permeate 2 (Water + Organics/ ETOH Mixture)	total	76415,10	[kg]
		Water	76357,13	[kg]
		ETOH	57,97	[kg]

WetLignin Process Settings

Input	Retentat 2 (Suspended Lignin Nanoparticles)		756,54	[kg]
Output	ETOH		0,54	[kg]
Output	Water to River		717,54	[kg]

Feed Preheating Settings

Input	Liquid from Membrane 1	total	74995,6	[kg]
		ETOH	6068,92	[kg]
		Water	68926,68	[kg]
Input	Thermal Energy Preheating		10659,6	[MJ]
Output	Preheated Liquid		74995,6	[kg]

Distillation Column Settings

Input	Preheated Liquid	total	74995,60	[kg]
		ETOH	6068,92	[kg]
		Water	68926,68	[kg]
Input	Thermal Energy for Destillation		27039,10	[MJ]
Output	Destillation Residue		65238,80	[kg]
Output	Recovered Liquid	total	9756,80	[kg]
		ETOH	6008,69	[kg]
		Water	3748,11	[kg]

Liquid Residue Rectification Settings

Input	Destillation Residue		65238,80	[kg]
Output	ETOH		60,22	[kg]
Output	Water to River		65178,58	[kg]

7.4.2 Scenario 2: OS-LHW

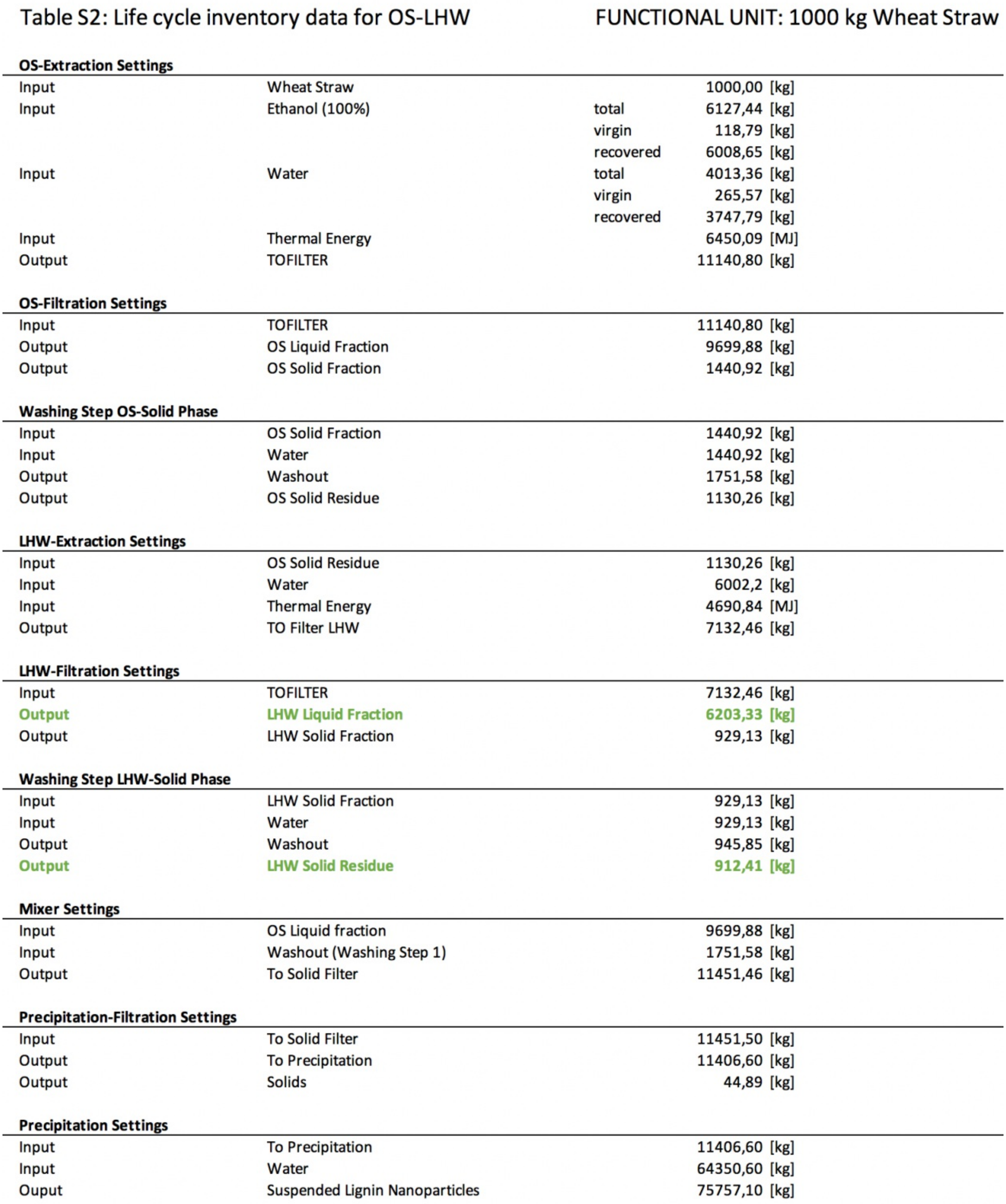


Table S2: Life cycle inventory data for OS-LHW

FUNCTIONAL UNIT: 1000 kg Wheat Straw

OS-Extraction Settings				
Input	Wheat Straw		1000,00	[kg]
Input	Ethanol (100%)	total	6127,44	[kg]
		virgin	118,79	[kg]
		recovered	6008,65	[kg]
Input	Water	total	4013,36	[kg]
		virgin	265,57	[kg]
		recovered	3747,79	[kg]
Input	Thermal Energy		6450,09	[MJ]
Output	TOFILTER		11140,80	[kg]
OS-Filtration Settings				
Input	TOFILTER		11140,80	[kg]
Output	OS Liquid Fraction		9699,88	[kg]
Output	OS Solid Fraction		1440,92	[kg]
Washing Step OS-Solid Phase				
Input	OS Solid Fraction		1440,92	[kg]
Input	Water		1440,92	[kg]
Output	Washout		1751,58	[kg]
Output	OS Solid Residue		1130,26	[kg]
LHW-Extraction Settings				
Input	OS Solid Residue		1130,26	[kg]
Input	Water		6002,2	[kg]
Input	Thermal Energy		4690,84	[MJ]
Output	TO Filter LHW		7132,46	[kg]
LHW-Filtration Settings				
Input	TOFILTER		7132,46	[kg]
Output	LHW Liquid Fraction		6203,33	[kg]
Output	LHW Solid Fraction		929,13	[kg]
Washing Step LHW-Solid Phase				
Input	LHW Solid Fraction		929,13	[kg]
Input	Water		929,13	[kg]
Output	Washout		945,85	[kg]
Output	LHW Solid Residue		912,41	[kg]
Mixer Settings				
Input	OS Liquid fraction		9699,88	[kg]
Input	Washout (Washing Step 1)		1751,58	[kg]
Output	To Solid Filter		11451,46	[kg]
Precipitation-Filtration Settings				
Input	To Solid Filter		11451,50	[kg]
Output	To Precipitation		11406,60	[kg]
Output	Solids		44,89	[kg]
Precipitation Settings				
Input	To Precipitation		11406,60	[kg]
Input	Water		64350,60	[kg]
Ouput	Suspended Lignin Nanoparticles		75757,10	[kg]

Membrane 1 Settings

Input	Suspended Lignin Nanoparticles		75757,1	[kg]
Output	Retentat 1 (Suspended Lignin Nanoparticles)		761,539	[kg]
Output	Permeate 1 (Water + Organics/ ETOH Mixture)	total	74995,6	[kg]
		Water	68926,68	[kg]
		ETOH	6068,92	[kg]

Mixer Settings

Input	Suspended Lignin Nanoparticles		761,54	[kg]
Input	Water		76410,06	[kg]
Output	Suspended Lignin Nanoparticles		77171,60	[kg]

Membrane 2 Settings

Input	Suspended Lignin Nanoparticles		77171,60	[kg]
Output	**Retentat 2 (Suspended Lignin Nanoparticles)**		**756,54**	**[kg]**
Output	Permeate 2 (Water + Organics/ ETOH Mixture)	total	76415,10	[kg]
		Water	76357,13	[kg]
		ETOH	57,97	[kg]

Feed Preheating Settings

Input	Liquid from Membrane 1	total	74995,6	[kg]
		ETOH	6068,92	[kg]
		Water	68926,68	[kg]
Input	Thermal Energy Preheating		10659,6	[MJ]
Output	Preheated Liquid		74995,6	[kg]

Distillation Column Settings

Input	Preheated Liquid	total	74995,6	[kg]
		ETOH	6068,92	[kg]
		Water	68926,68	[kg]
Input	Thermal Energy for Destillation		27039,1	[MJ]
Output	Destillation Residue		65238,8	[kg]
Output	Recovered Liquid	total	9756,44	[kg]
		ETOH	6008,65	[kg]
		Water	3747,79	[kg]

7.4.3 Scenario 3: LHW-OS

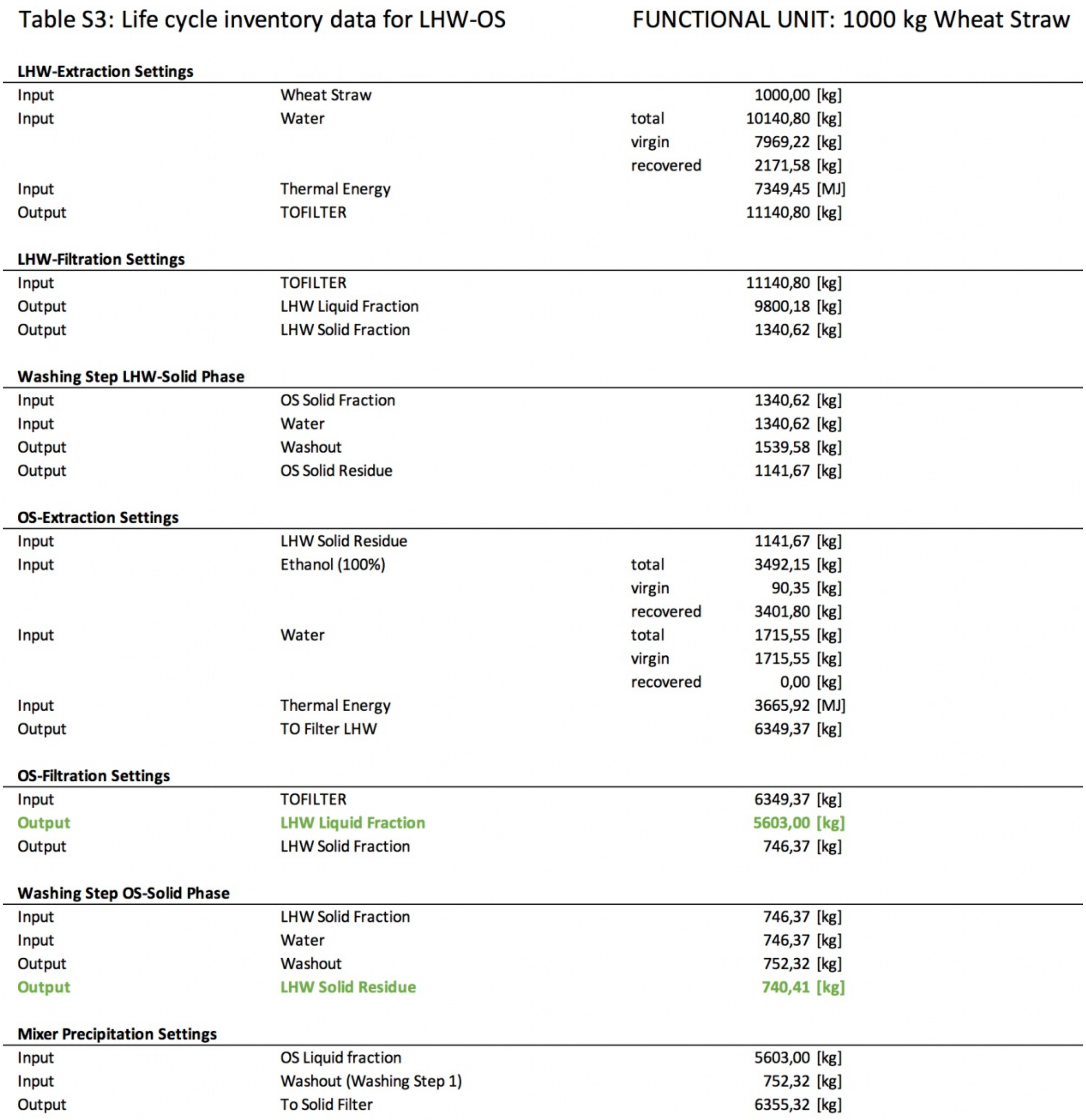


Table S3: Life cycle inventory data for LHW-OS FUNCTIONAL UNIT: 1000 kg Wheat Straw

LHW-Extraction Settings				
Input	Wheat Straw		1000,00	[kg]
Input	Water	total	10140,80	[kg]
		virgin	7969,22	[kg]
		recovered	2171,58	[kg]
Input	Thermal Energy		7349,45	[MJ]
Output	TOFILTER		11140,80	[kg]
LHW-Filtration Settings				
Input	TOFILTER		11140,80	[kg]
Output	LHW Liquid Fraction		9800,18	[kg]
Output	LHW Solid Fraction		1340,62	[kg]
Washing Step LHW-Solid Phase				
Input	OS Solid Fraction		1340,62	[kg]
Input	Water		1340,62	[kg]
Output	Washout		1539,58	[kg]
Output	OS Solid Residue		1141,67	[kg]
OS-Extraction Settings				
Input	LHW Solid Residue		1141,67	[kg]
Input	Ethanol (100%)	total	3492,15	[kg]
		virgin	90,35	[kg]
		recovered	3401,80	[kg]
Input	Water	total	1715,55	[kg]
		virgin	1715,55	[kg]
		recovered	0,00	[kg]
Input	Thermal Energy		3665,92	[MJ]
Output	TO Filter LHW		6349,37	[kg]
OS-Filtration Settings				
Input	TOFILTER		6349,37	[kg]
Output	**LHW Liquid Fraction**		**5603,00**	**[kg]**
Output	LHW Solid Fraction		746,37	[kg]
Washing Step OS-Solid Phase				
Input	LHW Solid Fraction		746,37	[kg]
Input	Water		746,37	[kg]
Output	Washout		752,32	[kg]
Output	**LHW Solid Residue**		**740,41**	**[kg]**
Mixer Precipitation Settings				
Input	OS Liquid fraction		5603,00	[kg]
Input	Washout (Washing Step 1)		752,32	[kg]
Output	To Solid Filter		6355,32	[kg]

Precipitation Settings				
Input	To Precipitation		6337,27	[kg]
Input	Water		35811,10	[kg]
Ouput	Suspended Lignin Nanoparticles		42148,37	[kg]

Membrane 1 Settings				
Input	Suspended Lignin Nanoparticles		42148,37	[kg]
Output	Retentat 1 (Suspended Lignin Nanoparticles)		712,43	[kg]
Output	Permeate 1 (Water + Organics/ ETOH Mixture)	total	41435,9	[kg]
		Water	37999,87	[kg]
		ETOH	3436,03	[kg]

Mixer Settings				
Input	Suspended Lignin Nanoparticles		712,43	[kg]
Input	Water		42257,80	[kg]
Output	Suspended Lignin Nanoparticles		42970,23	[kg]

Membrane 2 Settings				
Input	Suspended Lignin Nanoparticles		42970,20	[kg]
Output	**Retentat 2 (Suspended Lignin Nanoparticles)**		**712,33**	**[kg]**
Output	Permeate 2 (Water + Organics/ ETOH Mixture)	total	42257,90	[kg]
		Water	42202,67	[kg]
		ETOH	55,23	[kg]

Feed Preheating Settings				
Input	Liquid from Membrane 1	total	41435,9	[kg]
		ETOH	3436,03	[kg]
		Water	37999,87	[kg]
Input	Thermal Energy Preheating		5893,19	[MJ]
Output	Preheated Liquid		41435,9	[kg]

Distillation Column Settings				
Input	Preheated Liquid	total	41435,9	[kg]
		ETOH	3436,03	[kg]
		Water	37999,87	[kg]
Input	Thermal Energy for Destillation		14960,6	[MJ]
Output	Destillation Residue		35862,5	[kg]
Output	Recovered Liquid	total	5573,38	[kg]
		ETOH	3401,80	[kg]
		Water	2171,58	[kg]

HCELLW_Process				
Input	Destillation Residue		35862,5	[kg]
Output	Ethanol		34,24	[kg]
	Water		35828,26	[kg]

7.4.4 Composition Intermediates

Cellulose Phase

[g]	CELLULOS	HEM-C5	HEM-C6	LIGNIN-S	LIGNIN-L	C6 Sugar	C5 Sugar	ACETIC ACID	HMF	FURFURAL	EXTRACT	WATER	ETHANOL	ASH-L	ASH-S
OS	303,29	192,48	10,12	79,40	0	0	0	0	0	0	0	535,89	0	0	9,08
OS-LHW	281,87	111,61	4,61	54,35	0	0	0	0	0	0	0	458,96	0	0	1,02
LHW-OS	294,25	93,24	3,10	37,13	0	0	0	0	0	0	0	310,35	0	0	2,35

Sugar-Stream

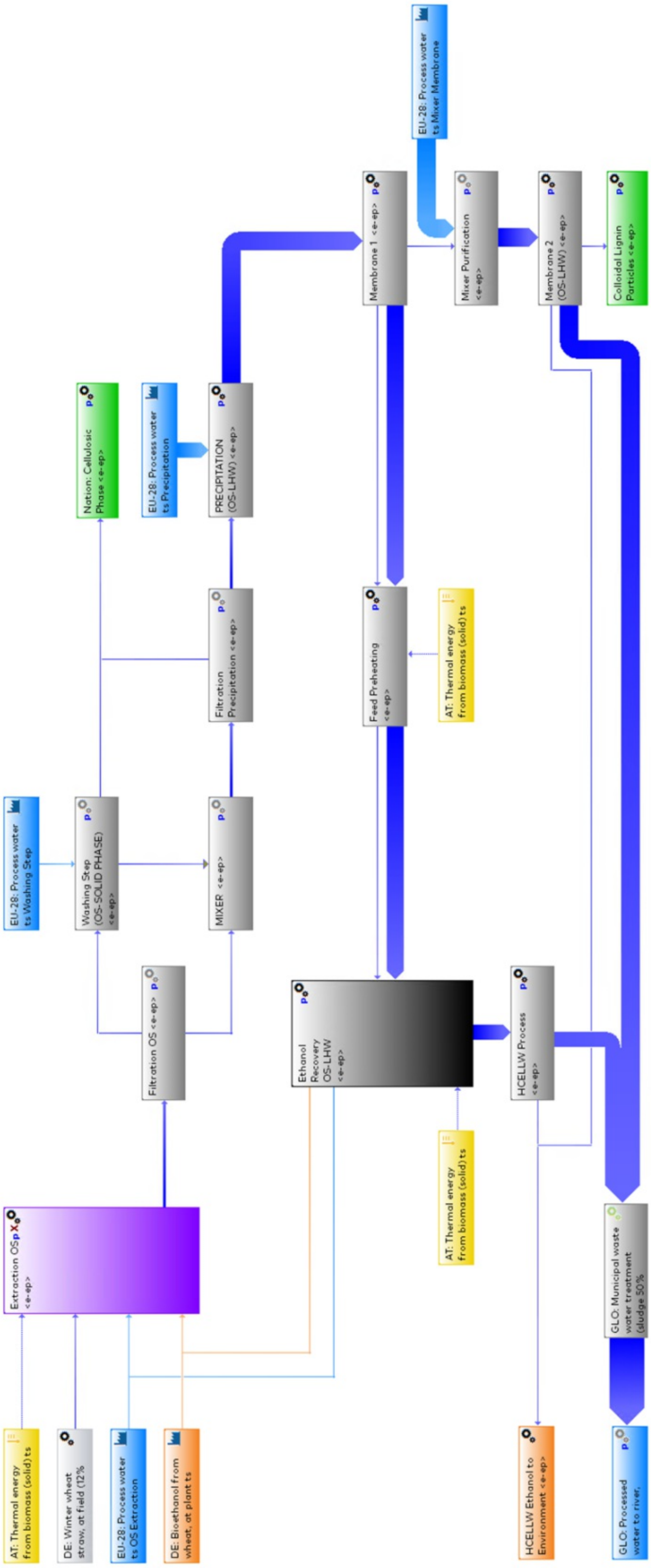
[g]	CELLULOS	HEM-C5	HEM-C6	LIGNIN-S	LIGNIN-L	C6 Sugar	C5 Sugar	ACETIC ACID	HMF	FURFURAL	EXTRACT	WATER	ETHANOL	ASH-L	ASH-S
OS	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
OS-LHW	13,70	5,43	0,22	2,64	20,81	12,92	66,78	4,9	0,17	5,23	0	6063,03	0	7,45	0,05
LHW-OS	9,32	3,19	0,11	3,33	44,91	20,76	94,84	17,44	0,34	7,07	111,04	9481,23	0	6,50	0,09

CLP-Suspension

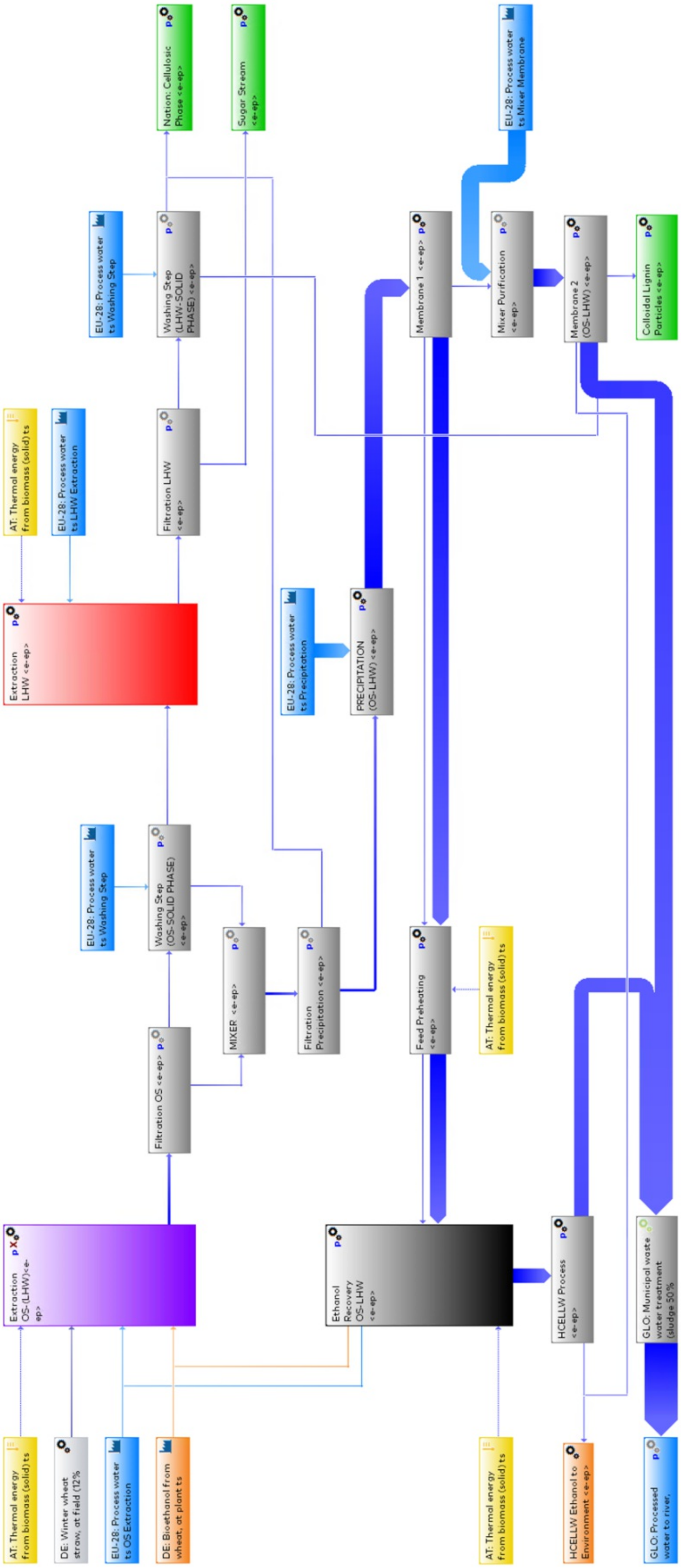
[g]	CELLULOS	HEM-C5	HEM-C6	LIGNIN-S	LIGNIN-L	C6 Sugar	C5 Sugar	ACETIC ACID	HMF	FURFURAL	EXTRACT	WATER	ETHANOL	ASH-L	ASH-S
OS	0	0	0	38,08	0,0034	0,0004	0,0003	0,0015	0	0	0,02	717,54	0,55	0	0,35
OS-LHW	0	0	0	38,08	0,0034	0,0004	0,0003	0,0015	0	0	0,02	717,54	0,55	0	0,35
LHW-OS	0	0	0	35,63	0,0090	0,0003	0,0020	0,0001	0	0	0,00	675,75	0,88	0	0,05

7.5 GaBi Process Plans

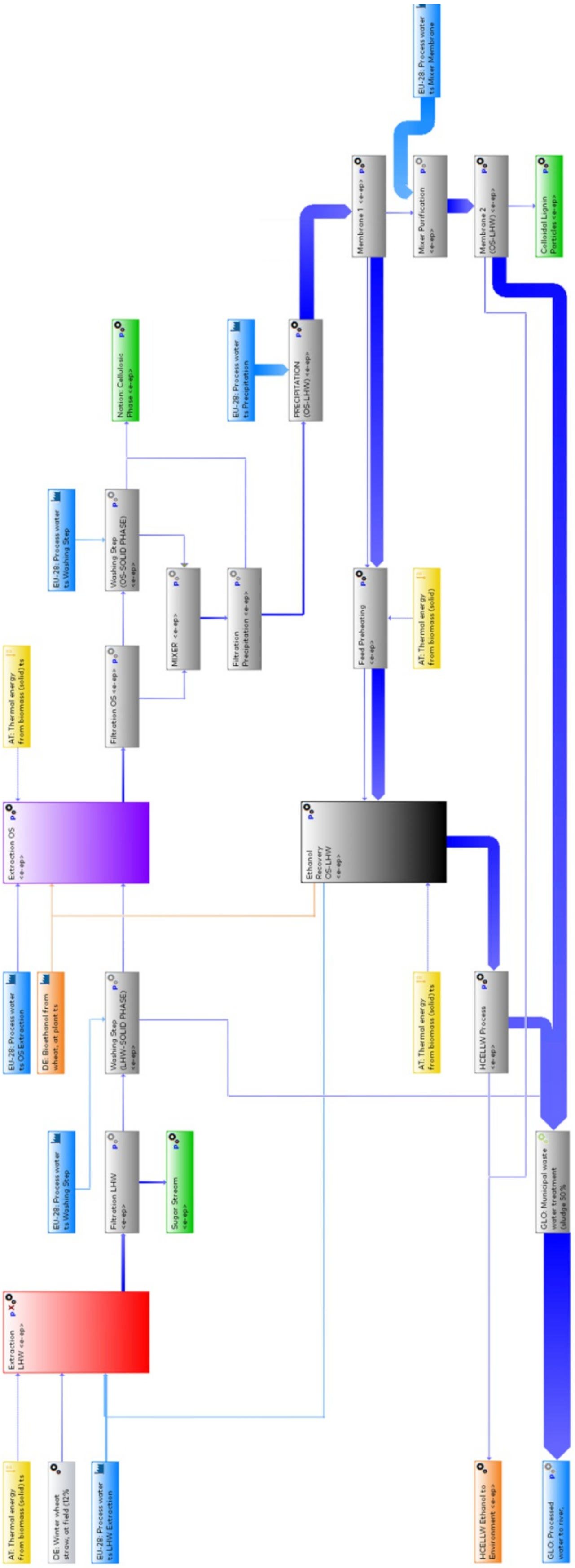
7.5.1 Scenario 1: OS (Base Case Scenario)



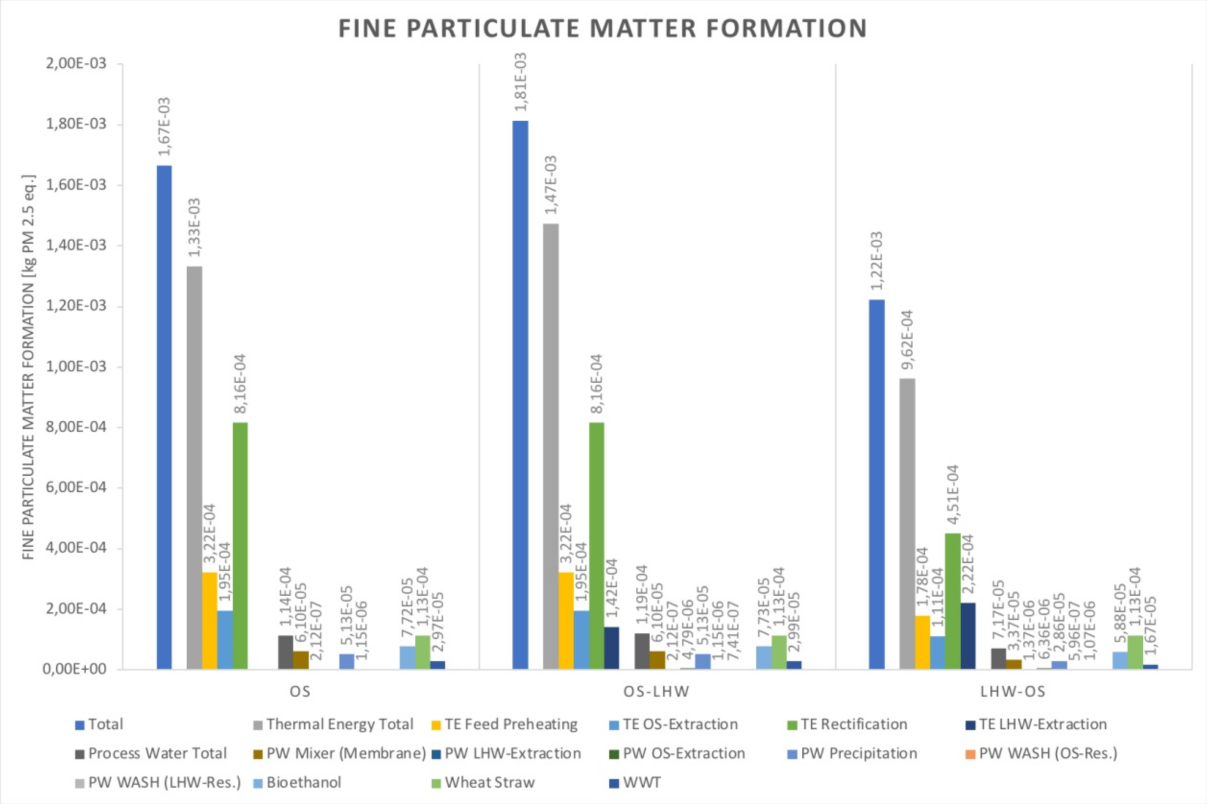
7.5.2 Scenario 2: OS-LHW

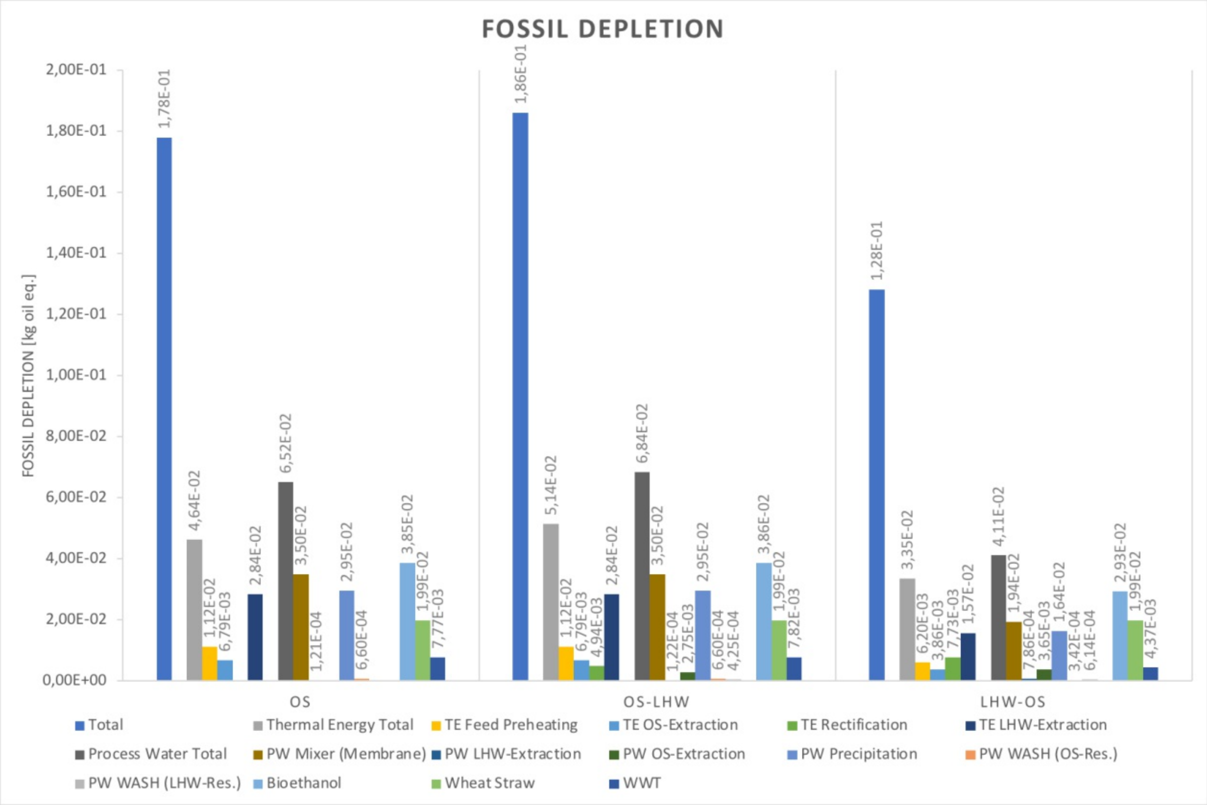


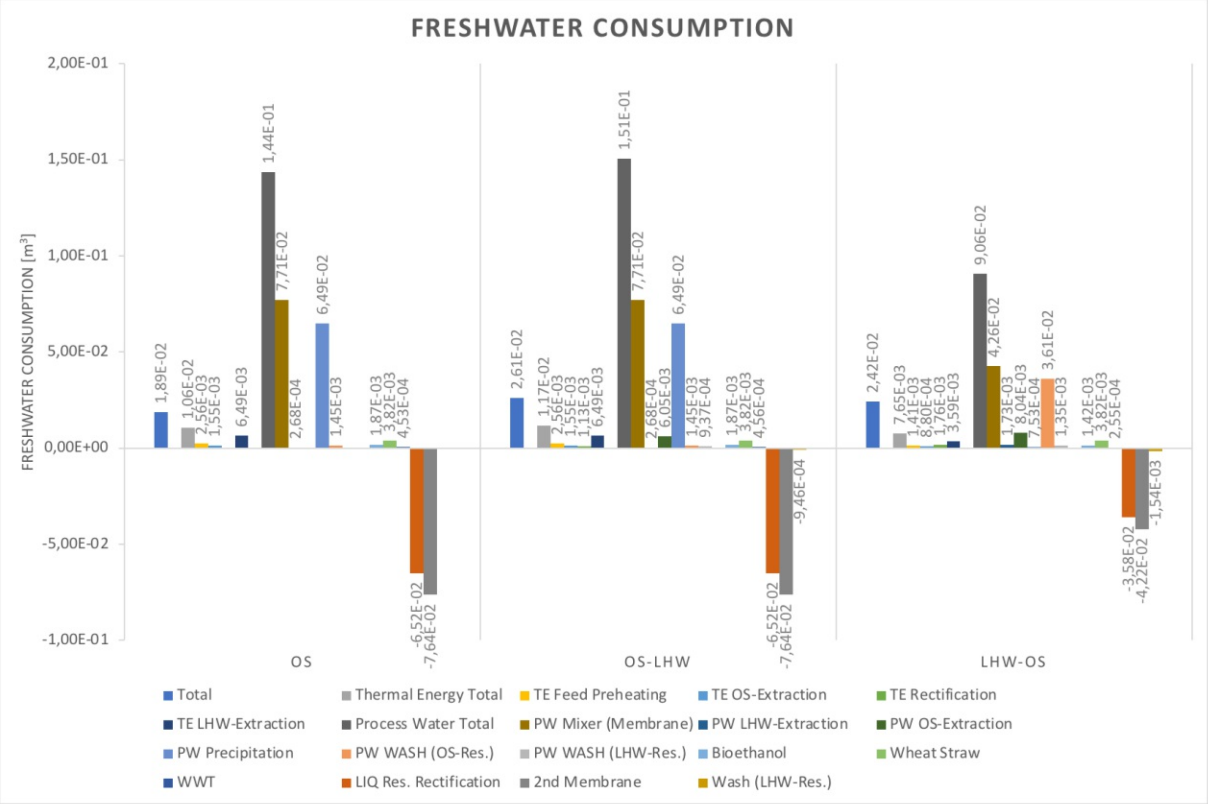
7.5.3 Scenario 3: LHW-OS



7.6 Results from the additional LCIA- ReCiPe midpoint categories






FRESHWATER CONSUMPTION
FRESHWATER CONSUMPTION [m³]
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1,50E-01
1,00E-01
5,00E-02
0,00E+00
-5,00E-02
-1,00E-01
1,89E-02
1,06E-02
2,56E-03
1,55E-03
6,49E-03
1,44E-01
7,71E-02
2,68E-04
6,49E-02
1,45E-03
1,87E-03
3,82E-03
4,53E-04
-6,52E-02
-7,64E-02
OS
2,61E-02
1,17E-02
2,56E-03
1,55E-03
1,13E-03
6,49E-03
1,51E-01
7,71E-02
2,68E-04
6,05E-03
6,49E-02
1,45E-03
9,37E-04
1,87E-03
3,82E-03
4,56E-04
-6,52E-02
-7,64E-02
-9,46E-04
OS-LHW
2,42E-02
7,65E-03
1,41E-03
8,80E-04
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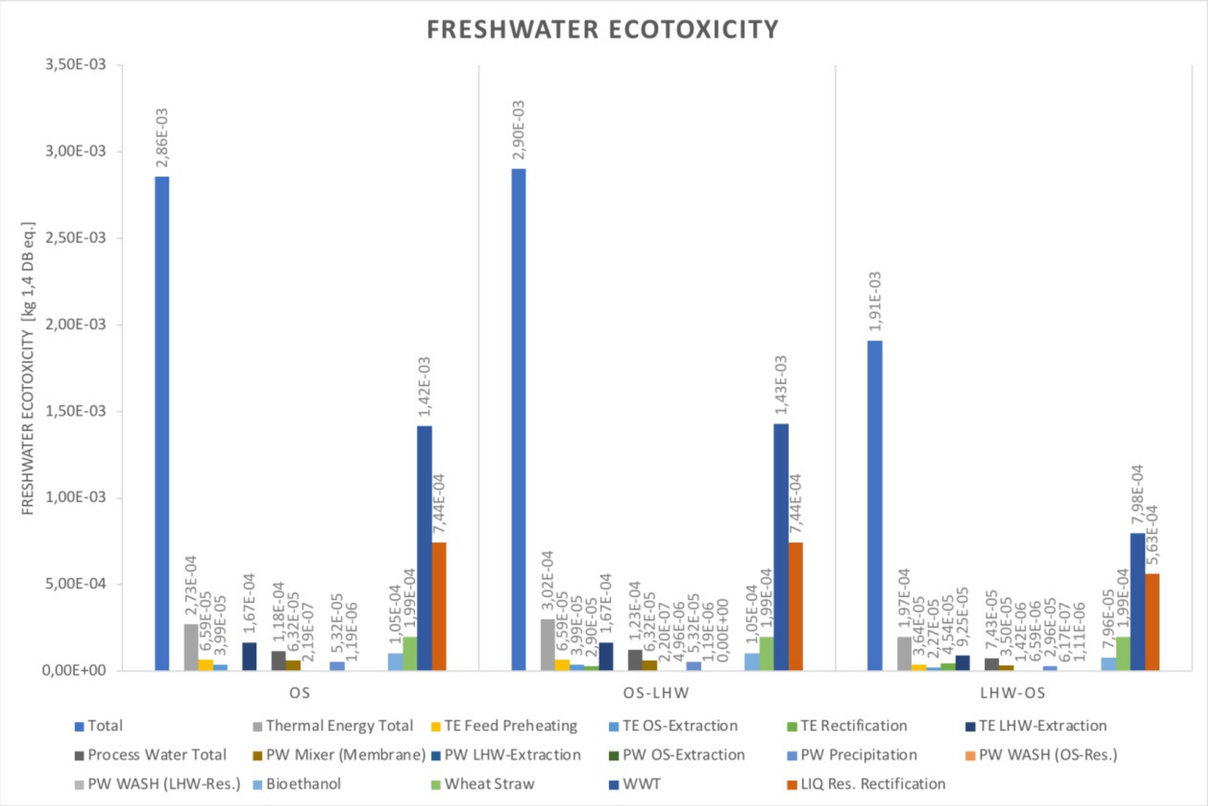
3,59E-03
9,06E-02
4,26E-02
1,73E-03
8,04E-03
7,53E-04
3,61E-02
1,35E-03
1,42E-03
3,82E-03
2,55E-04
-3,58E-02
-4,22E-02
-1,54E-03
LHW-OS
Total
Thermal Energy Total
TE Feed Preheating
TE OS-Extraction
TE Rectification
TE LHW-Extraction
Process Water Total
PW Mixer (Membrane)
PW LHW-Extraction
PW OS-Extraction
PW Precipitation
PW WASH (OS-Res.)
PW WASH (LHW-Res.)
Bioethanol
Wheat Straw
WWT
LIQ Res. Rectification
2nd Membrane
Wash (LHW-Res.)


FRESHWATER ECOTOXICITY
FRESHWATER ECOTOXICITY [kg 1,4 DB eq.]
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3,00E-03
2,50E-03
2,00E-03
1,50E-03
1,00E-03
5,00E-04
0,00E+00
2,86E-03
2,73E-04
6,59E-05
3,99E-05
1,67E-04
1,18E-04
6,32E-05
2,19E-07
5,32E-05
1,19E-06
1,05E-04
1,99E-04
1,42E-03
7,44E-04
OS
2,90E-03
3,02E-04
6,59E-05
3,99E-05
2,90E-05
1,67E-04
1,23E-04
6,32E-05
2,20E-07
4,96E-06
5,32E-05
1,19E-06
0,00E+00
1,05E-04
1,99E-04
1,43E-03
7,44E-04
OS-LHW
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1,97E-04
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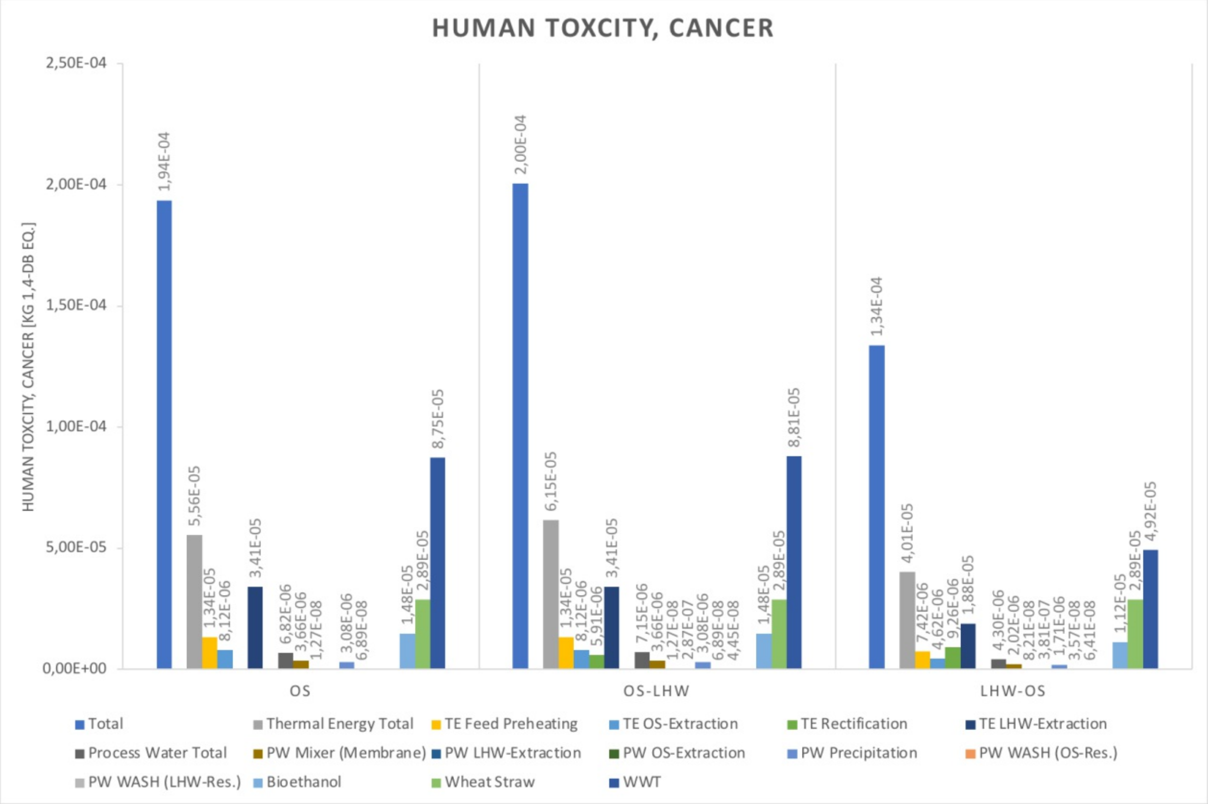
2,27E-05
4,54E-05
9,25E-05
7,43E-05
3,50E-05
1,42E-06
6,59E-06
2,96E-05
6,17E-07
1,11E-06
7,96E-05
1,99E-04
7,98E-04
5,63E-04
LHW-OS
Total
Thermal Energy Total
TE Feed Preheating
TE OS-Extraction
TE Rectification
TE LHW-Extraction
Process Water Total
PW Mixer (Membrane)
PW LHW-Extraction
PW OS-Extraction
PW Precipitation
PW WASH (OS-Res.)
PW WASH (LHW-Res.)
Bioethanol
Wheat Straw
WWT
LIQ Res. Rectification


HUMAN TOXCITY, CANCER
HUMAN TOXCITY, CANCER [KG 1,4-DB EQ.]
2,50E-04
2,00E-04
1,50E-04
1,00E-04
5,00E-05
0,00E+00
1,94E-04
5,56E-05
1,34E-05
8,12E-06
3,41E-05
6,82E-06
3,66E-06
1,27E-08
3,08E-06
6,89E-08
1,48E-05
2,89E-05
8,75E-05
2,00E-04
6,15E-05
1,34E-05
8,12E-06
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3,41E-05
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1,27E-08
2,87E-07
3,08E-06
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4,45E-08
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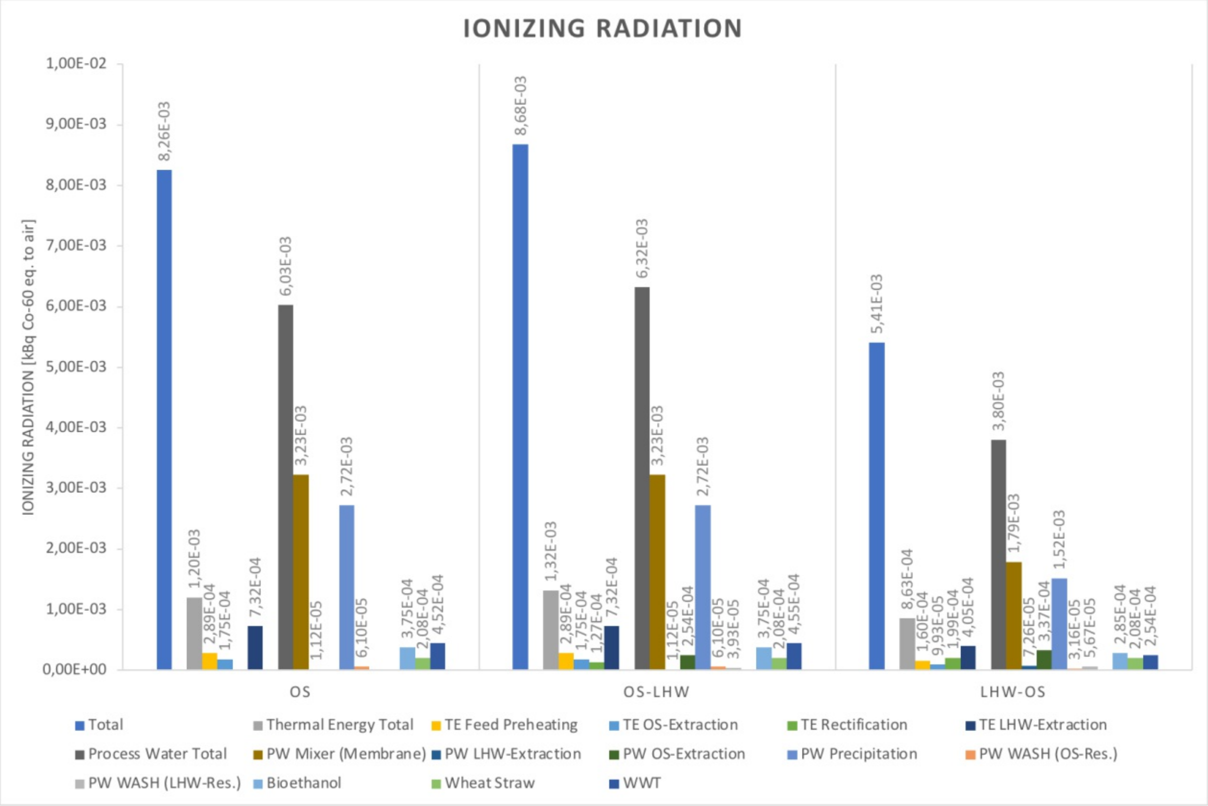
8,81E-05
1,34E-04
4,01E-05
7,42E-06
4,62E-06
9,26E-06
1,88E-05
4,30E-06
2,02E-06
8,21E-08
3,81E-07
1,71E-06
3,57E-08
6,41E-08
1,12E-05
2,89E-05
4,92E-05
OS
OS-LHW
LHW-OS
Total
Thermal Energy Total
TE Feed Preheating
TE OS-Extraction
TE Rectification
TE LHW-Extraction
Process Water Total
PW Mixer (Membrane)
PW LHW-Extraction
PW OS-Extraction
PW Precipitation
PW WASH (OS-Res.)
PW WASH (LHW-Res.)
Bioethanol
Wheat Straw
WWT


IONIZING RADIATION
IONIZING RADIATION [kBq Co-60 eq. to air]
1,00E-02
9,00E-03
8,00E-03
7,00E-03
6,00E-03
5,00E-03
4,00E-03
3,00E-03
2,00E-03
1,00E-03
0,00E+00
8,26E-03
1,20E-03
2,89E-04
1,75E-04
7,32E-04
6,03E-03
3,23E-03
1,12E-05
2,72E-03
6,10E-05
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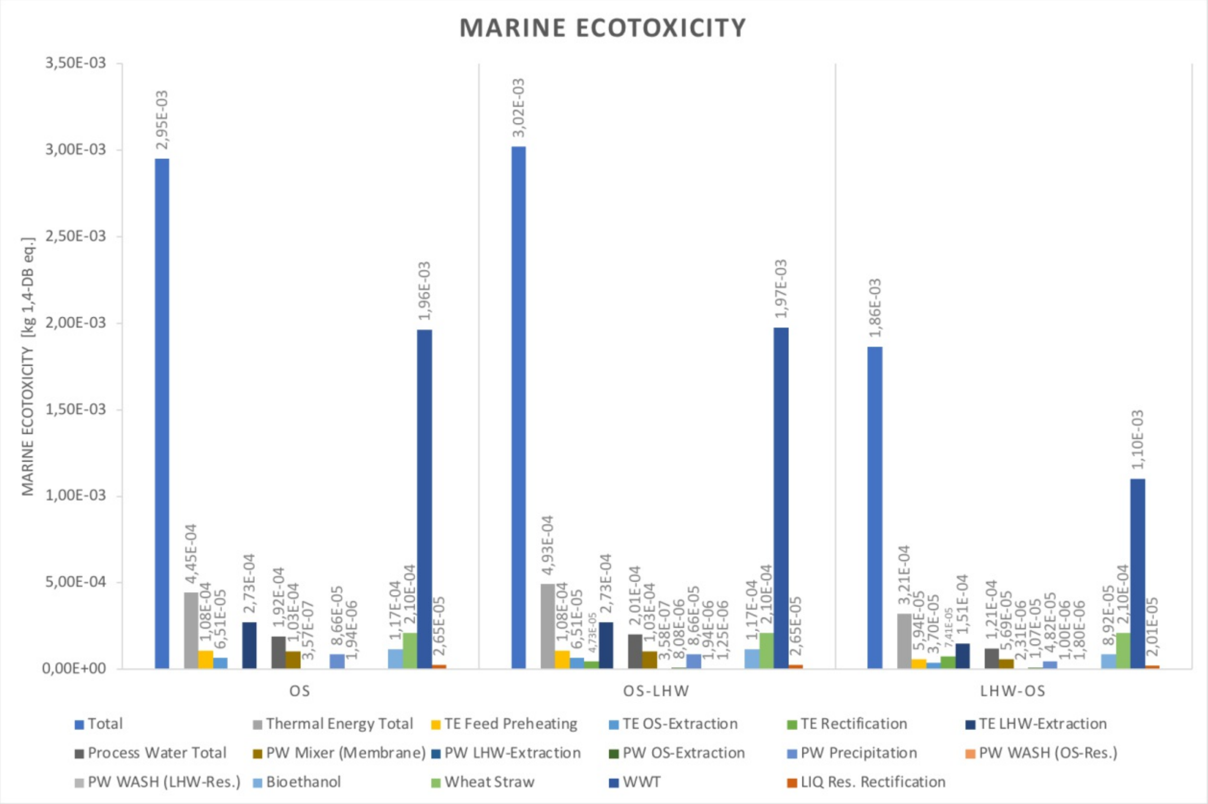
2,54E-04
2,72E-03
6,10E-05
3,93E-05
3,75E-04
2,08E-04
4,55E-04
5,41E-03
8,63E-04
1,60E-04
9,93E-05
1,99E-04
4,05E-04
3,80E-03
1,79E-03
7,26E-05
3,37E-04
1,52E-03
3,16E-05
5,67E-05
2,85E-04
2,08E-04
2,54E-04
OS
OS-LHW
LHW-OS
Total
Thermal Energy Total
TE Feed Preheating
TE OS-Extraction
TE Rectification
TE LHW-Extraction
Process Water Total
PW Mixer (Membrane)
PW LHW-Extraction
PW OS-Extraction
PW Precipitation
PW WASH (OS-Res.)
PW WASH (LHW-Res.)
Bioethanol
Wheat Straw
WWT


MARINE ECOTOXICITY
MARINE ECOTOXICITY [kg 1,4-DB eq.]
3,50E-03
3,00E-03
2,50E-03
2,00E-03
1,50E-03
1,00E-03
5,00E-04
0,00E+00
OS
2,95E-03
4,45E-04
1,08E-04
6,51E-05
2,73E-04
1,92E-04
1,03E-04
3,57E-07
8,66E-05
1,94E-06
1,17E-04
2,10E-04
1,96E-03
2,65E-05
OS-LHW
3,02E-03
4,93E-04
1,08E-04
6,51E-05
4,73E-05
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1,03E-04
3,58E-07
8,08E-06
8,66E-05
1,94E-06
1,25E-06
1,17E-04
2,10E-04
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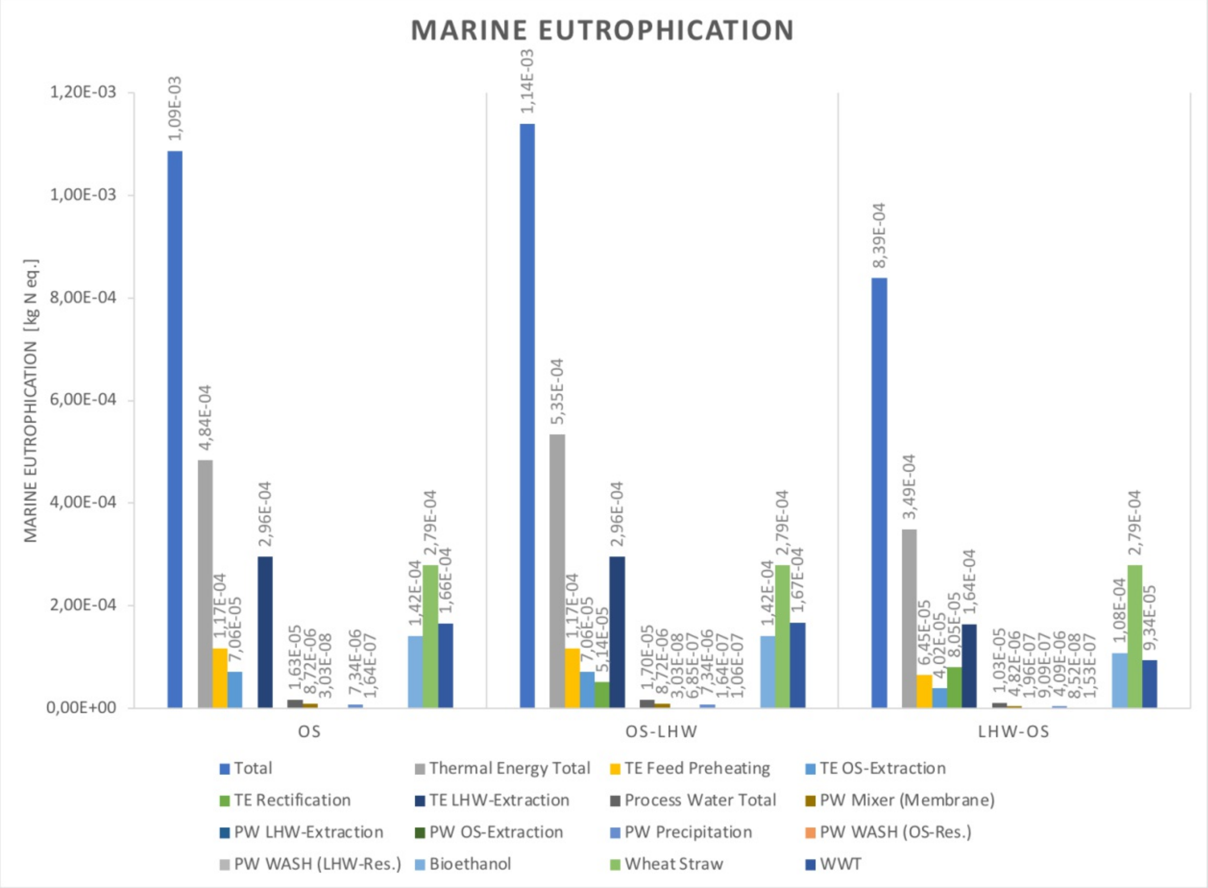
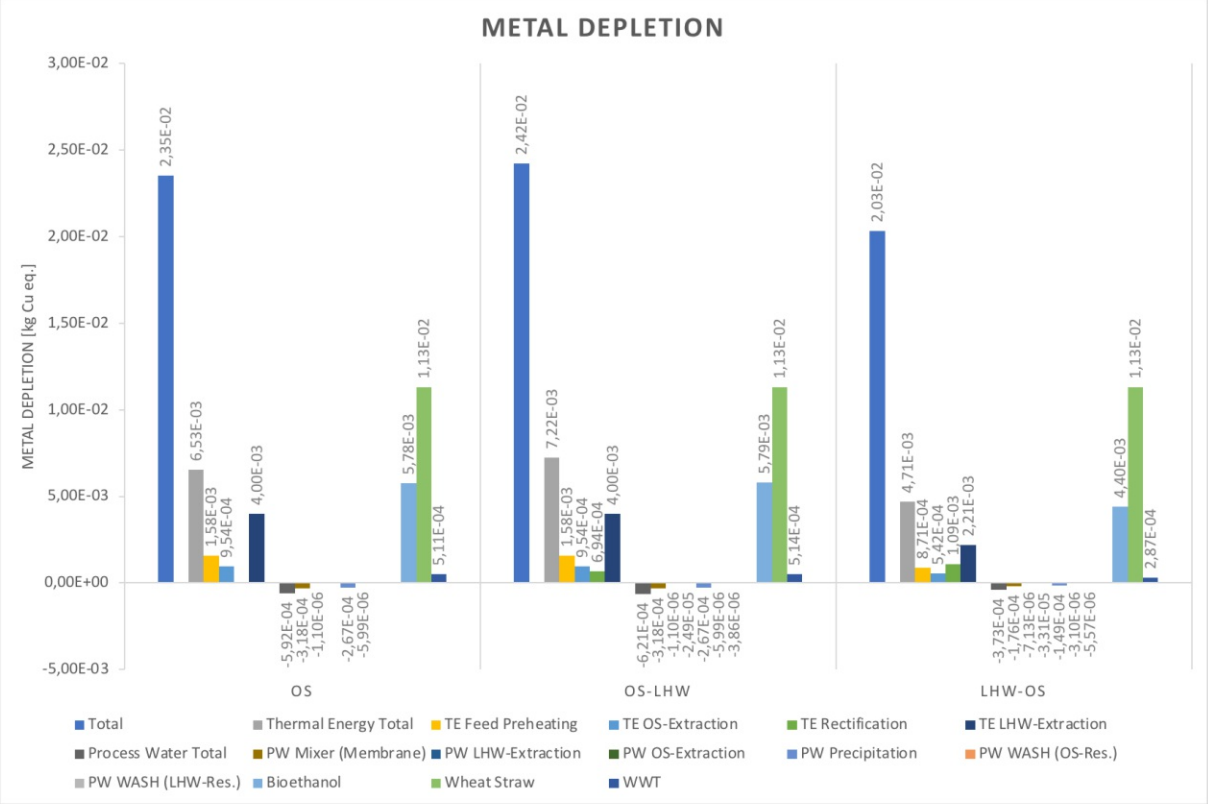
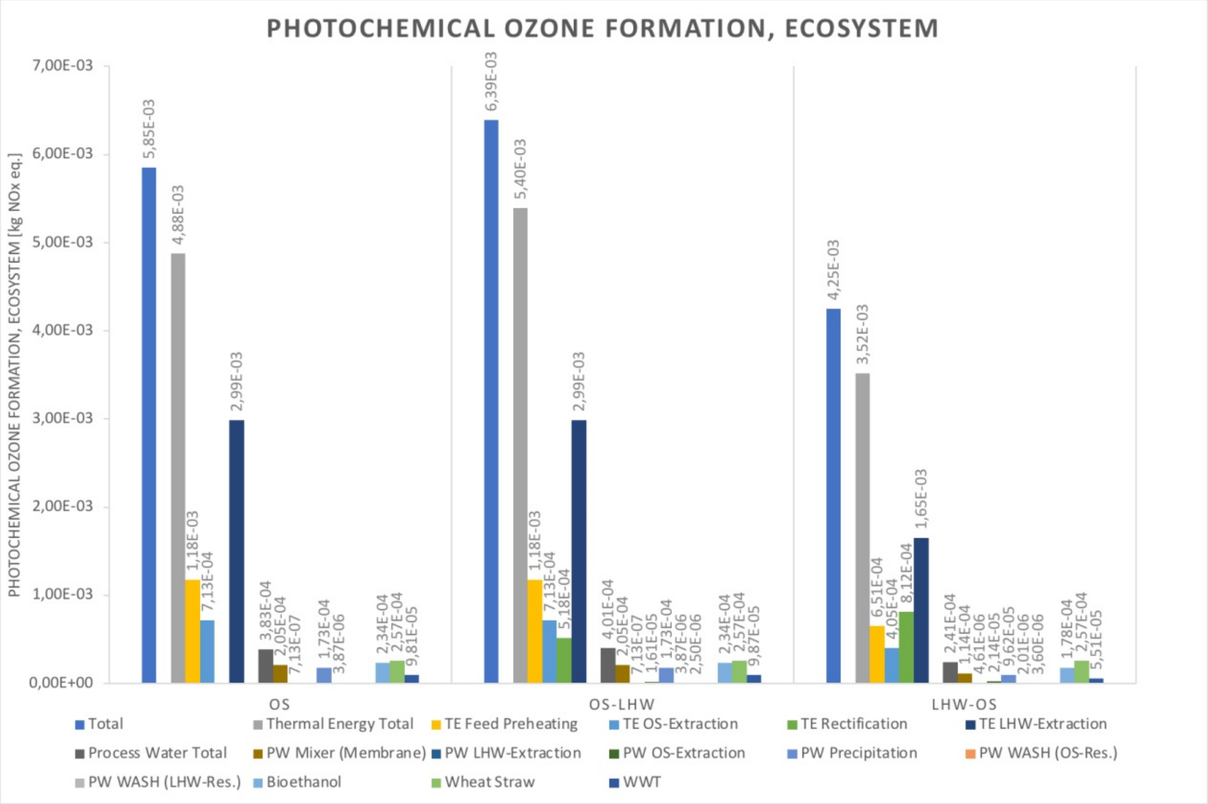
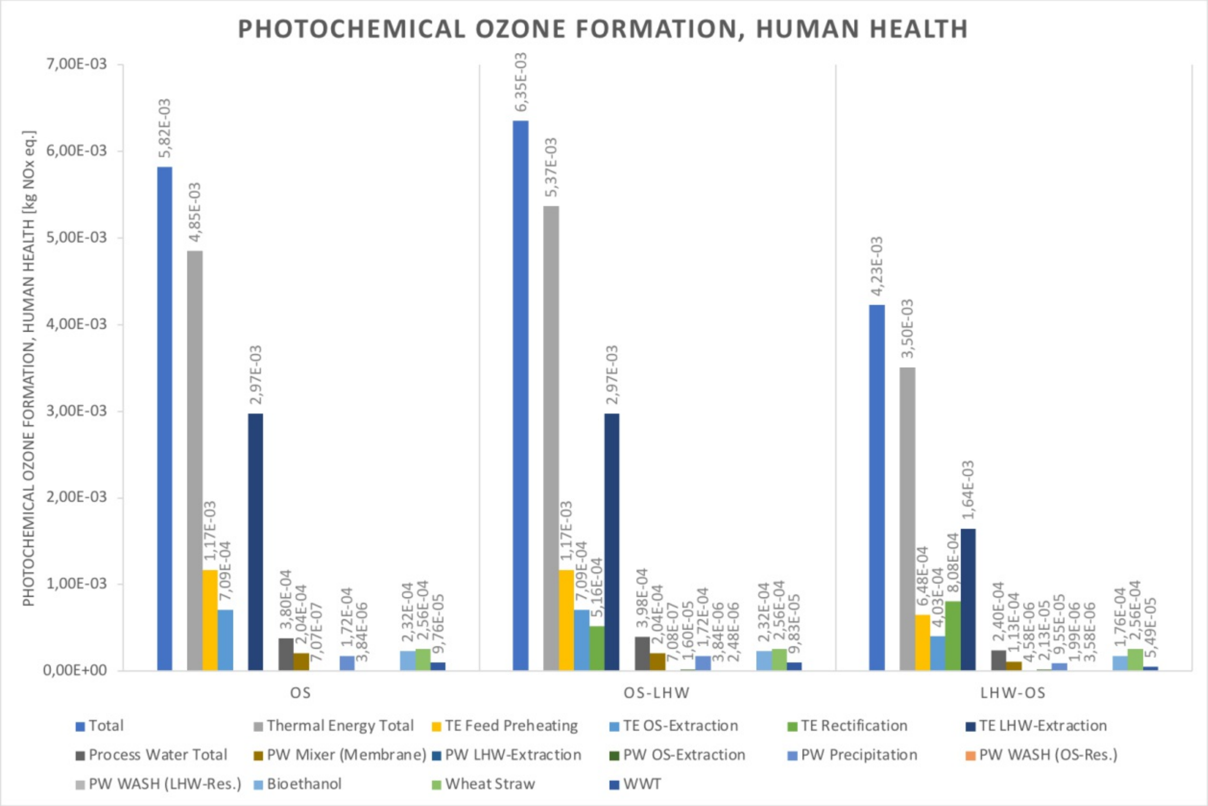
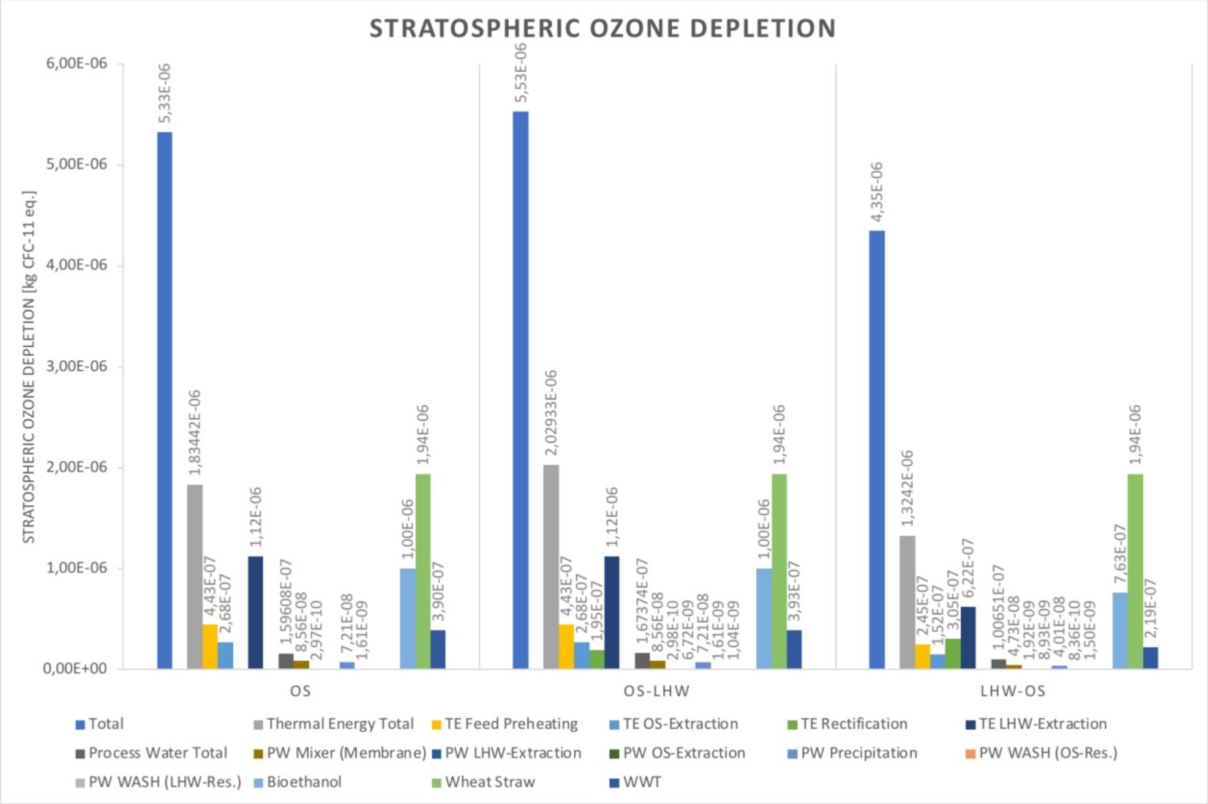
2,65E-05
LHW-OS
1,86E-03
3,21E-04
5,94E-05
3,70E-05
7,41E-05
1,51E-04
1,21E-04
5,69E-05
2,31E-06
1,07E-05
4,82E-05
1,00E-06
1,80E-06
8,92E-05
2,10E-04
1,10E-03
2,01E-05
Total
Thermal Energy Total
TE Feed Preheating
TE OS-Extraction
TE Rectification
TE LHW-Extraction
Process Water Total
PW Mixer (Membrane)
PW LHW-Extraction
PW OS-Extraction
PW Precipitation
PW WASH (OS-Res.)
PW WASH (LHW-Res.)
Bioethanol
Wheat Straw
WWT
LIQ Res. Rectification

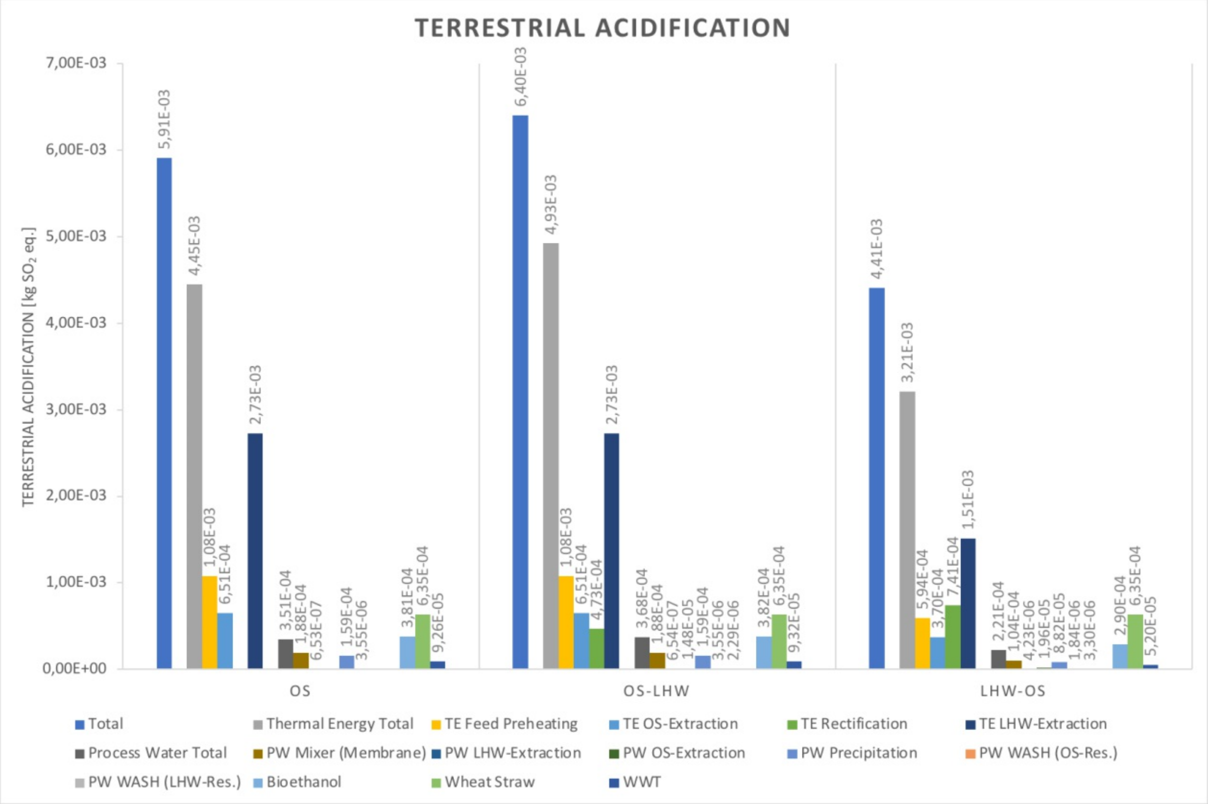

MARINE EUTROPHICATION
MARINE EUTROPHICATION [kg N eq.]
1,20E-03
1,00E-03
8,00E-04
6,00E-04
4,00E-04
2,00E-04
0,00E+00
OS
1,09E-03
4,84E-04
1,17E-04
7,06E-05
2,96E-04
1,63E-05
8,72E-06
3,03E-08
7,34E-06
1,64E-07
1,42E-04
2,79E-04
1,66E-04
OS-LHW
1,14E-03
5,35E-04
1,17E-04
7,06E-05
5,14E-05
2,96E-04
1,70E-05
8,72E-06
3,03E-08
6,85E-07
7,34E-06
1,64E-07
1,06E-07
1,42E-04
2,79E-04
1,67E-04
LHW-OS
8,39E-04
3,49E-04
6,45E-05
4,02E-05
8,05E-05
1,64E-04
1,03E-05
4,82E-06
1,96E-07
9,09E-07
4,09E-06
8,52E-08
1,53E-07
1,08E-04
2,79E-04
9,34E-05
Total
Thermal Energy Total
TE Feed Preheating
TE OS-Extraction
TE Rectification
TE LHW-Extraction
Process Water Total
PW Mixer (Membrane)
PW LHW-Extraction
PW OS-Extraction
PW Precipitation
PW WASH (OS-Res.)
PW WASH (LHW-Res.)
Bioethanol
Wheat Straw
WWT

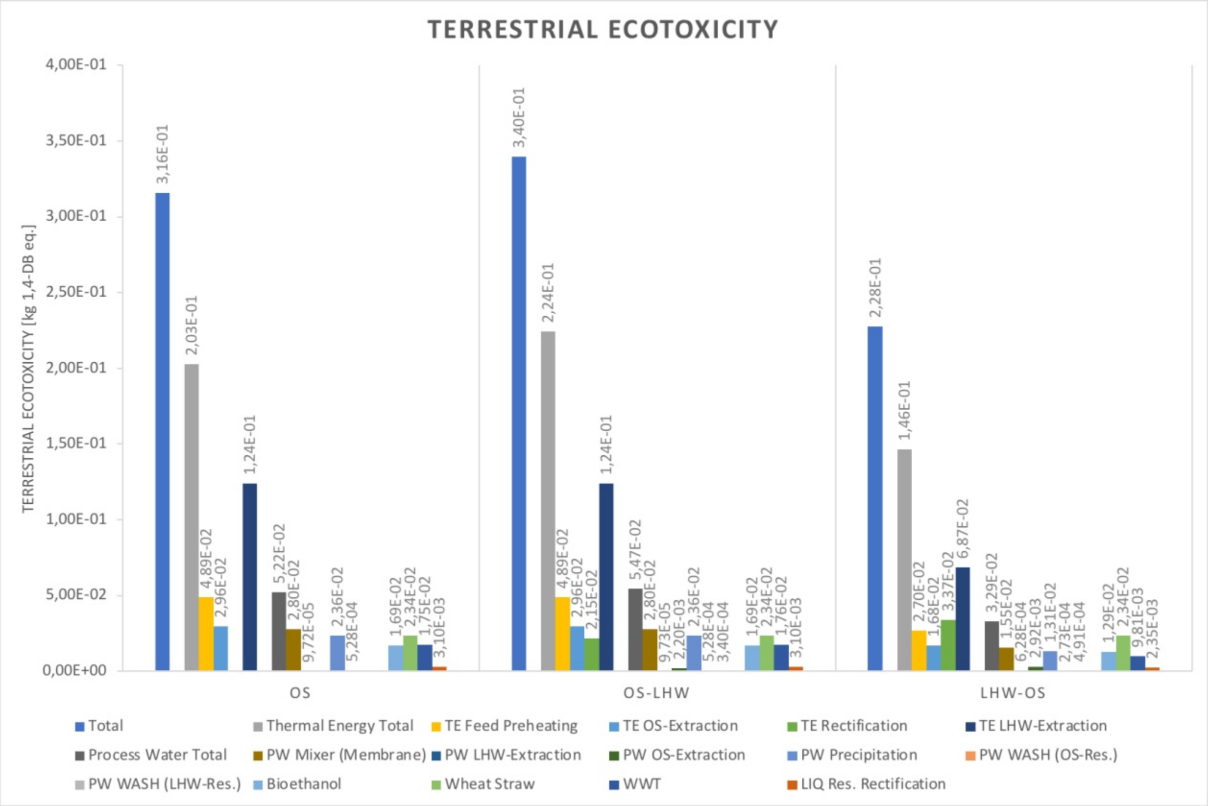

METAL DEPLETION
METAL DEPLETION [kg Cu eq.]
3,00E-02
2,50E-02
2,00E-02
1,50E-02
1,00E-02
5,00E-03
0,00E+00
-5,00E-03
OS
2,35E-02
6,53E-03
1,58E-03
9,54E-04
4,00E-03
-5,92E-04
-3,18E-04
-1,10E-06
-2,67E-04
-5,99E-06
5,78E-03
1,13E-02
5,11E-04
OS-LHW
2,42E-02
7,22E-03
1,58E-03
9,54E-04
6,94E-04
4,00E-03
-6,21E-04
-3,18E-04
-1,10E-06
-2,49E-05
-2,67E-04
-5,99E-06
-3,86E-06
5,79E-03
1,13E-02
5,14E-04
LHW-OS
2,03E-02
4,71E-03
8,71E-04
5,42E-04
1,09E-03
2,21E-03
-3,73E-04
-1,76E-04
-7,13E-06
-3,31E-05
-1,49E-04
-3,10E-06
-5,57E-06
4,40E-03
1,13E-02
2,87E-04
Total
Thermal Energy Total
TE Feed Preheating
TE OS-Extraction
TE Rectification
TE LHW-Extraction
Process Water Total
PW Mixer (Membrane)
PW LHW-Extraction
PW OS-Extraction
PW Precipitation
PW WASH (OS-Res.)
PW WASH (LHW-Res.)
Bioethanol
Wheat Straw
WWT


PHOTOCHEMICAL OZONE FORMATION, ECOSYSTEM
PHOTOCHEMICAL OZONE FORMATION, ECOSYSTEM [kg NOx eq.]
7,00E-03
6,00E-03
5,00E-03
4,00E-03
3,00E-03
2,00E-03
1,00E-03
0,00E+00
OS
5,85E-03
4,88E-03
1,18E-03
7,13E-04
2,99E-03
3,83E-04
2,05E-04
7,13E-07
1,73E-04
3,87E-06
2,34E-04
2,57E-04
9,81E-05
OS-LHW
6,39E-03
5,40E-03
1,18E-03
7,13E-04
5,18E-04
2,99E-03
4,01E-04
2,05E-04
7,13E-07
1,61E-05
1,73E-04
3,87E-06
2,50E-06
2,34E-04
2,57E-04
9,87E-05
LHW-OS
4,25E-03
3,52E-03
6,51E-04
4,05E-04
8,12E-04
1,65E-03
2,41E-04
1,14E-04
4,61E-06
2,14E-05
9,62E-05
2,01E-06
3,60E-06
1,78E-04
2,57E-04
5,51E-05
Total
Thermal Energy Total
TE Feed Preheating
TE OS-Extraction
TE Rectification
TE LHW-Extraction
Process Water Total
PW Mixer (Membrane)
PW LHW-Extraction
PW OS-Extraction
PW Precipitation
PW WASH (OS-Res.)
PW WASH (LHW-Res.)
Bioethanol
Wheat Straw
WWT


PHOTOCHEMICAL OZONE FORMATION, HUMAN HEALTH
PHOTOCHEMICAL OZONE FORMATION, HUMAN HEALTH [kg NOx eq.]
7,00E-03
6,00E-03
5,00E-03
4,00E-03
3,00E-03
2,00E-03
1,00E-03
0,00E+00
5,82E-03
4,85E-03
1,17E-03
7,09E-04
2,97E-03
3,80E-04
2,04E-04
7,07E-07
1,72E-04
3,84E-06
2,32E-04
2,56E-04
9,76E-05
6,35E-03
5,37E-03
1,17E-03
7,09E-04
5,16E-04
2,97E-03
3,98E-04
2,04E-04
7,08E-07
1,60E-05
1,72E-04
3,84E-06
2,48E-06
2,32E-04
2,56E-04
9,83E-05
4,23E-03
3,50E-03
6,48E-04
4,03E-04
8,08E-04
1,64E-03
2,40E-04
1,13E-04
4,58E-06
2,13E-05
9,55E-05
1,99E-06
3,58E-06
1,76E-04
2,56E-04
5,49E-05
OS
OS-LHW
LHW-OS
Total
Thermal Energy Total
TE Feed Preheating
TE OS-Extraction
TE Rectification
TE LHW-Extraction
Process Water Total
PW Mixer (Membrane)
PW LHW-Extraction
PW OS-Extraction
PW Precipitation
PW WASH (OS-Res.)
PW WASH (LHW-Res.)
Bioethanol
Wheat Straw
WWT


STRATOSPHERIC OZONE DEPLETION
STRATOSPHERIC OZONE DEPLETION [kg CFC-11 eq.]
6,00E-06
5,00E-06
4,00E-06
3,00E-06
2,00E-06
1,00E-06
0,00E+00
5,33E-06
1,83442E-06
4,43E-07
2,68E-07
1,12E-06
1,59608E-07
8,56E-08
2,97E-10
7,21E-08
1,61E-09
1,00E-06
1,94E-06
3,90E-07
5,53E-06
2,02933E-06
4,43E-07
2,68E-07
1,95E-07
1,12E-06
1,67374E-07
8,56E-08
2,98E-10
6,72E-09
7,21E-08
1,61E-09
1,04E-09
1,00E-06
1,94E-06
3,93E-07
4,35E-06
1,3242E-06
2,45E-07
1,52E-07
3,05E-07
6,22E-07
1,00651E-07
4,73E-08
1,92E-09
8,93E-09
4,01E-08
8,36E-10
1,50E-09
7,63E-07
1,94E-06
2,19E-07
OS
OS-LHW
LHW-OS
Total
Thermal Energy Total
TE Feed Preheating
TE OS-Extraction
TE Rectification
TE LHW-Extraction
Process Water Total
PW Mixer (Membrane)
PW LHW-Extraction
PW OS-Extraction
PW Precipitation
PW WASH (OS-Res.)
PW WASH (LHW-Res.)
Bioethanol
Wheat Straw
WWT


TERRESTRIAL ACIDIFICATION
TERRESTRIAL ACIDIFICATION [kg SO_2 eq.]
7,00E-03
6,00E-03
5,00E-03
4,00E-03
3,00E-03
2,00E-03
1,00E-03
0,00E+00
5,91E-03
4,45E-03
1,08E-03
6,51E-04
2,73E-03
3,51E-04
1,88E-04
6,53E-07
1,59E-04
3,55E-06
3,81E-04
6,35E-04
9,26E-05
6,40E-03
4,93E-03
1,08E-03
6,51E-04
4,73E-04
2,73E-03
3,68E-04
1,88E-04
6,54E-07
1,48E-05
1,59E-04
3,55E-06
2,29E-06
3,82E-04
6,35E-04
9,32E-05
4,41E-03
3,21E-03
5,94E-04
3,70E-04
7,41E-04
1,51E-03
2,21E-04
1,04E-04
4,23E-06
1,96E-05
8,82E-05
1,84E-06
3,30E-06
2,90E-04
6,35E-04
5,20E-05
OS
OS-LHW
LHW-OS
Total
Thermal Energy Total
TE Feed Preheating
TE OS-Extraction
TE Rectification
TE LHW-Extraction
Process Water Total
PW Mixer (Membrane)
PW LHW-Extraction
PW OS-Extraction
PW Precipitation
PW WASH (OS-Res.)
PW WASH (LHW-Res.)
Bioethanol
Wheat Straw
WWT


TERRESTRIAL ECOTOXICITY
TERRESTRIAL ECOTOXICITY [kg 1,4-DB eq.]
4,00E-01
3,50E-01
3,00E-01
2,50E-01
2,00E-01
1,50E-01
1,00E-01
5,00E-02
0,00E+00
3,16E-01
2,03E-01
4,89E-02
2,96E-02
1,24E-01
5,22E-02
2,80E-02
9,72E-05
2,36E-02
5,28E-04
1,69E-02
2,34E-02
1,75E-02
3,10E-03
3,40E-01
2,24E-01
4,89E-02
2,96E-02
2,15E-02
1,24E-01
5,47E-02
2,80E-02
9,73E-05
2,20E-03
2,36E-02
5,28E-04
3,40E-04
1,69E-02
2,34E-02
1,76E-02
3,10E-03
2,28E-01
1,46E-01
2,70E-02
1,68E-02
3,37E-02
6,87E-02
3,29E-02
1,55E-02
6,28E-04
2,92E-03
1,31E-02
2,73E-04
4,91E-04
1,29E-02
2,34E-02
9,81E-03
2,35E-03
OS
OS-LHW
LHW-OS
Total
Thermal Energy Total
TE Feed Preheating
TE OS-Extraction
TE Rectification
TE LHW-Extraction
Process Water Total
PW Mixer (Membrane)
PW LHW-Extraction
PW OS-Extraction
PW Precipitation
PW WASH (OS-Res.)
PW WASH (LHW-Res.)
Bioethanol
Wheat Straw
WWT
LIQ Res. Rectification