UNIVERSITÀ DEGLI STUDI DI PADOVA

DIPARTIMENTO DI INGEGNERIA INDUSTRIALE

CORSO DI LAUREA MAGISTRALE IN CHEMICAL AND PROCESS ENGINEERING

Tesi di Laurea Magistrale in

Chemical and Process Engineering

Consequential life cycle assessment of hemicellulose extraction process from kraft mill for pentane and higher hydrocarbons production.

Thesis Supervisor: Prof. Alessandro Manzardo

Foreign Tutor: Prof. Joseph S.M. Samec

Laureando: DANIEL CRACCO

ACCADEMIC YEAR: 2023-2024

Abstract

The sustainable utilization of forest resources stands as a critical topic in biorefineries, addressing contemporary global environmental challenges such as climate change, land use, water scarcity, and the depletion of fossil resources. To enhance the sustainability and profitability of biomass-based plants, capable of competing with and replacing the use of fossil resources, this thesis explores the potential of elevating side-streams to high-value end-products.

The primary focus lies in augmenting the sustainability of a forest biomass-based biorefinery through the production of chemicals derived from hemicellulose. This involves a comprehensive investigation into the environmental impacts through a consequential Life Cycle Assessment.

In the product system considered, hemicellulose is extracted from birch wood chips in a pre-hydrolysis step during a Kraft pulping process, followed by its conversion into Furfural utilizing Beta-Zeolites as catalysts. Subsequently, Furfural undergoes direct hydro-processing, leading to the production of pentane and higher hydrocarbons, facilitated by a combination of Pd/C and ZSM-5 Zeolites. Gaseous by-products, comprising <C5 hydrocarbons, can be reformed to yield green hydrogen and biogenic CO_2.

Post-extraction, wood chips undergo Kraft pulping to obtain Dissolving Grade Pulp, utilized in textile production. The incorporation of a pre-hydrolysis step proves to be an effective way of de-bottlenecking the recovery boiler of the pulp mill which represent the bottleneck of the whole process, enhancing pulp production while concurrently generating bio-based chemicals.

Environmental performances and hot spots in this alternative process are investigated through a Consequential Life Cycle Assessment. Primary data, derived from prior laboratory experiments, analyses, and measurements, form the basis for mass and energy balances. Secondary data from databases such as ecoQuery are employed in the inventory construction.

Two scenarios are examined, A first scenario (S1-Burn) addressing pre-hydrolysis coupled with the kraft pulping process to yield unbleached pulp without the integration of the hydrocarbons value chain, in this case the pre-hydrolysis liquor is burnt co-generation facility to recover heat and power. The second scenario (S2-HC) investigates the potential

environmental impacts of upgrading hemicellulose to hydrocarbons and burning the hemicellulose residues in the same co-generation plant, producing heat and power with high efficiency.

A Contribution Analysis was performed, which provides insights into the contribution of each analysis group in the product system to various impact categories. Performance in both scenarios is further explored through five different sensitivity analysis, investigating the performances when the pre-hydrolysis liquor and the hemicellulose residues are burnt in the recovery boiler of the plant, the benefits of locating the integrated kraft mill in an European context, the drawbacks of decreasing the yield of hydrocarbons by 10%, the impacts of decoupling the hydrocarbons value chain process from the pulp mill, and the sensitivity to a change in the impact assessment method.

Five distinct impact categories were investigated to assess the efficacy of the different scenarios: Climate change [Kg CO2 eq.], Land use [Pt], Water use [m3 depriv.], Resource use – fossil [MJ], and Resource use – mineral and metals [Kg Sb eq.].

The findings reveal that S2-HC, under an average European context, delivers the best performances in the climate change and fossil resources use impact categories, with a benefit of (-) 0.721 KgCO2 eq and (-) 6.85 MJ respectively. The best performances in Land use and mineral resources use are delivered by S1-Burn in a Swedish + Finland context, with an impact of (+) 84.8 Pt and (+) 4.06E-06 Kg Sb eq. S1-Burn under an average European context delivers the best outcomes in the water use with a benefit of (-) 2.54E-02 m3 depriv.

The results highlight that the production of pentane and higher hydrocarbons from hemicellulose, discarded during the kraft pulping process, coupled with the recovery of heat and power from a co-generation plant through the incineration of residuals not converted into furfural, can significantly enhances the sustainability and environmental performance of a kraft mill within an average European scenario.

Table of Contents

Introduction

The sustainable use of forest resources is of paramount importance in biorefineries for facing the current global environmental challenges such as global warming, land use, water scarcity and fossil resources depletion. The exploitation of renewable resources in place of fossil resources can be an effective way to reduce the concentration of Greenhouse gasses (GHG) in the atmosphere, plants have the potential to sequester large amounts of carbon from CO_2 present in the atmosphere and from soil, counterbalancing the emissions of biogenic CO_2 when they are used for heat and electric energy production. Biogenic carbon can be defined as carbon arising from biological sources and has a much shorter timescale for carbon cycling than fossil carbon.

Exploiting renewable resources and upgrading side-streams to a higher value end-products, which can represent a storage of carbon, is an effective way to improve the sustainability and profitability of a process to compete with fossil fuels and to replace them.

In the product system considered, hemicellulose is extracted from birch wood *via* pre-hydrolysis during a Kraft pulping process, followed by its conversion into Furfural utilizing Beta-Zeolites as catalysts. Subsequently, Furfural undergoes direct hydro-processing to obtain pentane, higher hydrocarbons and gaseous by-products comprising <C5 hydrocarbons, facilitated by a combination of Pd/C and ZSM-5 Zeolites. Post-extraction, wood chips undergo Kraft pulping to obtain Dissolving Grade Pulp, utilized in textile production.

The aim of this thesis project is to assess the environmental impacts, through a Consequential Life Cycle Assessment, of a type II Lignocellulosic feedstock Biorefinery which aims to produce Dissolving Grade Pulp and chemicals as by-products from hardwood.

Chapter 1

Lignocellulosic biomass

Wood is a lignocellulosic material composed by cellulose, hemicellulose, lignin, and the so-called extractives, which are lipophilic compounds present in bark and refer to the non-structural part of the biomass. When pulping wood and wood chips there are some variables to be considered:

- Moisture content, which is the percentage of water relative to the dry or wet mass of the wood, a lower moisture content can reduce the energy requirements in chemical pulping and the transportation costs.
- Wood density or specific gravity: will affect the load to the digester.
- Tension and compression strength properties, they will depend on growing factors, trees growing in sunny, wet, and warm locations will grow fast and will have coarse and stiff fibres, trees growing in dry and cold locations are slow growing with fine and dense fibres.
- Bark content and chemical composition: cellulose, hemicellulose, lignin, and extractives contents.
- Chips dimensions and bulk density
- Wood species: Softwood or Hardwood.

Softwoods are woods from the gymnosperms subdivision, also commonly known as conifers or evergreen trees. Their cellulose microfibrils are oriented in 10-30 degrees from the main longitudinal axis of the fibre, resulting in a high tensile strength.

In this work the starting material are wood chips from hardwood, for this reason a brief introduction to hardwood chemical composition from Bajpai (2018a) is needed: Hardwoods are woods from the angiosperm subdivision, also commonly known as broadleaves and they lose their leaves in winter. The structure and morphology of hardwood is way more complex; the fibres are shorter than the softwood ones with a lower strength.

Cellulose is a polymer of D-glucose connected by β-(1→4) linkages, as shown in Figure 1.1, with a degree of polymerization above 10'000. 50%-70% of cellulose present in wood is crystalline. Cellulose is the most abundant component in biomasses and is responsible for the structural strength of plants.
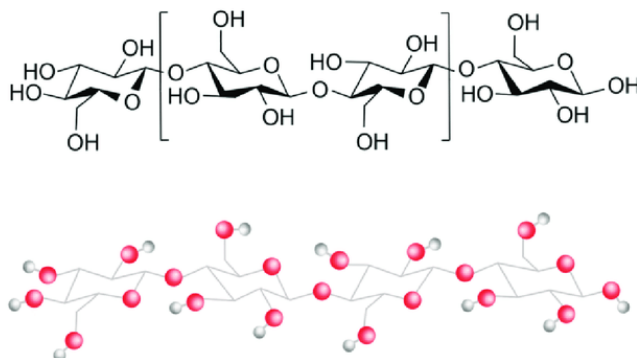
Figure 1.1. Structure of the Cellulose polymer.

Hemicelluloses are a class of polymers of both 6C and 5C sugars like mannose, galactose and 4-O-methyl-D-glucuronic acid or xylose and arabinose. The degree of polymerization is of 100-200 sugar units per hemicellulose molecule. Glucuronoxylans (xylans) are the principal hemicellulose of hardwoods and make up 15%-30% of hardwoods.
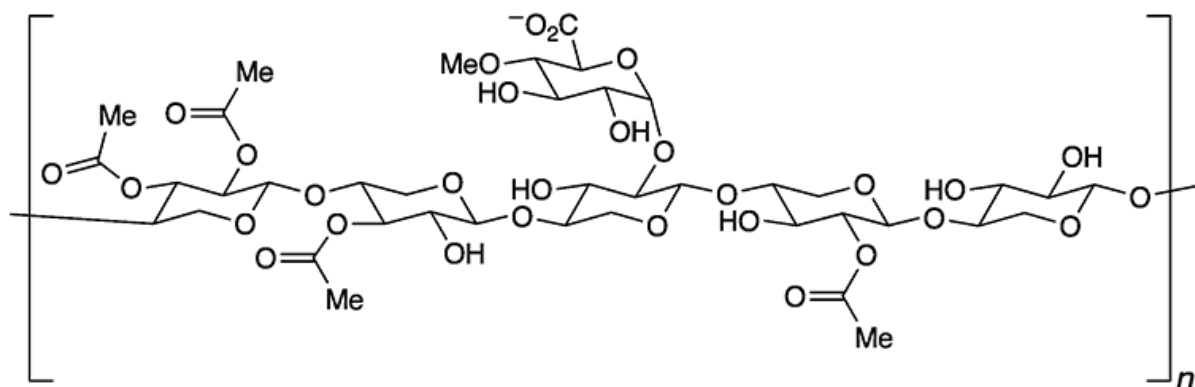
Figure 1.2. Structure of the hemicellulose polymer of xylans

Another component is the lignin, which is a polymer consisting of phenylpropane units and has an amorphous and three-dimensional structure, it acts as a resin contributing to the rigidity and protection of the cell walls in the plant. It has the role of binding the fibers

together and it needs to be removed during pulping processes. Hardwoods contain both coniferyl alcohol and sinapyl alcohol as lignin monomers.

The β-O-4 linkage is the most important and abundant in lignin structure, connecting the phenolic groups of different monomers through an ether bond. Other linkages like β-5 and β-β also play a role in giving the characteristic three-dimensional structure, strength, and rigidity. Lignin is becoming an attractive source of aromatic compounds for different applications through valorization in biorefineries.

Finally, extractives are compounds which are soluble by definition in organic solvents or water. There are a lot of compounds, and their composition varies a lot with wood species. Hardwoods have very small amounts of extractives such as terpenes, turpentines and fatty acids.

Chapter 2

Pulping fundamentals

Pulping is the process of breaking down physically and/or chemically wood or other lignocellulosic starting materials to obtain "market pulp" that can be sold or used to produce paper and textiles. There are four main categories of pulping processes: chemical, semi-chemical, chemi-mechanical and mechanical pulping. Different pulping processes give different yields in pulp, where Yield is calculated in every step of the process and indicates the amount of product recovered compared to the amount of starting material. Kraft pulping yield for brown paper is between 65-70%, 47%-50% for bleachable pulps and 43%-45% after the bleaching step.

$$Yield \ [\%] = \frac{dry \ product \ mass}{starting \ material \ mass} \times 100$$

(1.1)

2.1 Conventional Kraft Pulping process

This work focuses on the Kraft pulping process for Dissolving Grade Pulp production and integration with a hemicellulose removal and upgrading process. The first Kraft mill went into operation in Sweden in 1890. The Kraft pulping process is a full chemical method which implement sodium hydroxide (NaOH) and sodium sulphite (Na_2S) at relatively high temperatures (180°C) in steam, the chemicals involved have the role to break down the lignin structure that binds the cellulose fibres together to obtain in the end a high strength pulp, from which derives the name "Kraft" which means "strong" in Swedish and German. The advantage of this type of process is that it can tolerate all types of wood, the drawback are the emissions of sulfur in its reduced forms that gives a sulfur odour. In Kraft pulping is important to have a uniform wood chips size and thickness to ensure uniform cooking. According to Bajpai (2018b) the degree of cooking in a Kraft mill is defined as soft, medium and hard depending on the pulp to be obtained: soft cooks are for bleachable grades pulp and

will have a lignin content of 3%-5.2% for softwoods or 1.8%-2.4% for hardwoods, medium cooks are for bags and papers, hard cooks are for top linerboards.

The wood chips are sent to a pre-steaming section where they are wetted and preheated with steam to help the filling of wood cavities of white liquor and achieve a uniform degree of cooking. The cooking is carried out in digesters, which can be batch or continuous operation units, with the batch representing the majority of the processes. Typically, delignification requires around two hours at 170°C-180°C depending on the type of wood, the white liquor is mixture of the active chemicals involved and some impurities coming from wood, corrosion and from the recovery process. Under these digesting conditions the white liquor dissolves lignin and hemicellulose to give soluble fragments. Once the cooking is complete the content of the digester is sent to an atmospheric tank called "blow tank" then it is sent to pulp washers where the cooking spent liquor is separated, the resulting pulp is then sent to further washing and, eventually, bleaching. The spent cooking liquor is combined with the pulp washing water to form a weak black liquor which is concentrated in a multiple-effect evaporator to 55% solids, then is further concentrated to 65% in a direct-contact evaporator by contact with the flue gasses from the furnace. The "strong" Black Liquor is then burnt in the recovery boiler operation, which has two main roles:

1. The hemicellulose and lignin operate as reducing agents in the regeneration of process chemicals, reducing sulfoxides to sulfides.
2. Heat and power that are generated from the combustion are utilized internally in the pulp mill operations.

The resulting inorganics generated in the recovery boiler comprises sodium sulfides and sodium carbonate, which are quenched in water to give "green liquor". To recover the sodium hydroxide, ion exchange with calcium oxide is performed in the slacker. The resulting calcium, hydroxide is dehydrated in the lime kiln.
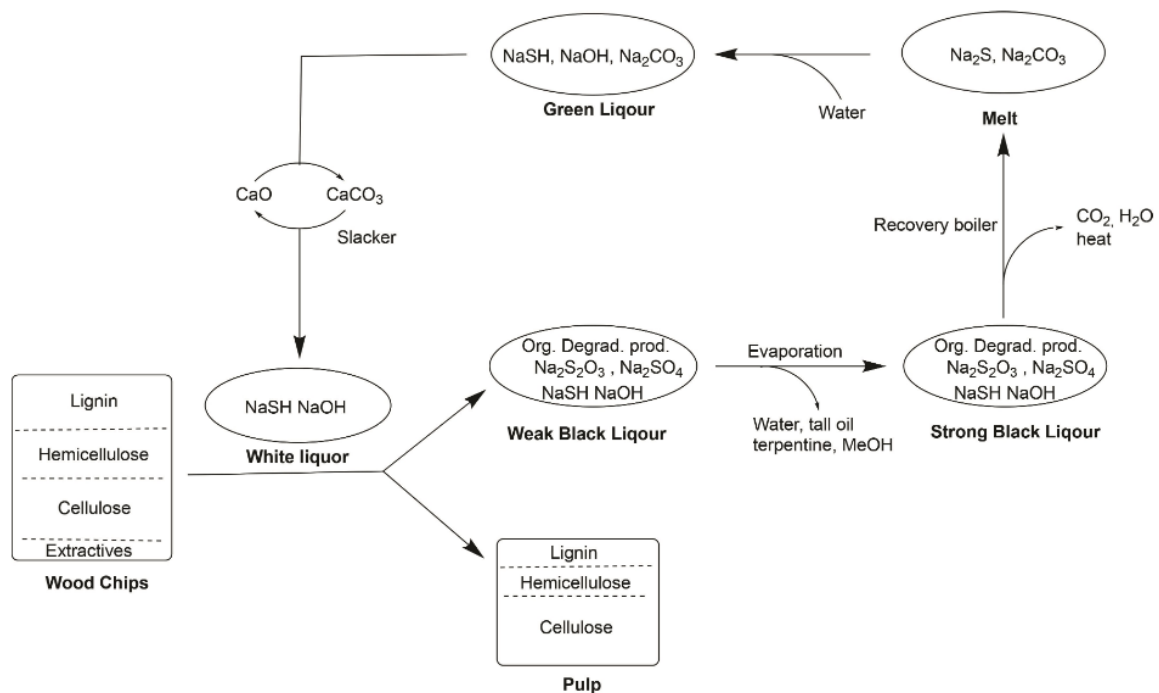
Figure 2.1: Simplified illustration over the kraft process. Sulfide and hydroxide ions are reactants in white liquor during the process. Weak black liquor is generated and concentrated during evaporation to yield strong black liquor.

2.2 The Recovery Boiler in Kraft pulping

As mentioned in the previous section, recovery boilers in pulp mills have several functions. Combustion of the organic material in the black liquor, mainly hemicellulose and lignin, to generate high pressure steam used to generate electricity in a turbine and low-pressure steam for process heating, to reduce the inorganic sulfur compounds to sodium sulfide, to regenerate the spent chemicals and dissolve them to produce green liquor, to avoid the releasing hazardous streams in the environment. Black liquor dry solid flow, defined as the mass ratio of dried black liquor to unit of black liquor before drying, is the key criteria for establishing the required size of the boiler and the Black liquor heating value is needed to define the boiler capacity. A dry solid content below 20% results in a negative net heating value of the black liquor, which means that all the heat provided by the combustion of organics is spent to evaporate the water content, on the other hand, with high dry solids content the temperature of the adiabatic combustion increase, but this parameter is limited by the available evaporation technology that can handle highly viscous liquors.

The state of the art for recovery boilers provided by Vakkilainen (2005) is characterized by one drum boiler, black liquor dry solid at 80% generating steam at 9.2 MPa/490°C, lower

emissions of TRS (Total reduced sulfur compounds), SO_2 and particulate with the design driving to Black liquor with 90% dry solids and higher pressures and temperatures due the increasing demand of power. What is important to highlight is that the recovery boiler operates at maximum capacity, representing the bottleneck of the process and limiting the production of pulp.

2.3 Dissolving Grade Pulp

Dissolving Grade Pulp is a high-valuable product obtainable from various types of biomasses according to Bajpai (2018c): wood raw materials from softwoods or hardwoods, non-wood raw materials like bagasse, bamboo (designed and put in production in China) and corn stalk. DGP is rich in cellulose (>95%) and dissolved in a liquor prior to regeneration to produce the fibre. DGP has peculiar properties such as a uniform molecular weight distribution and a high level of brightness. The production of regenerated cellulose, and thus of dissolving pulp, can be performed through the kraft pulping process with a preliminary hemicellulose extraction and delignification because the subsequent processes require a low hemicellulose content, and further bleaching. It can be converted in viscose or lyocell fibres, or chemically converted in cellulose derivatives like cellulose triacetate to form fibres or films. It is estimated that further increase in cotton production is not possible due to land use and irrigation. Furthermore, sulfite pulp mills cannot supply the increasing demand of textile fibers. In this context, re-structuring kraft pulp mills from making paper pulp to dissolving pulp is prosperous.

Trends in dissolving pulp markets worldwide are growing consistently. The dissolving pulp industry exhibited prospective growth in developing countries in recent years with an annual global production of cellulose pulp of approximately 18 million tons reported by Balkissoon et al. (2022). Since DGP is a high purity product, the other major components separated like hemicellulose and lignin can be upgraded to higher value products in a so-called Integrated Dissolving pulp biorefinery.
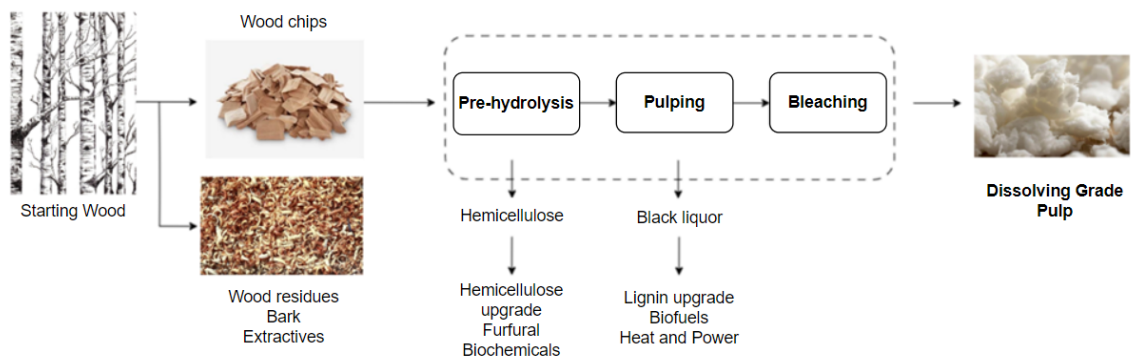
Figure 3.2. Dissolving Grade Pulp manufacture

As previously stated, DGP can be produced via Kraft pulping but requires a Pre-hydrolysis step to separate the hemicellulose in a Pre-Hydrolysis Liquor (PHL). Furthermore, to achieve high purity and brightness, bleaching is required. For these reasons, and due to a dissolving pulp yield of 30%-35%, the production costs are higher compared to a paper Kraft mill.

Chapter 3

Integrated Dissolving Grade Pulp biorefinery process

As explained in chapter §2.3, to produce DGP, hemicellulose and lignin need to be separated to achieve the desired product specifications. In a conventional Kraft mill these side-streams are burnt to a low value in the recovery boiler, which operates at the maximum capacity resulting in the bottleneck of the process. The separation of hemicellulose and lignin lowers the load to the recovery boiler, allowing for higher intakes of starting wood to the process, increasing the production of pulp destined to DGP production. The increased production is usually referred to as "marginal tonnage". Previous studies, such as Argyropoulos et al. (2023) and Marson et al. (2023), focused on the separation and valorisation of Kraft Lignin and the associated environmental consequences by adopting this strategy. Witthayolankowit et al. (2024) study investigates the environmental sustainability of the valorization of Tops and Branches (which are materials from forestry that are either left in the forest or collected and incinerated to a low value) with the production of biofuels from lignin.

Lebedeva and Samec (2023) instead, investigated the possibility of valorising the hemicellulose extracted in the pre-hydrolysis step to obtain hydrocarbons in the biofuel range. The aim of this thesis work is to assess the environmental impacts and hotspots of an Integrated Dissolving Grade Pulp Biorefinery performing such separation and valorization.

A short description of the hemicellulose to hydrocarbons value chain will follow, but it is noteworthy that the proposed process is still at a conceptual level, with all the data and results based on laboratory research by Lebedeva and Samec (2023).

The starting raw material is birch wood in the form of wood chips that firstly undergoes to a pre-hydrolysis step to take away hemicellulose. The pre-hydrolysis treated wood then is sent to the Kraft pulping process and subsequent bleaching to achieve the desired regenerated cellulose for textile fibres production. The Pre-Hydrolysis liquor is used to produce furfural and then directly hydro-processed to generate pentane and higher liquid hydrocarbons that can be potential candidates to be used as green fuels.

A conceptual scheme for the hemicellulose recovery and upgrade is shown in Figure 3.1
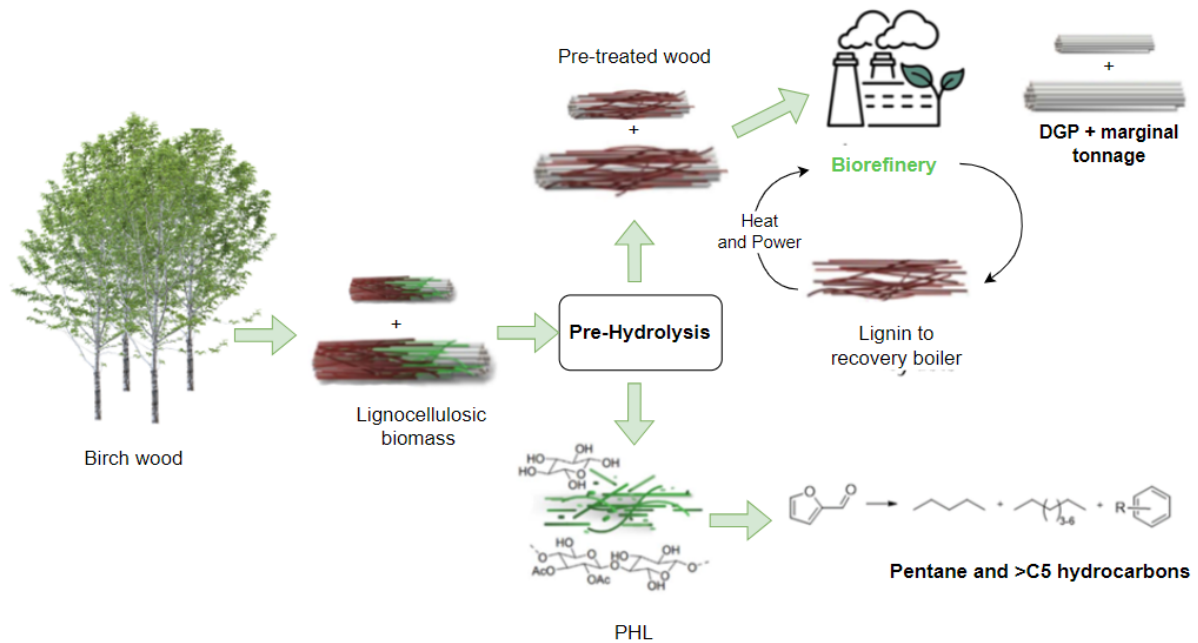
Figure 4.1. DGP and PHL proposed value chains.

A more detailed Block Flow diagram of the proposed process is shown in Figure 4.2 and described in §4.1.3 discussing the system boundaries of the cLCA study.

3.1 Pre-Hydrolysis step

The starting lignocellulosic biomass is from birch wood as it is considered a favoured species to produce pre-hydrolysis kraft pulp. The composition determined by Lebedeva and Samec (2023) through a standardized protocol is reported in Table 3.1.

Table 3.1. *Birch wood composition*

PRE-TREATED BIRCH WOOD COMPOSITION	
Component	**Quantity (wt%)**
Cellulose	32.40
Hemicellulose	25
Of which xylose	32
Lignin	19
Bark	7.55
Sawdust	0.60

After harvesting the birch wood is chipped into wood chips. In the Pre-Hydrolysis step birch wood chips undergoes stirring in an autoclave and heated up to 200°C, within 40 minutes 97 wt% of the xylan, which is the component we are interested in, was solubilized in the pre-hydrolysis liquor. In this condition a pre-hydrolysis liquor composed mostly by hemicellulose is obtained with a small presence of glucans in 0.4 wt%.

3.2 De-hydration to furfural

The xylose (the main monomer of xylan chains) in the pre-hydrolysis liquor can be further converted into furfural through zeolites with a defined pore size, these catalysts can give a confinement control to avoid the formation of humin as side-product from condensation reactions resulting from the hemicellulose hydrolysis. Lebedeva and Samec (2023) states that using Beta zeolites with a SiO_2/Al_2O_3 molar ratio of 25 a conversion of 83% of xylose to furfural can be obtained. The reaction was performed at 180°C in a dioxane/water mixture 20:1 and after 2h the Yield to furfural reached a value of 94%, and from the stoichiometry of the reaction (3.1), for every molecule of furfural obtained, 3 molecules of water are produced.

(3.1)

Particular attention must be given to the choice of solvents to be used in the chemical industry, they are responsible for a major part of the environmental performances of the processes, representing in many cases the hot-spots from a sustainability point of view, impacting at the same time on costs, safety and health related hazards. Moreover, different indirect environmental impacts are associated with the use of solvents in a chemical process, such as resource depletion when producing petrochemical based solvent, emissions due to their incineration of high energy investments for their separation and recycling. 1-4 Dioxane is a hazardous solvent with high persistency, flammability and reactivity. Capello et. al reported the performances of different solvents regarding their intrinsic hazards and environmental impacts through their life cycle. Dioxane is characterized by high EHS scores indicating elevated safety and health hazards; from a life-cycle perspective its responsible for

environmental impacts related to its production and when incinerated doesn't provide high environmental credits due to its low net calorific value.

De-hydration of xylose can be carried out also through the implementation of Ethyl acetate as solvent which is a safer chemical from the intrinsic hazards point of view but present the same Life-cycle related problem of dioxane. Ethyl acetate is made from ethanol, which can be produced from the fermentation of biomass, solving the problem of fossil resource depletion and significantly reducing the global worming potential related to ethyl acetate usage. Thus, de-hydration of xylose to obtain furfural was then performed in ethyl acetate under the same condition, giving a lower yield of furfural equal to 74% but achieving better environmental performances.

3.3 Hydro-processing to obtain hydrocarbons

A direct hydrotreatment was hypothesized to obtain a mixture of pentanes and higher hydrocarbons from furfural. The oxygen content in the bio-based feed may give rise to uncontrolled exothermic reactions during hydrotreating, a way to control these reactions is the implementation of a liquid carrier. For this reason, when hydro-processing furfural in a continuous process, the implementation of a hydrocarbon carrier liquid constituted by the pentane produced could allow a 100% biobased feed to the reaction. The Hydro-Deoxygenation reaction was run at 400°C with a Hydrogen pressure of 10 bar and using Pd/C and ZSM-5 zeolites as catalysts. Under these conditions we achieved a full consumption of the starting material and full deoxygenation, with a yield of 34.4 wt% to Pentane, 6.6 wt% to saturated higher hydrocarbons (decane) and 3.5 wt% to aromatics (1-ethyl 2,4-dimethylbenzene).

$$\text{furfural} + 6H_2 \longrightarrow \text{pentane} + 2H_2O \tag{3.2}$$

$$2\times\text{furfural} + 7H_2 \longrightarrow \text{1-ethyl 2,4-dimethylbenzene} + 4H_2O \tag{3.3}$$

$$2\times\text{furfural} + 11H_2 \longrightarrow \text{decane} + 2H_2O \tag{3.4}$$

$$\text{furfural} + 7H_2 \longrightarrow \text{butane} + CH_4 + 2H_2O \tag{3.5}$$
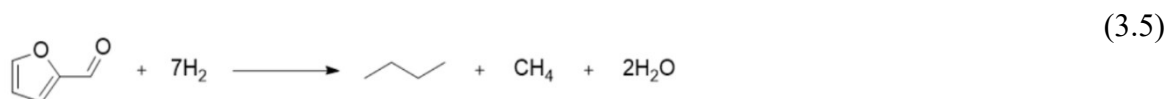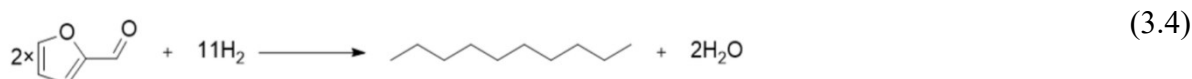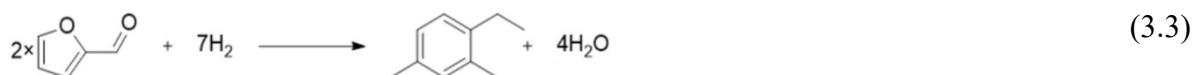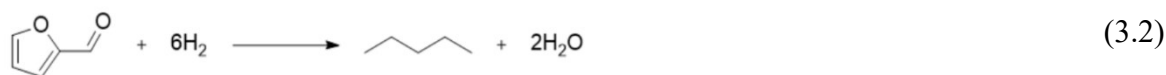
During HDO reactions C_4 intermediates are produced *via* furfural decarbonylation with a product ratio $C_4:C_5$ of 1:2., assuming that the C_4 intermediates are converted to butane, the off gasses of the HDO process are butane, CH_4 and biogenic CO_2. then for every reaction also water is produced as shown in (3.2) to (3.5) reactions.

3.4 Hydrogen manufacturing Unit

Furthermore, a hydrogen manufacturing unit was hypothesized to recover green hydrogen from Butane and CH_4 produced from the HDO reactions *via* steam reforming and water gas shift reactions. The water produced in the previous sections might be used after separation and treatment to integrate the steam needed. The green hydrogen generated can be recycled in the plant to partially satisfy the hydrogen demand in the HDO section.

$$\wedge\!\!\!\vee \quad + \quad 8H_2O \quad \longrightarrow \quad 13H_2 \quad + \quad 4CO_2 \tag{3.6}$$

$$CH_4 \quad + \quad 2H_2O \quad \longrightarrow \quad 4H_2 \quad + \quad CO_2 \tag{3.7}$$
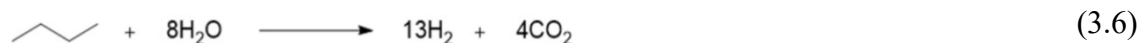
Given the exothermic behaviour of the hydrotreating reactions, heat is produced which is assumed to be exploited to generate the steam needed and to keep the high temperatures required by the endothermic steam reforming reactions.

Chapter 4

The Life-Cycle Assessment study

Life Cycle Assessment is a systematic and comprehensive method to investigate and evaluate the environmental impacts associated with a product, a process or a service with a life-cycle perspective. LCA is a powerful tool to identify the risks and opportunities for improvement related to a product system, it is useful for decision-making to promote sustainability in various industries.

LCA is regulated by ISO 14040 and ISO 14044 and provide the standard definition: "Compilation and evaluation of the inputs, outputs and the potential environmental impacts of a product system throughout its life cycle".

LCA studies are structured in four main phases:

1. Goal and scope definition: the objectives of the assessment, the functions of the system and its system boundaries are clearly defined.

2. Life Cycle Inventory analysis (LCI): Compilation of the inventory with all inputs and outputs through data collection, mass and energy balances.

3. Life Cycle Impact Assessment (LCIA): The potential environmental impacts are evaluated from the inventory flows. Every inventory flow is assigned to an impact category and characterized into potential environmental impacts through Category indicators.

4. Interpretation: The final step focusses on the interpretation of the LCA results and to draw conclusions to assess the significance of the environmental impacts, to identify the key contributions to the impact categories and to identify opportunities to improve the product system.
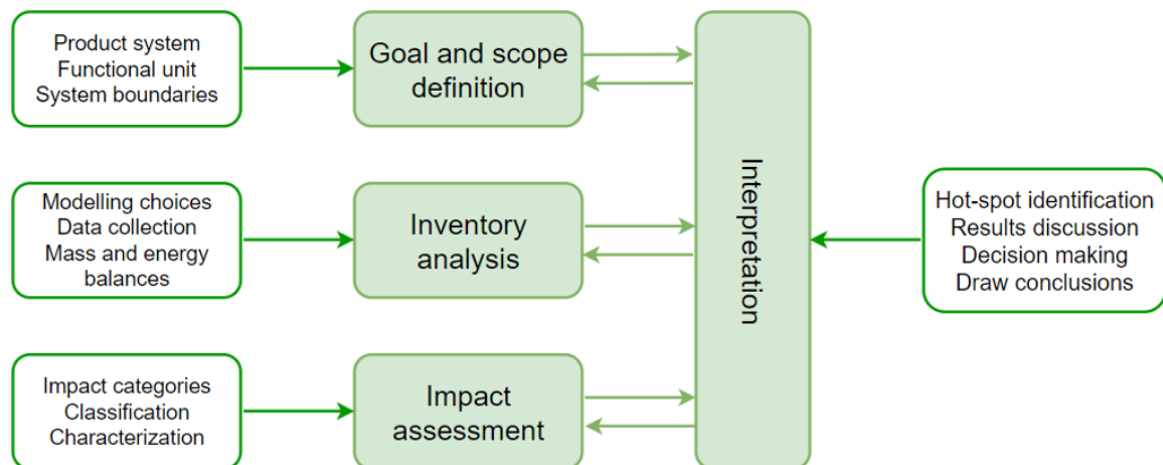
Figure 4.1. *LCA structure*

4.1 Goal and Scope Definition

The study is carried out with the intentions to give a clear representation of the potential environmental impacts of an integrated process to produce high value co-products from the side-streams of the DGP industry and to compare its performances with the same kraft pulping process producing regenerated cellulose for the DGP production with the aim of decision making between the two process management approaches.

The reason behind the study is the necessity to find a way to meet the major needs and challenges of this century without compromising the health and the needs of the future generations, i.e. without negatively affecting climate change, land use, resource depletion or water scarcity and pollution.

LCA studies can be performed following a consequential (cLCA) or an attributional (aLCA) approach. This study follows a consequential methodology, usually considered a more complete approach because it takes into account both the direct impacts and the consequences of a change in the elementary flows and changes in the market, this means considering all the chain effects, giving an overall view of the impacts associated with this product system. On contrary, the attributional approach directly attributes the environmental impacts to their source, without considering the chain effects when the elementary flows change. Another advantage of consequential approach is that it avoids the use of allocation procedures: allocation is necessary in attributional LCA when different co-products are addressed by the

product system and it's difficult to attribute an impact to a product or another, in such cases allocation by different criteria like mass or profit given by the products. According to the suggestions of ISO 14040 and ISO 14044, allocation has been avoided thanks to the consequential approach, allowing to account for all the chain effects when a change in the elementary flows or a change in the market occur.

The study is representative in a North Europe context (constituted by Sweden and Finland), with a broader European context investigated subsequently with in the sensitivity analysis.

The key audience for this study are the scientific communities of forestry, textile, biofuel production, chemical engineering and LCA. Hopefully, the study will also reach outside the scientific community in the same sectors.

4.1.1 Product System and Functional Unit

The definition of the Product System is part of the Goal & Scope definition, it represents the collection of the Unit Processes, connected by material and energy flows, that perform one or more defined functions inside the system under study and which defines the Life Cycle of a product. The Unit Process is the smallest element considered in the Life Cycle Inventory Analysis, for which all the inputs and outputs are specified.

The Product System for this work is the DGP Biorefinery Process integrated with the hemicellulose extraction from pre-hydrolysis liquors and upgrading to hydrocarbons described in Chapter §3.

The Product System was investigated and compared under two different Scenarios:

❖ A first Scenario (S1-Burn) representing the kraft pulping with a pre-hydrolysis stage for hemicellulose extraction and subsequent burning in a co-generation plant to generate heat and power from a bio-based material.

❖ A second scenario (S2-HC) in which the hemicellulose extracted in the pre-hydrolysis section is upgraded to pentane and higher hydrocarbons in a biofuel range, the hemicellulose residues are burnt in a co-generation plant to deliver heat and power.

The Functional Unit purpose is to give a reference value to which all the input and outputs data to the Unit Process are normalized when building the inventory of the Product System, furthermore it will be a useful basis to quantify the performances of the product system.

The Functional Unit for this Product System will be 1 Kg of Unbleached grade pulp.

4.1.2 System boundaries

The system boundaries define which processes will be included in the LCA study, depending on functional limitations, territorial limitations, temporal limitations, or cut-off rules.

A "Cradle to gate" approach was chosen, i.e. every unit process from the raw materials extraction to the output of the kraft pulping process are accounted for.

The bleaching process of the pulp to achieve the desired grade for DGP was excluded from the scope of the study since the complexity of the process, associated with all the chemicals needed for bleaching, would strongly affect the results, giving a difficult interpretation of the impact assessment results, diverting from our attention the impacts associated with only the hemicellulose extraction and the hydrocarbons value chain. The use phase and the end-life of the dissolving pulp are equal in both the scenarios to be compared, and since the FU delivered is the same, these stages can be excluded as well without affecting the results of the comparison according to ISO 14044. For kraft pulping processes, pre-hydrolysis liquor upgrading process to biofuels and for the whole product system a series of diagrams for system boundary are depicted in Figures 4.2 – 4.5.
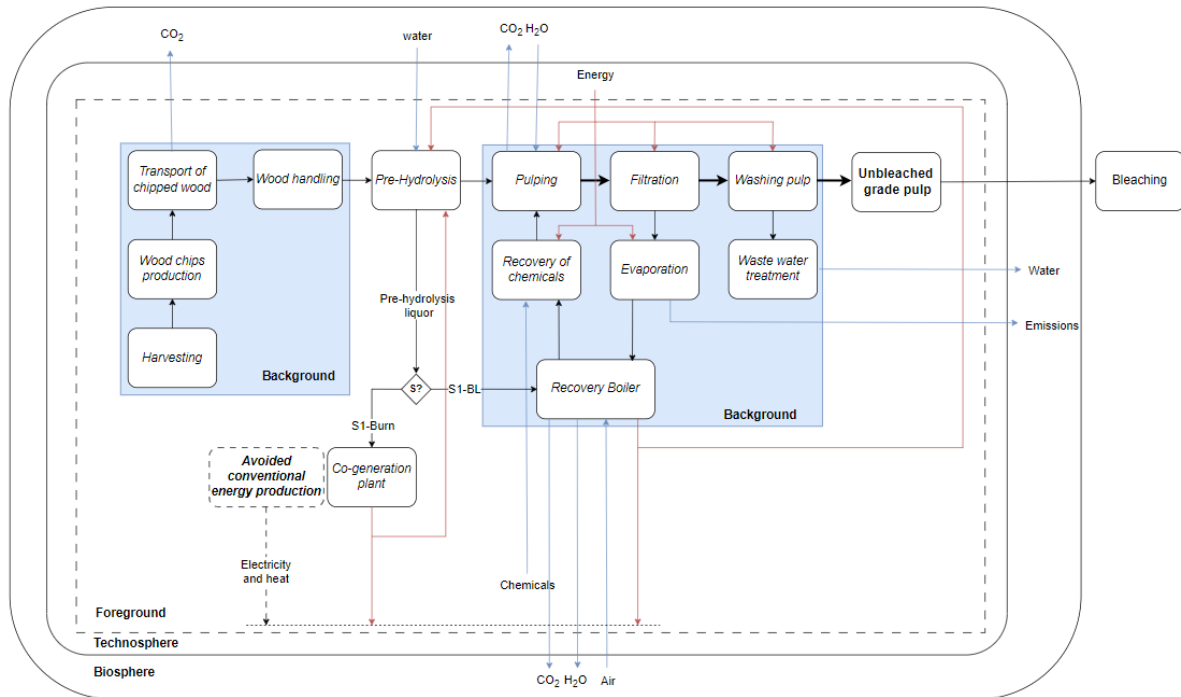
Figure 4.2. *System boundaries for S1-Burn, hemicellulose extraction via pre-hydrolysis and incineration in co-generation plant for heat and power production.*
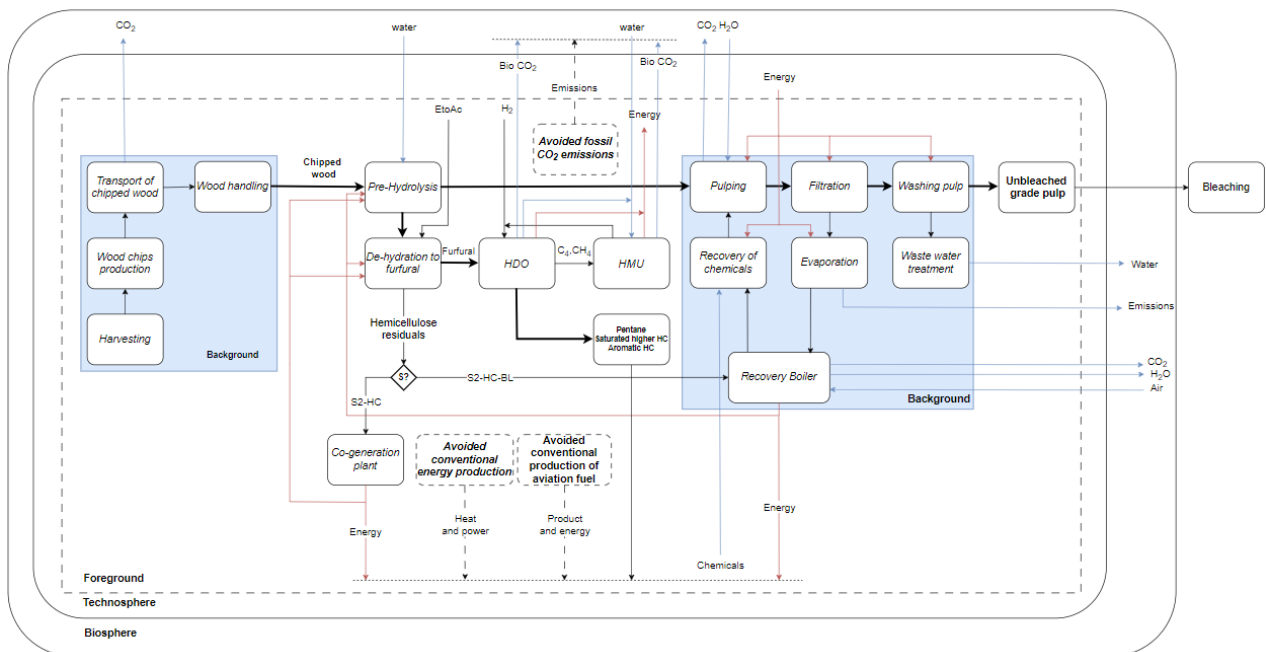
Figure 4.3. *System boundaries for S2-AF, hemicellulose extraction, upgrade to hydrocarbons and incineration in co-generation plant or recovery boiler for heat and power production.*
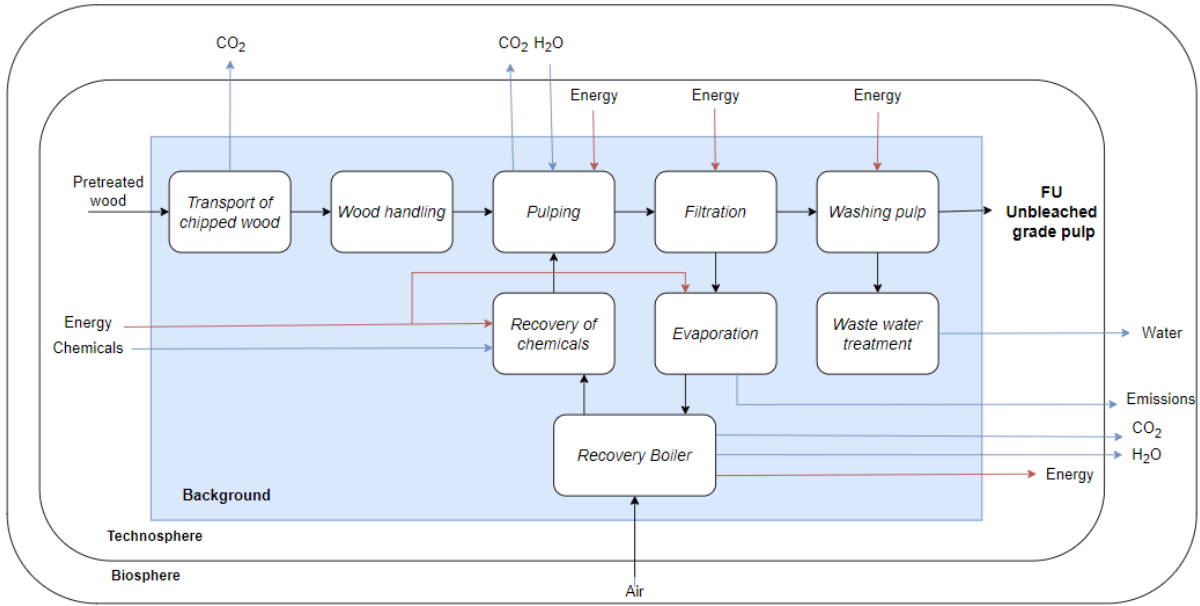
Figure 4.4. *Kraft pulping process, treated with a black-box approach.*
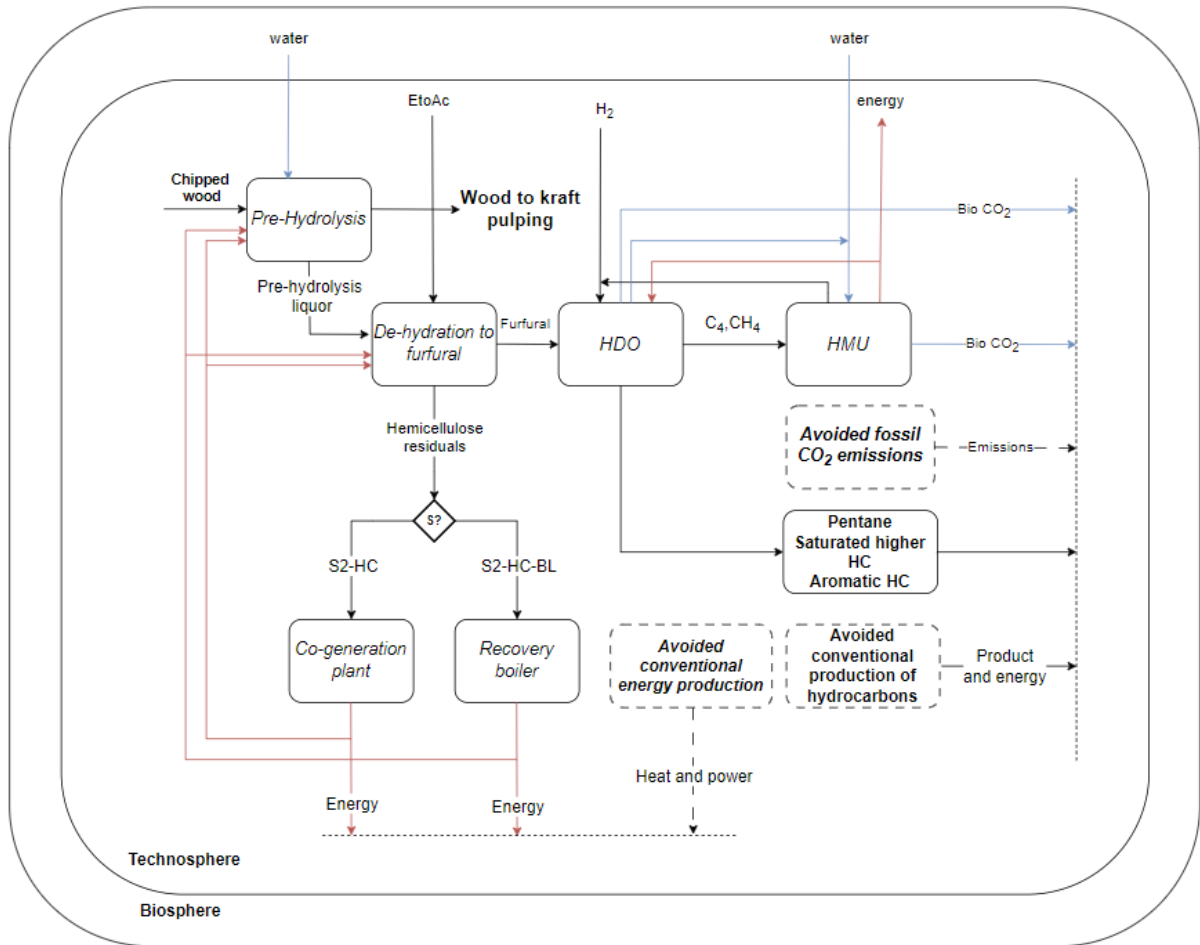
Figure 4.5. *System boundaries for hemicellulose extraction via pre-hydrolysis and upgrade to hydrocarbons, incineration of residues in co-generation plant or recovery boiler for heat and power production.*

In the inventory analysis phase, which will be discussed in §4.2, all the unit processes nested in the kraft pulping process shown in Figure 4.4, data retrieved from Ecoinvent 3.9.1 database, were calculated together with a black box approach. In all the system boundaries schemes reported there is a distinction between background and foreground frameworks, for the unit processes in the background, secondary data has been used. For the foreground, primary data has been used for yields of unbleached pulp and mass balances of the upgrading value chain. Secondary data has also been used in the foreground to estimate the theoretical energy consumption in the unit processes.

4.2 Life-Cycle Inventory analysis (LCI)

The LCI phase comprises the quantification and compilation of all the inputs and outputs related to the flows inside the product system through its entire Life Cycle or within the system boundaries.

4.2.1 Inventory building in SimaPro

Data processing and system modelling was carried out using the LCA software SimaPro (v9.5.0.2) and background data from Ecoinvent 3.9.1. EF 3.0 version 1.01 (2019) was the methodology chosen for the impact assessment.

For the pulping process, secondary data was retrieved from Ecoinvent 3.9.1 consequential and adapted to a hardwood-based starting material and neglecting all the chemicals involved in the bleaching step.

The calculation of constant scaling factors was the most conservative approach to adapt all the elementary flows to a hardwood biomass input, given that no datasets related to the production of unbleached pulp from hardwood (UPH) were available in Ecoinvent 3.9.1 consequential. These scaling factors were calculated as the ratio (4.1) between the total amount of wood input in the case of bleached pulp from hardwood (BPH) and bleached pulp from softwood (BPS). The dataset was finally built applying the scaling factor of 0.89 for every elementary flow through the simple equation (4.2), except for "pulpwood, hardwood, measured as solid wood under bark" and "wood chips, wet, measured as dry mass" for which

the scaling factors calculated were 1,03 and 0.234 respectively. The dataset built can be found in Table A1 in the Appendix section.

$$CSF = \frac{Kg \ of \ wood \ input \ (BPH)}{Kg \ of \ wood \ input \ (BPS)}$$

(4.1)

$$UPH = CSF \times UPS$$
(4.2)

Sources of data used in the study are summarized in Table 4.1.

Table 4.1. *Data sources*

DATA SOURCE DISTINCTION		
	Data type	**Data source**
Kraft pulping dataset	Secondary	Ecoinvent 3.9.1 consequential
Birch wood composition	Primary	Laboratory
Yield to Unbleached pulp	Primary	Laboratory
Yield of pre-hydrolysis liquor	Primary	Laboratory
Yields in the hydrocarbons value chain	Primary	Laboratory
Yield to hydrocarbons	Primary	Laboratory
Catalysts consumption	Secondary	Witthayolankowit et al. (2023)
Solvents and chemicals consumption	Calculated	Laboratory
Carbon content in wood fractions	Secondary	Ecoinvent 3.9.1 consequential
Low Heating Value of Black liquor	Secondary	Ecoinvent 3.9.1 consequential
Low Heating Value of hemicellulose	Secondary	Furlan et al. (2013)
Low Heating of Value lignin	Secondary	Energimyndigheten
Recovery boiler efficiency to heat and electricity.	Calculated	Ecoinvent 3.9.1 consequential
Co-generation plant efficiency to heat and electricity.	Secondary	Ecoinvent 3.9.1 consequential

4.2.2 Mass and Energy balances

The mass balances needed to calculate the material flows in the inventory of the product system were carried out on the basis of primary data from laboratory previous analysis and measurements.

The amount of starting birch wood was calculated on the basis of the amount of pre-treated wood material needed to produce 1 kg of unbleached sulfate pulp, calculated when the dataset for the pulping of hardwood was build following the procedure described in §4.2.1.

The amount of pre-treated wood needed to produce 1 kg of pulp is 2,26 kg and it is composed mainly of cellulose and lignin after the pre-hydrolysis step. Lebedeva and Samec (2023) report a hemicellulose extraction efficiency of 97%, given the composition of birch wood (Table 3.1) the amount of starting wood is equal to 2.98 kg.

As previously mentioned in §2.1, for bleachable pulps the degree of cooking is soft, obtaining a lignin content from 1.8% to 2.4% when dealing with hardwoods. For this reason, a strong delignification of 98% is assumed, obtaining an Unbleached Sulfate Pulp with a composition of 96.6% cellulose, 2.2% of hemicellulose and 1.1% of lignin.

The amount of water needed in the pre-hydrolysis unit process is ten times the amount of startin wood material, but a recovery and recycle system was assumed with a loss of 5% of water each cycle, the water loss was set as an emission to air to adopt a conservative approach, the loss set as an emission to water would imply a benefit in the Water use impact category during the LCIA phase thanks to the reintroduction of water in a basin.

The amount of ethyl acetate used for Furfural production was 11.5 times the amount of PHL during the laboratory experimentation phase, the proportion was assumed to be constant when adapting the amount of ethyl acetate for 1 kg of pulp. A such large amount of ethyl acetate would represent a crucial hot-spot for the process from an environmental point of view. A separation and recycling of the solvent from Furfural and water would be the best practice in an industrial scale to lower the environmental burdens, health hazards and costs. An assumption of 2% loss of solvent every 5 runs was assumed and tested through the simulation of a distillation column and a decanter with Aspen Plus software. An almost complete separation of ethyl acetate resulted with a loss < 1%, supporting the hypothesis and significantly lowering the associated environmental impacts.

The modelling of the consumption of catalysts during De-hydration and HDO processes was based on the LCA study by Witthayolankowit et al. (2023), the amount of zeolites and palladium was set equal to the usage of such catalysts in the hydrotreating sections of Diesel production in petroleum refinery operations , the value was retrieved from the dataset "Disel, low-sulfur, diesel production, low-sulfur, petroleum refinery operations" from Ecoinvent

3.9.1 consequential. The catalyst bed will be more consumed using the bio-feed as compared to traditional fossil feeds such as vacuum gas oils, both because more material passes through the catalyst bed (factor 1.8) as well as the bio-feed contains more oxygen and this will wear the catalyst by an estimated factor of 3 as compared to vacuum gas oils according to Witthayolankowit et al. (2023);   Thus, all the input data of the database concerning the catalyst bed is multiplied by a factor of 5.4 to compensate for this.

The amount of hydrogen demand in HDO process and retrieved from the HMU process was calculated from the stoichiometry of the reactions in §3.3 and used to calculate the make-up. Industrially, the hydrogen used in hydrotreating operations is in strong excess, a recycling of the excess was assumed. This considerably lowers the demand of hydrogen by 78%.

The characterization and quantification of the HDO products by Lebedeva and Samec (2023) was performed through GC-MS/FID, the Yields of hydrocarbons were defined as:

$$Y \ [wt\%] = \frac{m_{prod}}{m_{sm}} \times 100$$

(4.3)

The input and output flows for the inventory analysis of the product system calculated from the mass and energy balances are listed in Table 4.2.

Table 4.2. *Inventory input and output data for conversion of birch wood to USP for DGP and hydrocarbons production.*

FORESTRY HARVESTING

Input	value	Unit	Data source
Birch wood, standing	2.98	kg	Calculated data
Diesel	0.00418	kg	Ecoinvent v3.9.1
Output			
Birch wood	2.98	kg	Calculated data

CHIPPING

Input	Value	unit	Data source
Birch wood	2.98	kg	Calculated data
Diesel	0.005	kg	Ecoinvent v3.9.1
Output			
Birch wood chips	2.98	kg	Ecoinvent v3.9.1

PRE-HYDROLYSIS

Input	Value	unit	Data source
Birch wood chips	2.98	kg	Calculated data
Water, river (5% make-up)	1.49	dm^3	Primary data
Output			
Wood without hemicellulose	2.26	kg	Primary data
Pre-hydrolysis liquor	0.723	kg	Primary data
Water, air emission	1.49	dm^3	Primary data

PULPING

Input	Value	Unit	Data source
Wood without hemicellulose	2.26	kg	Primary data
Electricity	0.126	kWh	Secondary data
Other Chemicals	See Table A1		Secondary data
Output			
Unbleached pulp	1	kg	Primary data
Heat	1.119	MJ	Secondary data
Electricity	0.122	kWh	Secondary data
Emission to air	See Table A1		Secondary data
Emission to water	See Table A1		Secondary data

DE-HYDRATION

Input	Value	unit	Data source
Pre-hydrolysis liquor	0.723	kg	Primary data
Ethyl acetate (make-up)	0.0332	kg	Calculated data
Zeolites	0.000244	kg	Secondary data
Output			
Furfural	0.11	kg	Calculated data
Hemicellulose residuals	0.552	kg	Calculated data
Water	0.0619	dm^3	Calculated data

HYDROTREATMENT (HDO) OF FURFURAL

Input	value	unit	Data source
Furfural	0.11	kg	Calculated data

Hydrogen (make-up)	0.00254	kg	Calculated data
Pd catalyst	1.1E-07	kg	Ecoinvent v3.9.1
Zeolites	0.000244	kg	Ecoinvent v3.9.1
Output			
Pentane	0.0377	kg	Calculated data
Kerosene	0.0111	kg	Calculated data
Water	0.032	dm^3	Calculated data
Butane	0.0152	kg	Calculated data
Methane	0.00419	kg	Calculated data
CO_2 biogenic	0.0207	kg	Calculated data

HYDROGEN MANUFACTURING UNIT (HMU)

Input	value	unit	Data source
Butane	0.0152	kg	Calculated data
Methane	0.00419	kg	Calculated data
Water	0.0151	dm^3	Calculated data
Output			
CO_2 biogenic	0.0578	kg	Calculated data

INCINERATION in co-generation plant (S1-Burn)

Input	value	unit	Data source
Lignin in black liquor	0.555	kg	Calculated data
Hemicellulose residuals	0.718	kg	Calculated data
Output			
Power	0.592	kWh	Calculated data
Heat	6.39	MJ	Calculated data

INCINERATION in co-generation plant (S2-HC)

Input	value	unit	Data source
Lignin in black liquor	0.555	kg	Calculated data
Hemicellulose residuals	0.552	kg	Calculated data
Output			
Power	0.5	kWh	Calculated data
Heat	5.2	MJ	Calculated data

Table 4.3. *Low Heating Values*

Low heating values of components in the Black Liquor		
Component	**LHV [MJ/kg]**	**Data source**
Hemicellulose	16.4	Furlan et al. (2013)
Lignin	21.6	Energimyndigheten
Black Liquor	19.8	Ecoinvent v3.9.1 consequential

The LHVs where useful to calculate the theoretical energy that can be obtained burning the amounts of Lignin and hemicellulose in the black liquor for a conventional kraft mill

producing 1kg of Pulp. These values where compared to the heat and power listed as co-products in the dataset calculated from Ecoinvent 3.9.1 consequential. The efficiency of the recovery boiler was calculated to be 13%, with an overall efficiency towards electricity and heat of 3.7% and 9.3% respectively.

For both S1-Burn and S2-HC secondary data for the values of efficiencies to heat and electricity from a co-generation unit were taken from Ecoinvent 3.9.1 and are 45% and 15% respectively (Table A11 §Appendix).

The heat needed in UP1 and UP2 for the pre-hydrolysis and de-hydration is assumed to be taken from the recovery boiler of the mill. This assumption will be tested during the sensitivity analysis phase.

A representation of the mass balance for the hemicellulose valorization chain is shown in Figure 4.6.
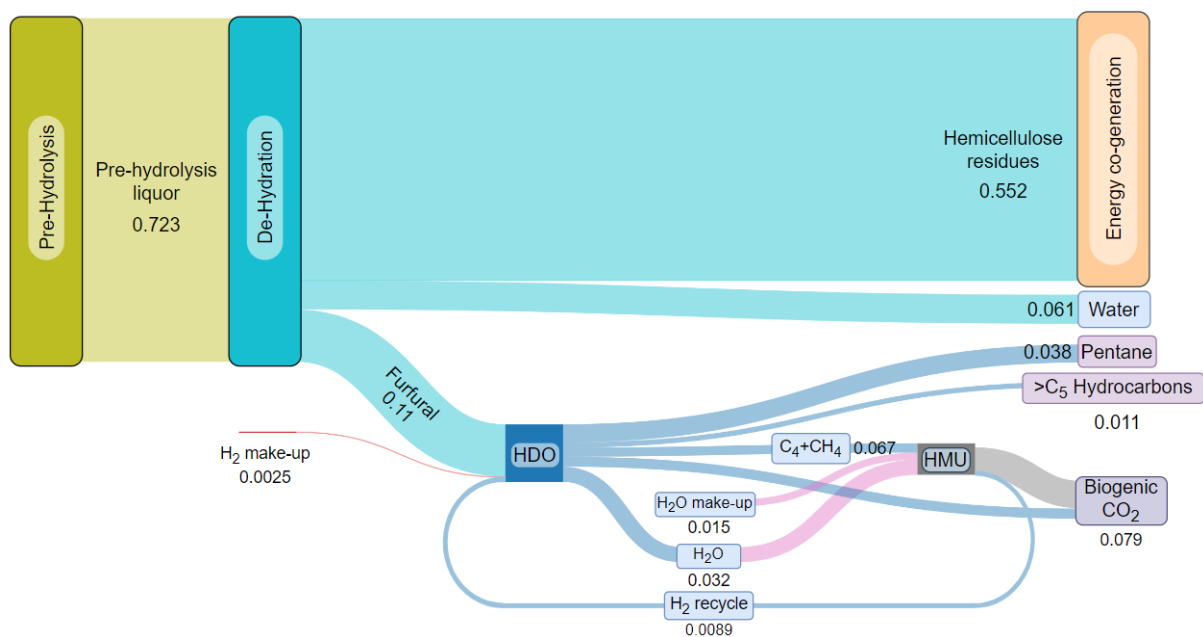
Figure 4.6. *Mass balance for hemicellulose valorization chain, all values are expressed in [kg]*

4.2.3 Modelling strategies

Building the inventory in SimaPro means developing a structure of datasets linked together by the inputs and outputs, the product system was divided into two unit processes for S1-Burn and four unit processes for S2-HC.

Datasets in SimaPro are treated like black boxes, when building one all the inputs and outputs need to be specified and divided into different areas of concern:

- ❖ The Main Product delivered by the dataset which can be a material or energy related, the units need to be specified and a brief description of the dataset may be included.

- ❖ The Avoided products are the co-products delivered by the unit process, the term "avoided" means that the material or the energy produced avoid the production of the same amount through the conventional production pathways. The avoided products can be listed also in the input section with a minus sign.

- ❖ The inputs are divided in three sections: from nature; from Technosphere: materials/fuels; from Technosphere: electricity/heat, depending on the source and the nature of the input.

- ❖ Emissions are the outputs that doesn't represent a product or co-product and can be divided in emissions to air or to water depending on the destination of the flow.

- ❖ All the output flows that represent a waste material of the process are listed in the "Waste to treatment" section.

The top dataset is the one delivering the Functional Unit to which all the other datasets are linked through a network and scaled according to the FU, the top dataset under study is the dataset counting for the kraft pulping process and the incineration of the black liquor in the recovery boiler of the mill. The dataset with all the flows can be found in Table A1 in the Appendix section.

The dataset of the first unit process (UP1) represents the pre-hydrolysis of the starting material, present in both S1-Burn and S2-HC. In this unit processes the two value chain are separated, the main output is the pre-treated wood to be sent to the Kraft Pulping UP and the avoided product is the amount of Pre-Hydrolysis liquor that will be burnt in the co-generation facility (S1-Burn scenario) or will undergo the hydrocarbons route (S2-HC scenario). The input and the emission flows can be found in Table A2 in Appendix section.

The second unit process (UP2) represent the de-hydration of xylose in the PHL to furfural. The main function of this unit process is the consumption of the PHL, thus the main product is the amount of PHL with a minus sign and the avoided product is the amount of furfural produced, which will be listed as the consumption in UP3.

The hemicellulose residues which are comprised of the other compounds not converted to furfural will be burnt in the co-generation plant, for this reason a dataset for the generation of energy from the co-generation plant was built. In such dataset, the main product is 1kg of hemicellulose burnt, the input is another dataset which count for the impacts related to the combustion of wood-based materials, the avoided products are the heat [MJ] and electricity [kWh] produced from burning 1kg of hemicellulose and calculated through the LHV [MJ/kg] of the material and the efficiencies of the co-generation plant through equation 4.4 and 4.5. With this methodology, in UP2 the only dataset to be recalled is the one for the combustion of hemicellulose in the co-generation facility specifying only the amount in kg of the residues. For sake of clarity, the dataset is reported in Table A10.

$$Heat\ [MJ] = m_{biomass}[kg] \times LHV\left[\tfrac{MJ}{kg}\right] \times \eta_Q \tag{4.4}$$

$$Electricity\ [kWh] = m_{biomass} \times LHV\left[\tfrac{MJ}{kg}\right] \times \eta_{el} \tag{4.5}$$

The last unit process of the hydrocarbons production pathway is UP3, which treat as a black box the HDO and HMU steps together. The main function is the consumption of furfural, thus in the main product section the amount of furfural is set with a minus sign and the avoided products are the pentane and the >C5 hydrocarbons which are modelled as substitution of kerosene in the software. Even though the hydrocarbons are the main products of the side value chain it is correct to list them as avoided products because the production from fossil-based raw materials is avoided and substituted with the production from a bio-based source. Two datasets were built for pentane and kerosene in which the avoided production of pentane and kerosene from a conventional pathway is specified. To account for the emission of Biogenic CO_2 at their end of life, a dataset named "Avoided CO_2" was built in which in the "emission to air" field, for 1 kg of Biogenic CO_2 produced 1kg of fossil CO_2 is avoided. This dataset is recalled in the input section of the pentane and kerosene datasets specifying the amount of CO_2 released by these products at their end of life and calculated as:

$$Bio\ CO_2 = \frac{MW_C \cdot n_C}{MW_{HC}} \cdot \frac{MW_{CO2}}{MW_C} \quad (HC: C_5H_{12};\ kerosene) \tag{4.6}$$

The datasets for the pentane and kerosene products can be found in Tables A5-A6, while the dataset for the Avoided fossil CO_2 is shown in Table A7 in Appendix section.

The black box methodology allows us to list in this process only the make-up of hydrogen needed in the HDO process and only the make-up of water needed to generate the steam excess needed in the MSR and WGS reactions. The biogenic CO_2 produced by both processes is listed as an emission to air. As explained in section §3.4, the heat generated from HDO is entirely exploited to provide the heat necessary in the HMU section, in this way there are no terms related to energy in this UP. The dataset structure of UP3 can be found in Table A4 in Appendix A section.

To model the consumption and production electricity in the product system, an average of the marginal electricity of Sweden and Finland was considered, then for heat the substitution of biomass and coal were adopted for Sweden and Finland according to the procedure described by Marson et al., (2023). Datasets related to the consumption and production of heat and electricity can be found in Tables A8-A9 of Appendix A section.

4.3 Life-Cycle Impact Assessment (LCIA)

LCIA step is comprised of two mandatory phases and two optional phases. The first is the Classification, which is the assignment of the material/energy flows listed in the LCI to the appropriate EF (Environmental Footprint) impact category. For example, all the flows that may results in GHG emissions are assigned to the climate change impact category. It is important to underline that an input or output may contribute to more than one EF impact category. The second phase is the Characterization, which refers to the calculation of the contributions of each classified flow to their respective EF impact category through the characterization indicators of each EF Impact category. The characterization indicators are reference units that represent the intensity of a classified input or output relative to a common reference impact given by a reference substance. For example, when calculating the impacts to climate change, all the GHG emissions given by the flows classified into the climate change category are weighted in terms of their intensity relative to the one of Carbon Dioxide. This allows the aggregation of all the potential impacts and the expression of the impacts with a unique reference unit. Normalizing and Weighting are the non-mandatory phases, Normalization is the step in which the life cycle impact assessment results are multiplied by normalisation factors to calculate and compare the magnitude of their contributions to the EF

impact categories relative to a reference unit. As a result, dimensionless, normalised results are obtained. Weighting supports the communication of the results by multiplying the normalized results by a set of weighting factors (in %) which reflect the perceived relative importance of the life cycle impact categories considered. ISO 14044 states that weighting shall not me addressed when conducting comparative LCA intended to be disclosed to the public. These two optional phases are not addressed in this study.

4.3.1 Impact categories

The impact assessment results are displayed using 16 midpoint impact categories from the Environmental Footprint (EF) method 3.0 according to Zampadori & Pant (2019). Only five categories are presented and discussed in the main text: climate change (GWP-total), land use (SQP), water use (WDP), resource use of fossils (ADP-fossil), and mineral and metal resources (ADP-min&met). The performances of the different scenarios in all the 16 categories are shown in the Appendix Section.

The full set of impact categories and their related unit of measure is reported in Table 4.4.

Table 4.4. *List of impact categories and related models*

Impact category	Impact category indicator	Unit
Climate change	Radiative forcing as global warming potential	kg CO_2 eq
Ozone depletion	Ozone Depletion Potential	kg CFC 11 eq
Ionising radiation	Human exposure efficiency relative to U^{235}	kBq U-235 eq
Photochemical ozone formation	Tropospheric ozone concentration increase	kg NMVOC eq
Particulate matter	Impact on human health	disease inc.
Human toxicity, non-cancer	Comparative Toxic Unit for humans	CTUh
Human toxicity, cancer	Comparative Toxic Unit for humans	CTUh
Acidification	Accumulated Exceedance	mol H^+ eq
Eutrophication, freshwater	Fraction of nutrients reaching freshwater end compartment (P)	kg P eq
Eutrophication, marine	Fraction of nutrients reaching marine end compartment (N)	kg N eq
Eutrophication, terrestrial	Accumulated Exceedance	mol N eq
Ecotoxicity, freshwater	Comparative Toxic Unit for ecosystems	CTUe

Land use	This index is the result of the aggregation, performed by JRC, of the 4 indicators provided by LANCA model as indicators for land use (Soil quality index, Biotic production, Erosion resistance, Mechanical filtration, Groundwater replenishment)	Pt
Water use	User deprivation potential (deprivation-weighted water consumption)	m^3 depriv.
Resource use, fossils	Abiotic resource depletion – fossil fuels	MJ
Resource use, minerals and metals	Abiotic resource depletion	kg Sb eq

It should be noted, however, that the LCA methodology is currently limited in the assessment of environmental aspects such as biodiversity according to Damiani et al. (2023), for which methodologies that can comprehensively capture all dimensions are not yet available.

The five impact categories will be referred as: GWP-total (climate change), SQP (Land use), WDP (water use), ADP-fossil (fossil resource use) and ADP-min&met (mineral resource use) for sake of brevity.

4.3.2 Contribution analysis

A contribution analysis was performed considering the main processes related to the environmental impacts in the different impact categories, in the specific the product system was divided in 7 groups:

- Raw materials: This group includes wood chips as a raw material for pulping, which is linked to the harvesting and chipping datasets, which are responsible for most of the impacts related to this group.

- Pulping and incineration: represents the dataset related to pulping, which include the chemicals involved in the kraft pulping process and all the emissions. In this group also the dataset related to the combustion of hemicellulose and the associated impacts are included.

- Solvents and chemicals: Here are grouped together the solvents and chemicals needed in the hydrocarbons production chain.

- Catalysis: address the impacts related to zeolites, molecular sieves and all the other catalysts involved in the hydrocarbons production chain.

- Avoided products: comprises the products from the hydrocarbons value chain, modelled as pentane and kerosene in SimaPro inventory.

- Avoided CO_2: comprises the datasets that model the avoided fossil CO_2 which is substituted with biogenic CO_2 when the hydrocarbons are used and burned.
- Energy: Comprised the consumption of energy and the avoid of energy from the grid, with the substitution with energy produced from biobased sources.

Such analysis was helpful since the benefits in climate change from production of energy from burning the residual biomass in a more efficient co-generation plant was large making difficult to understand the benefits from the avoided products and avoided fossil CO_2, a contribution analysis can disclose the results in a much clearer way.

4.3.3 Sensitivity analysis

The aim of the sensitivity analysis is to investigate the influence of different modelling and operating choices on the Scenarios, i.e. the sensitivity of the Scenarios when some parameters representing the modelling strategies are manipulated. Five sensitivity analysis were developed:

A first sensitivity analysis on the product system proposed was addressed to see the actual benefits of burning the pre-hydrolysis liquor in S1-Burn and the hemicellulose residue in S1-HC in a co-generation plant instead of exploiting the recovery boiler of the mill. The two scenarios with the incineration in the recovery boiler are called respectively S1-BL and S2-HC-BL, the input and outputs regarding the incineration are reported in Table 4.5.

Table 4.5. *Input and output structure for incineration in the recovery boiler of the mill.*

INCINERATION in recovery boiler (S1-BL)			
Input	**value**	**unit**	**Data source**
Lignin in black liquor	0.555	kg	Calculated data
Hemicellulose in black liquor	0.718	kg	Calculated data
Output			
Power	0.241	kWh	Calculated data
Heat	2.21	MJ	Calculated data
INCINERATION in recovery boiler (S2-HC-BL)			
Input	**value**	**unit**	**Data source**
Lignin in black liquor	0.555	kg	Calculated data
Hemicellulose residuals	0.552	kg	Calculated data
Output			
Power	0.213	kWh	Calculated data
Heat	1.95	MJ	Calculated data

Another sensitivity analysis was performed by a change in the location of the integrated pulp mill to an average European scenario, switching to a European network for heat and electricity through three parameters: RER, SE and FI and implemented as shown in Tables A8 and A9, §Appendix A.

Sensitivity analysis was implemented also to investigate a worse scenario where the yields to aviation fuels (modelled as kerosene) are decreased by 10%, assuming a constant yield of unbleached grade pulp. This was done by multiplying the amounts of pentane and kerosene in UP3 dataset by a parameter (1-LowY) where LowY could be switched from 0 to 0.1 to account for 10% less hydrocarbon products.

Another sensitivity analysis was useful to understand the consequences in decoupling the upgrading process from the kraft pulp mill, in this scenario another facility would buy the pre-hydrolysis liquor from the kraft pulp mill and couldn't exploit the energy retrieved from the mill to run the unit processes in the upgrading value chain. To calculate the energy necessary to vaporize the water make-up and keep the steam in the Pre-hydrolysis section at the operating temperature the specific heat at constant pressure for water in the liquid and gas state (Cp,l and Cp,g @25°C) and the standard enthalpy of vaporization ΔH_{vap} were retrieved from NIST Chemistry WebBook.

$$Q = Q_{heat,1} + Q_{ph} + Q_{heat,2}$$

(4.7)

$$Q_{heat,1} = m[kg] \cdot C_{p,l}^{25°C}\left[\frac{KJ}{kg \cdot K}\right] \cdot (T_{eb} - 298.15)[K]$$

(4.8)

$$Q_{ph} = m[kg] \cdot \Delta H_{vap}^{25°C}$$

(4.9)

$$Q_{heat,2} = m[kg] \cdot C_{p,v}^{25°C}\left[\frac{KJ}{kg \cdot K}\right] \cdot \left(T_{ref} - T_{eb}\right)[K]$$

(4.10)

Then the energy needed to heat up the make-up of ethyl acetate and the recycle of ethyl acetate was calculated.

Then the heat of reaction was calculated through:

$$Qr = \sum\nolimits_{Products} ni\ [mol] \times \Delta H°f \left[\frac{KJ}{mol}\right] - \sum\nolimits_{Reagents} ni[mol] \times \Delta H°f \left[\frac{KJ}{mol}\right]$$
(4.11)

The standard heats of formation $\Delta H°f \left[\frac{KJ}{mol}\right]$ and the Cp,l [KJ/mol*K] of ethyl acetate were calculated from NIST and the Perry's Chemical Engineering Handbook, 8th edition.

A last sensitivity analysis was carried out to see the influence on the results when changing the impact assessment method from the EF Method 3.0 to ReCiPe, 2016, (midpoint) H. In this method the following impact categories were addressed: Global Warming, Water consumption, Land use, Mineral resource scarcity and Fossil resource scarcity, but all the impact categories are as well reported in Table C5 in Appendix section C.

The five sensitivity analysis are investigated calculating the variance between the values of the impacts in the five representative categories for the study according to the formula:

$$Var\ [\%] = \left.\frac{Difference\ between\ scenarios}{Value\ of\ the\ scenario\ of\ reference}\right|_{all\ impact\ categories} \qquad (4.12)$$

Chapter 5

Interpretation of the results

5.1 LCIA Results and discussion

Impact assessment was performed to compare the impacts of the two scenarios, the results for both scenarios and the variance are reported in Table 5.1:

Table 5.1. *Impact assessment of unbleached pulp production from S1-Burn and S2-HC.*

Impact category	Unit	S1-Burn	S2-HC	Var% between S1-Burn and S2-HC
Climate change (GWP-total)	kg CO_2 eq	2.34E-01	1.53E-01	-53%
Land use (SQP)	Pt	8.48E+01	1.36E+02	38%
Water use (WDP)	m^3 depriv.	1.05E-01	1.81E-01	42%
Resource use, fossils (ADP-fossil)	MJ	2.62E+00	1.66E+00	-58%
Resource use, minerals and metals (ADP-min&met.)	kg Sb eq	4.06E-06	5.52E-06	27%

S2-HC emerged as the superior performer in the GWP-total (0.153 kg CO_2eq/kg$_{USP}$) and ADP-fossil categories (1.66 MJ), while S1-Burn was the most performing in SQP, WDP and ADP-min&met. categories (84.8 Pt, 0.105 m^3 depriv, 4.06E-06 kg Sb eq respectively).

The results for the contribution analysis are depicted in Table 5.2 and 5.3 for both scenarios:

Table 5.2. *Contribution analysis, S1-Burn (Swedish + Finland scenario).*

Impact category	Unit	Total	Raw materials	Pulping and incineration	Energy
GWP-total	kg CO_2 eq	2.34E-01	6.60E-02	1.91E-01	-2.33E-02
SQP	Pt	8.48E+01	1.53E+02	-1.78E+01	-5.09E+01
WDS	m^3 depriv.	1.05E-01	3.84E-03	1.16E-01	-1.45E-02
ADP-fossil	MJ	2.62E+00	9.03E-01	1.96E+00	-2.44E-01
ADP-min&met	kg Sb eq	4.06E-06	-3.84E-07	6.43E-06	-1.99E-06

Table 5.3. *Contribution analysis, S1-Burn (European scenario).*

Impact category	Unit	Total	Raw materials	Pulping and incineration	Energy
GWP-total	kg CO_2 eq	1.91E-01	-8.92E-01	1.91E-01	-8.92E-01
SQP	Pt	-1.78E+01	-3.25E+01	-1.78E+01	-3.25E+01
WDP	m^3 depriv.	1.16E-01	-1.45E-01	1.16E-01	-1.45E-01
ADP-fossil	MJ	1.96E+00	-8.70E+00	1.96E+00	-8.70E+00
ADP-min&met.	kg Sb eq	6.43E-06	3.25E-06	6.43E-06	3.25E-06

Table 5.4. *Contribution analysis, S2-HC (Swedish + Finland scenario).*

Impact category	Unit	Total	Raw materials	Pulping and incineration	Chemicals	Catalysts	Avoided products	Energy	Avoided CO₂
GWP-total	kg CO_2 eq	1.53E-01	8.72E-02	1.91E-01	9.58E-02	1.39E-03	-4.97E-02	-2.35E-02	-1.50E-01
SQP	Pt	1.36E+02	2.03E+02	-1.78E+01	2.30E+00	2.13E-02	-6.97E-02	-5.13E+01	0.00E+00
WDP	m^3 depriv.	1.81E-01	5.07E-03	1.32E-01	5.97E-02	1.64E-03	-2.90E-03	-1.46E-02	0.00E+00
ADP-fossil	MJ	1.66E+00	1.19E+00	1.96E+00	2.36E+00	1.46E-02	-3.62E+00	-2.46E-01	0.00E+00
ADP-min&met.	kg Sb eq	5.52E-06	-5.07E-07	6.43E-06	1.53E-06	7.63E-08	-1.74E-09	-2.01E-06	0.00E+00

Table 5.5. *Contribution analysis, S2-HC (European scenario).*

Impact category	Unit	Total	Raw materials	Pulping and incineration	Chemicals	Catalysts	Avoided products	Energy	Avoided CO₂
GWP-total	kg CO_2 eq	-7.21E-01	8.72E-02	1.91E-01	9.58E-02	1.39E-03	-4.97E-02	-8.97E-01	-1.50E-01
SQP	Pt	1.54E+02	2.03E+02	-1.78E+01	2.30E+00	2.13E-02	-6.97E-02	-3.27E+01	0.00E+00
WDP	m^3 depriv.	4.90E-02	5.07E-03	1.32E-01	5.97E-02	1.64E-03	-2.90E-03	-1.46E-01	0.00E+00
ADP-fossil	MJ	-6.85E+00	1.19E+00	1.96E+00	2.36E+00	1.46E-02	-3.62E+00	-8.75E+00	0.00E+00
ADP-min&met.	kg Sb eq	1.08E-05	-5.07E-07	6.43E-06	1.53E-06	7.63E-08	-1.74E-09	3.27E-06	0.00E+00

The contribution analysis outcomes for all the 16 impact categories are listed from Table B2 to Table B5 in §Appendix, section B, along with the contribution plots for the specific scenarios.

In GWP-total for S2-HC, the principal factor contributing to reduced impacts was the avoidance of fossil CO_2 emissions relative to conventional hydrocarbons production, decreasing emissions by 0.15 kg CO_2eq/kg$_{USP}$. The efficacy of S1-Burn in the GWP-total, which utilizes pre-hydrolysis liquor as an energy source in a cogeneration plant, is highly contingent on the replaced energy mix.

Conversely, in the SQP category, S1-Burn outperforms S2-HC, attributable to the increased combustion of hemicellulose for heat production, thereby supplanting biomass-derived heat which accounts for a significant share in Northern Europe's energy mix. This substitution mitigates the wood chips consumption and reduces land use impacts. This interpretation is supported by the contribution analysis results, in the SQP impact category the largest contribution comes from Raw Materials, with a difference of 50 Pt between the scenarios.

The impacts to water use in S1-Burn are attributable mainly to the pulping and incineration processes, while in S2-HC they can be attributable also to the intensified use of solvents and catalysts. Giving that the contribution of pulping and incineration is similar in the two scenarios, the higher WDP indicator for S2-HC can be attributed to the solvents and catalyst productions.

In terms of ADP-fossil, S2-HC have higher impacts related to the production of the chemicals needed in upgrading value chain, which are compensated with the credits obtained from the avoided production of pentane and kerosene from petroleum sources, resulting in an overall better performance than S1-Burn.

For ADP-min&met, S2-HC have worse performances mainly due the implementation of solvents and catalysts in the hemicellulose to hydrocarbons value chain.

In Figure 5.1 and 5.2, the contribution of the different groups comparing S1-Burn and S2-HC in the Northern and European contexts respectively are depicted in terms of normalized impacts. The normalization was performed by dividing each contribute by the maximum between the sum of the positive or negative impacts through equation 5.1.

$$Normalized\ impact: \frac{Contribution\ to\ the\ impact\ category}{MAX(\sum positives, \sum negatives)} \qquad (5.1)$$
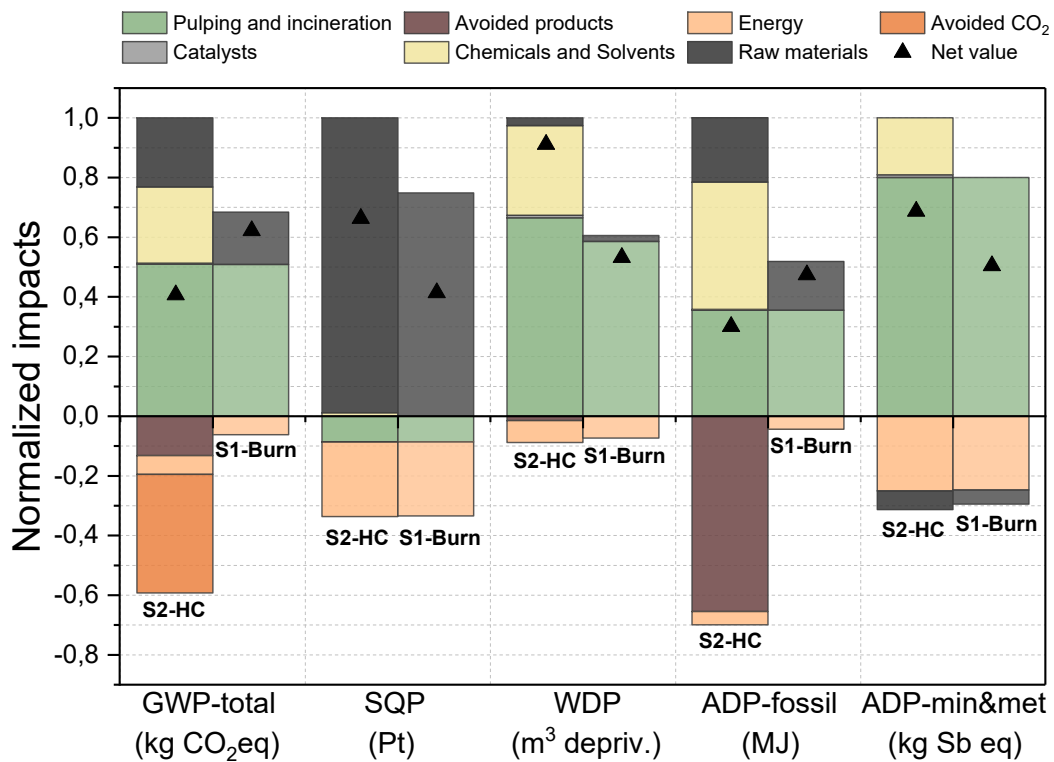
Figure 5.1. *Contribution analysis under a Northern context, comparison between scenarios. The contributions are displayed in terms of normalized impacts through equation 5.1.*
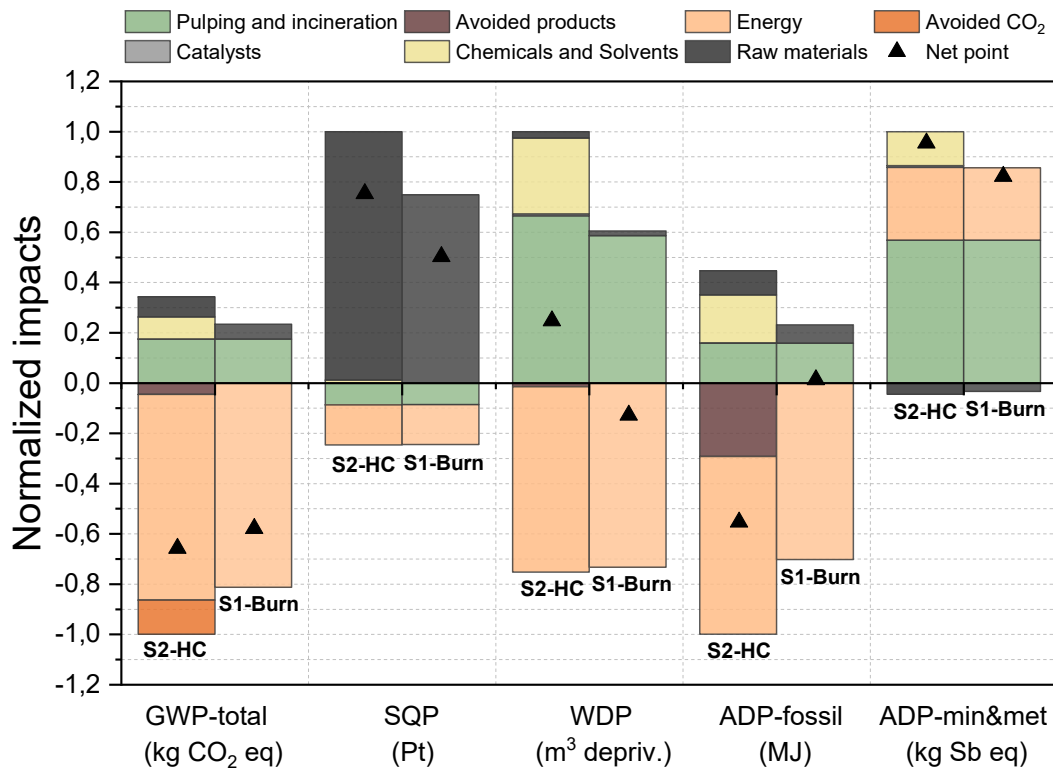
Figure 5.2. *Contribution analysis results under an average European context, comparison between scenarios. The contributions are displayed in terms of normalized impacts through equation 5.1.*

5.2 Sensitivity analysis results

Five sensitivity analyses assessed the effects of various modeling and operational parameters on the outcomes.

5.2.1 Incineration in the recovery boiler of the kraft mill

In this scenario the pre-hydrolysis liquor in the first scenario and the hemicellulose residues in the second scenario are incinerated in the recovery boiler with a lower efficiency respect to the co-generation unit, the results are listed in Table 5.6.

Table 5.6. *Sensitivity analysis comparing incineration in recovery boiler and in a co-generation plant.*

Impact category	Unit	S1-Burn	S1-BL	Var%
GWP-total	kg CO_2 eq	2.34E-01	2.52E-01	8%
SQP	Pt	8.48E+01	1.17E+02	38%
WDP	m^3 depriv.	1.05E-01	1.16E-01	10%
ADP-fossil	MJ	2.62E+00	2.88E+00	10%
ADP- min&met	kg Sb eq	4.06E-06	5.95E-06	47%

Impact category	Unit	S2-HC	S2-HC-BL	Var%
GWP-total	kg CO_2 eq	1.53E-01	1.71E-01	12%
SQP	Pt	1.36E+02	1.68E+02	24%
WDP	m^3 depriv.	1.81E-01	1.91E-01	6%
ADP-fossil	MJ	1.66E+00	1.92E+00	16%
ADP- min&met	kg Sb eq	5.52E-06	7.42E-06	34%

The comparison shows benefits in all the impact categories for both scenarios, highlighting that incinerating the wood-based residues in a co-generation unit might significantly enhance the environmental performances of the product system.

5.2.2 Hydrocarbons production in an average European location.

The location of the integrated pulp mill was hypothesized to be in an average European context as explained in §4.3.3. The outcomes for the five impact categories under study are depicted in Table 5.7.

Table 5.7. *Sensitivity analysis comparing the Northern context to average European context.*

S1-Burn				
Impact category	**Unit**	**Swedish + Finland scenario**	**European scenario**	**Var%**
GWP-total	kg CO_2 eq	2.34E-01	-6.34E-01	-371%
SQP	Pt	8.48E+01	1.03E+02	22%
WDP	m³ depriv.	1.05E-01	-2.54E-02	-124%
ADP-fossil	MJ	2.62E+00	-5.83E+00	-323%
ADP- min&met	kg Sb eq	4.06E-06	9.30E-06	129%

S2-HC				
Impact category	**Unit**	**Swedish + Finland scenario**	**European scenario**	**Var%**
GWP-total	kg CO_2 eq	1.53E-01	-7.21E-01	-572%
SQP	Pt	1.36E+02	1.54E+02	14%
WDP	m³ depriv.	1.81E-01	4.90E-02	-73%
ADP-fossil	MJ	1.66E+00	-6.85E+00	-513%
ADP- min&met	kg Sb eq	5.52E-06	1.08E-05	96%

Remarkable shifts for both S1-Burn and S2-HC resulted, particularly in GWP-total, WDP, and ADP-fossil. The impact on GWP-total is attributed to the higher emission factor of the European marginal energy mix (0.218 kgCO2eq/kWh) compared to the Northern mix (0.07 kgCO2eq/kWh), suggesting a net reduction in greenhouse gas emissions when replacing an energy mix dominated by fossil fuels. Locating the integrated pulp mill in an average European context resulted in an improvement in the overall environmental performances, except for the Land use and mineral resources depletion impact categories.

5.2.3 Hydrocarbons production with a decreased Yield

A separate sensitivity analysis evaluated the impact of a 10% lower yield to aviation fuels in the hydrodeoxygenation (HDO) section on S2-HC scenario.

Table 5.8. *Sensitivity analysis when the hydrocarbons Yield decrease by 10%.*

		S2-HC		
Impact category	**Unit**	**Proposed Scenario**	**Lower Yield scenario**	**Var%**
GWP-total	kg CO_2 eq	1.53E-01	1.72E-01	13%
SQP	Pt	1.36E+02	1.36E+02	0%
WDP	m^3 depriv.	1.81E-01	1.81E-01	0%
ADP-fossil	MJ	1.66E+00	1.99E+00	20%
ADP- min&met	kg Sb eq	5.52E-06	5.52E-06	0%

Although the GWP-total and ADP-fossil indicators deteriorated due the less amount of pentane and kerosene substituted, S2-HC still maintains a climate change advantage over S1-Burn, albeit with increased impacts on fossil resource use.

5.2.4 Hydrocarbons production in a separated facility

Another analysis for S2-HC assessed the effects of producing aviation fuels in an independent facility, predicting increased GWP-total and ADP-fossil due to higher energy demands.

Table 5.9. *Sensitivity analysis when upgrading hemicellulose in an independent facility.*

		S2-HC		
Impact category	**Unit**	**Integrated pulp mill scenario**	**Independent plant scenario**	**Var%**
GWP-total	kg CO_2 eq	1.53E-01	1.51E-01	-1%
SQP	Pt	1.36E+02	2.37E+02	74%
WDP	m^3 depriv.	1.81E-01	1.84E-01	2%
ADP-fossil	MJ	1.66E+00	6.02E-01	-64%
ADP- min&met	kg Sb eq	5.52E-06	2.71E-07	-95%

The results depicted in Table 5.9 showed a decrease in GWP-total, ADP-fossil and ADP-min&met, contrary to expectations, due to varying efficiencies between recovery boilers and co-generation plants in hemicellulose combustion. The impacts of the higher energy requirements from grid are counterbalanced with the higher exportation of energy from the mill.

5.2.5 LCIA using the ReCiPe, 2016, (Midpoint) Method

Lastly, altering the assessment to the ReCiPe 2016 (midpoint), H method in the final sensitivity analysis did not yield significant differences in the relevant impact categories under study as reported in Table 5.10, meaning a consistency of the product system to changes in the impact assessment method.

Table 5.10. *Sensitivity analysis comparing the different scenarios using ReCiPe 2016 (Midpoint), H.*

Impact category	Unit	S1–Burn	S2-HC	Var% between S1-Burn and S2-HC
Global warming	kg CO2 eq	2.33E-01	1.52E-01	-35%
Land use	m2a crop eq	7.58E-01	1.21E+00	59%
Mineral resource scarcity	kg Cu eq	6.15E-04	8.28E-04	35%
Fossil resource scarcity	kg oil eq	7.48E-02	5.61E-02	-25%
Water consumption	m3	8.10E-04	3.41E-03	321%

Conclusions

The objectives of this thesis work were to give a clear representation of the environmental impacts associated with the integrated biorefinery process producing Unbleached sulfate pulp and hydrocarbons in a biofuel range as co-products and to compare them to the conventional pre-hydrolysis kraft pulping. To fulfill this purpose, Consequential LCA was successfully applied.

Of the five environmental footprint impact categories, the scenario with the proposed value chain to obtain hydrocarbons performed better than the conventional pre-hydrolysis kraft pulping in the climate change and in the fossil resources use impact categories thanks to the avoided fossil CO_2 and the production of pentane and $>C_5$ hydrocarbons from bio-based resources.

The most remarkable outcomes from the sensitivity analysis highlighted that burning the hemicellulose residues discarded from the valorization processes in a co-generation facility, instead of the recovery boiler of the kraft mill, significatively increase the benefits arising from the recovery of heat and power from wood-based materials. Moreover, the location of the integrated pulp mill plays a significant role when assessing the environmental impacts of the product system. Locating the integrated pulp mill in an average European context resulted in an improvement in the overall environmental performances, except for the Land use and mineral resources depletion impact categories.

The major challenges addressed in the development of the model concerned the building of the mass and energy balances and the development of a suitable dataset accounting for the production of Unbleached Sulfate Pulp from hardwood; thus, the major limitation in the reliability of the results concerns the quality of the starting inventory data, which are all from secondary sources.

Furthermore, this study only analyzes the environmental performances of the proposed process and the associated risks and opportunities but does not address a design optimization and a techno-economic analysis, leaving room for further improvement.

The proposed value chain resulted to be a promising strategy to reduce the environmental impacts associated with the production of pulp destined to the production of Dissolving Grade Pulp for the textile industry, allowing a mitigation of the major challenges of this century.

Appendix

Appendix A: Inventory Analysis Datasets

Table A1. *Dataset structure for Unbleached Sulfate Pulp production from Hardwood, data calculated from Ecoinvent v3.9.1 consequential.*

Type	Name	Location	Unit	Value
Input from Technosphere: materials/fuels				
Type	**Name**	**Location**	**Unit**	**Value**
Fuel	Heavy fuel oil	RER	kg	2.6E-02
Fuel	Light fuel oil	RER	kg	3.62E-05
Fuel	Methanol, from biomass	CH	kg	1.27E-02
Other	Pulp factory	RER	Unit	4.79E-11
Material	Chemical, organic	GLO	kg	1.01E-04
Material	Bark chips, wet, measured as dry mass	RoW	kg	-2.234E-01
Material	Oxygen, liquid	RER	kg	1.34E-03
Material	Quicklime, milled, loose	CH	kg	2.21E-02
Material	Sawdust, wet, measured as dry mass	RoW	kg	-1.775E-02
Material	Sodium hydroxide, without water, 50% solution state	GLO	kg	1.60E-02
Material	Sulfuric acid	RER	kg	8.11E-03
Material	DC_UP1: Wood without hemicellulose	(Table A2)	kg	2.24
Transport	Transport, freight train	RER	Ton*km	1.99E-01
Transport	Transport, freight, lorry >32 metric ton, euro 5	RER	Ton*km	1.58E-01
Input from Technosphere: electricity/heat				
Type	**Name**	**Location**	**Unit**	**Value**
Energy	Electricity, consumption+substitution scenario	(Table A9)	kWh	1.25E-01
Input from environment				
Type	**Name**	**Location**	**Unit**	**Value**
Material	Water, unspecified natural origin	RER	m^3	5.84E-02
Material	oxygen	/	kg	1.58
Output to Technosphere				
Type	**Name**	**Location**	**Unit**	**Value**
Product (FU)	Unbleached sulfate pulp		kg	1
Avoided product	DC: Heat, consumption and substitution	(Table A8)	MJ	1.11
Avoided product	Electricity, consumption+substitution scenario	(Table A9)	kWh	1.21E-01
Emissions to Air				
Type	**Name**	**Location**	**Unit**	**Value**
Air Emission	Acetaldehyde		kg	1.59E-07

Air Emission	Acetic acid	kg	6.35E-07
Air Emission	Acetone	kg	1.59E-07
Air Emission	Ammonia	kg	1.08E-08
Air Emission	Arsenic ion	kg	1.38E-08
Air Emission	Benzene	kg	2.31E-11
Air Emission	Benzo(a)pyrene	kg	2.97E-11
Air Emission	Butane	kg	4.86E-10
Air Emission	Calcium	kg	1.16E-07
Air Emission	Carbon dioxide, fossil	kg	8.36E-02
Air Emission	Carbon dioxide, non-fossil	kg	2.09E+00
Air Emission	Carbon monoxide, fossil	kg	7.40E-06
Air Emission	Chromium III	kg	5.24E-09
Air Emission	Chromium VI	kg	5.29E-11
Air Emission	Cobalt II	kg	3.49E-08
Air Emission	Copper ion	kg	1.80E-08
Air Emission	Dinitrogen monoxide	kg	8.47E-07
Air Emission	Dioxins, measured as 2,3,7,8-tetrachlorodibenzo-p-dioxin	kg	4.77E-16
Air Emission	Ethanol	kg	3.17E-07
Air Emission	Formaldehyde	kg	4.78E-07
Air Emission	Hydrocarbons, aliphatic, alkanes, unspecified	kg	6.35E-07
Air Emission	Hydrocarbons, aliphatic, unsaturated	kg	3.17E-08
Air Emission	Hydrocarbons, aromatic	kg	1.59E-07
Air Emission	Hydrochloric acid	kg	1.53E-06
Air Emission	Hydrogen fluoride	kg	5.08E-08
Air Emission	Hydrogen sulfide	kg	8.67E-05
Air Emission	Iron ion	kg	8.67E-07
Air Emission	Lead II	kg	1.54E-07
Air Emission	Mercury II	kg	1.60E-10
Air Emission	Methane, fossil	kg	3.18E-06
Air Emission	Methanol	kg	5.39E-07
Air Emission	Molybdenum VI	kg	8.46E-09
Air Emission	Nickel II	kg	5.18E-07
Air Emission	Nitrogen oxides	kg	1.53E-03
Air Emission	PAH, polycyclic aromatic hydrocarbons	kg	6.14E-10
Air Emission	Particulate Matter, < 2.5 um	kg	6.62E-05
Air Emission	Particulate Matter, > 10 um	kg	2.54E-06
Air Emission	Particulate Matter, > 2.5 um and < 10um	kg	1.38E-04
Air Emission	Pentane	kg	3.23E-10
Air Emission	Phenol	kg	1.07E-08
Air Emission	Propane	kg	3.18E-08
Air Emission	Selenium IV	kg	1.27E-08

Air Emission	Sodium		kg	7.93E-07
Air Emission	Sulfur dioxide		kg	1.34E-05
Air Emission	Sulfur oxides		kg	1.00E-04
Air Emission	Toluene		kg	3.18E-08
Air Emission	Vanadium V		kg	1.06E-06
Air Emission	Water		kg	6.58E-01
Air Emission	Zinc		kg	5.92E-08

Emission to water

Type	Name	Location	Unit	Value
Emission to water	AOX, Adsorbable Organic Halogen		kg	1.34E-05
Emission to water	BOD5, Biological Oxygen Demand		kg	2.18E-03
Emission to water	COD, Chemical Oxygen Demand		kg	1.31E-02
Emission to water	DOC, Dissolved Organic Carbon		kg	2.09E-03
Emission to water	Nitrogen		kg	1.87E-04
Emission to water	Phosphorus		kg	1.78E-05
Emission to water	Suspended solids, unspecified		kg	1.08E-03
Emission to water	TOC, Total Organic Carbon		kg	2.09E-03
Emission to water	Water	RER	m³	5.84E-02

Waste to treatment

Type	Name	Location	Unit	Value
Waste	Green liquor dregs	GLO	kg	5.09E-03
Waste	hazardous waste, for incineration	CH	kg	2.66E-06
Waste	hazardous waste, for incineration	Europe without Switzerland	kg	1.02E-04
Waste	limestone residue	CH	kg	8.60E-02
Waste	wood ash mixture, pure	CH	kg	3.39E-05
Waste	wood ash mixture, pure	Europe without Switzerland	kg	1.65E-05

Table A2. *Dataset structure for Pre-hydrolysis of starting wood, UP1.*

Input from Technosphere: materials/fuels				
Type	**Name**	**Location**	**Unit**	**Value**
Material	Wood chips, wet, measured as dry mass	SE	kg	2.96

Input from technosphere: electricity/heat				
Type	**Name**	**Location**	**Unit**	**Value**
Energy	DC: Heat, consumption and substitution	(Table A8)	MJ	9.33*

Input from environment				
Type	**Name**	**Location**	**Unit**	**Value**
Material	Water, river	In water	dm^3	1.48

Output to Technosphere				
Type	**Name**	**Location**	**Unit**	**Value**
Product	DC_UP1: wood without hemicellulose	/	kg	1
Avoided product	DC_UP2: De-hydration to Furfural	/	kg	0.718

Emissions to Air			
Type	**Name**	**Unit**	**Value**
Air Emission	water	dm^3	1.48

*See Sensitivity #4 §4.3.3

Table A3. *Dataset structure for De-hydration of xylose to furfural, UP2.*

	Input from Technosphere: materials/fuels			
Type	**Name**	**Location**	**Unit**	**Value**
Material	Ethyl acetate, production from biomass	RER	kg	3.3E-02
Material	Zeolite, powder production	RER	kg	3.78E-05
	Input from Technosphere: electricity/heat			
Type	**Name**	**Location**	**Unit**	**Value**
Material	DC: Hemicellulose combustion in co-generation plant	(Table A10)	kg	5.48E-01
Energy	Heat, consumption and substitution	(Table A9)	MJ	1.44*
	Output to Technosphere			
Type	**Name**	**Location**	**Unit**	**Value**
Product	DC_UP2: De-hydration to Furfural	/	kg	-0.718
Avoided product	DC_UP3: HDO + HMU	/	kg	0.109
	Emissions to Air			
Type	**Name**	**Location**	**Unit**	**Value**
Air Emission	water	/	dm^3	6.12E-02

*See Sensitivity #4 §4.3.3

Table A4. *Dataset structure for hydrotreating of furfural and hydrogen recovery from HMU, UP3.*

	Input from Technosphere: materials/fuels			
Type	**Name**	**Location**	**Unit**	**Value**
Material	Hydrogen, gaseous, production from petroleum refinery operations	RoW	kg	2.5E-03
Material	Zeolite, powder production	RER	kg	3.78E-05
Material	Palladium, treatment of precious metal from electronics scrap	SE	kg	1.095E-07
	Input from environment			
Type	**Name**	**Location**	**Unit**	**Value**
Material	Water, river	SE	dm^3	1.5E-2
	Output to Technosphere			
Type	**Name**	**Location**	**Unit**	**Value**
Product	DC_UP3: HDO + HMU	/	kg	-0.109
Avoided product	DC: Pentane	(Table A5)	kg	3.74E-02*(1-LowY)
Avoided product	DC: Kerosene	(Table A6)	kg	1.1E-02*(1-LowY)
	Emissions to Air			
Type	**Name**	**Location**	**Unit**	**Value**
Air Emission	Carbon dioxide, biogenic	/	kg	7.78E-02

LowY = 0 - 0.1. To account for 10% less hydrocarbon products.

Table A5. *Dataset structure for product pentane.*

	Input from Technosphere: materials/fuels			
Type	**Name**	**Location**	**Unit**	**Value**
Material	DC: Avoided CO_2	(Table A7)	kg	3.06
	Output to Technosphere			
Type	**Name**	**Location**	**Unit**	**Value**
Product	DC: Pentane	/	kg	-1
Avoided product	Pentane production	RER	kg	1

Table A6. *Dataset structure for product kerosene.*

	Input from Technosphere: materials/fuels			
Type	**Name**	**Location**	**Unit**	**Value**
Material	DC: Avoided CO_2	(Table A7)	kg	3.12
	Output to Technosphere			
Type	**Name**	**Location**	**Unit**	**Value**
Product	DC: kerosene	/	kg	-1
Avoided product	Kerosene production, petroleum refinery operation	Europe without Switzerland	kg	1

Table A7. *Dataset structure for Avoided fossil CO$_2$.*

Output to Technosphere			
Type	**Name**	**Unit**	**Value**
Product	DC: Avoided CO$_2$	kg	1
Emissions to Air			
Type	**Name**	**Unit**	**Value**
Air Emission	Carbon dioxide, biogenic	kg	1
Air Emission	Carbon dioxide, fossil	kg	-1

Table A8. *Dataset structure for Heat, consumption and substitution.*

Input from Technosphere: electricity/heat				
Type	**Name**	**Location**	**Unit**	**Value**
Energy	Heat, district or industrial, other than natural gas, hard coal	SE	MJ	4.71E-02(SE+FI) (*)
Energy	Heat, district or industrial, other than natural gas, wood chips, 6667 kW, state-of-the-art 2014	SE	MJ	9.53E-01*(SE+FI)
Energy	Heat, district or industrial, other than natural gas, market for	RER	MJ	1*RER (*)
Output to Technosphere				
Type	**Name**	**Location**	**Unit**	**Value**
Product	DC: Heat, consumption and substitution	/	MJ	1

*SE=0/0.5; FI=0/0.5; RER=0/1. Parameters adopted in Sensitivity #2 to switch from north Europe scenario to average European scenario.

Table A9. *Dataset structure for electricity, input and substitution scenarios.*

Input from Technosphere: electricity/heat				
Type	**Name**	**Location**	**Unit**	**Value**
Energy	Electricity, high voltage, market for	RER	MJ	1*RER
Energy	MARGINAL Electricity, high voltage, market for	FI	MJ	1*FI
Energy	MARGINAL Electricity, high voltage, market for	SE	MJ	1*SE
Output to Technosphere				
Type	**Name**	**Location**	**Unit**	**Value**
Product	Electricity, input and substitution scenarios	/	kWh	1

*SE=0/0.5; FI=0/0.5; RER=0/1. Parameters adopted in Sensitivity #2 to switch from north Europe scenario to average European scenario.

Table A10. *Dataset structure for hemicellulose combustion in a co-generation facility.*

Input from Technosphere: materials/fuels				
Type	**Name**	**Location**	**Unit**	**Value**
Material	DC: Heat, district or industrial, other than natural gas, co-generation of heat and power, wood chips, 6667 kW, state-of-the-art 2014	(Table A11)	kg	1
Output to Technosphere				
Type	**Name**	**Location**	**Unit**	**Value**
Product	DC: Hemicellulose combustion in a co-generation plant	/	kg	-1
Avoided product	DC: Heat, consumption and substitution	/	MJ	7.38
Avoided product	Electricity, input and substitution scenarios	/	kWh	6.833E-01

Table A11. *Dataset structure for combustion of wood materials in co-generation units.*

	Input from Technosphere: materials/fuels			
Type	**Name**	**Location**	**Unit**	**Value**
Material	Ammonia, anhydrous, liquid	RER	kg	1.82E-08
Material	Chemical, organic	GLO	kg	1.30E-05
Material	Chlorine, liquid	RER	kg	7.29E-07
Unit	Dust collector, electrostatic precipitator, for industrial use	GLO	p	1.16E-09
Material	Lubricating oil	RER	kg	7.29E-06
Material	NOx retained, by selective catalytic reduction	GLO	kg	1.78E-04
Material	Sodium chloride, powder	GLO	kg	9.11E-06
Material	Water, decarbonised	RoW	kg	0.001749

	Input from Technosphere: electricity/heat			
Type	**Name**		**Unit**	**Value**
Unit	Furnace, wood chips, with silo, 5000kW	GLO	p	1.16E-09
Unit	Heat and power co-generation unit, organic Rankine cycle, 1000kW electrical	GLO	p	1.16E-09

	Output to Technosphere			
Type	**Name**		**Unit**	**Value**
Product	DC: Heat, district or industrial, other than natural gas, heat and power co-generation, wood chips, 6667 kW, state-of-the-art 2014	SE	kg	1.17578E-01

	Emissions to Air		
Type	**Name**	**Unit**	**Value**
Emissions to air	Acetaldehyde	kg	1.36E-07
Emissions to air	Ammonia	kg	3.78E-05
Emissions to air	Arsenic	kg	2.22E-09
Emissions to air	Benzene	kg	2.02E-06
Emissions to air	Benzene, ethyl-	kg	6.67E-08
Emissions to air	Benzene, hexachloro-	kg	1.60E-14
Emissions to air	Benzo(a)pyrene	kg	1.11E-09
Emissions to air	Bromine	kg	1.33E-07
Emissions to air	Cadmium	kg	1.56E-09
Emissions to air	Calcium	kg	1.30E-05
Emissions to air	Carbon dioxide, biogenic	kg	2.13333E-01
Emissions to air	Carbon monoxide, biogenic	kg	2.22E-04
Emissions to air	Chlorine	kg	4.00E-07
Emissions to air	Chromium	kg	8.80E-09
Emissions to air	Chromium VI	kg	8.89E-11
Emissions to air	Copper	kg	4.89E-08
Emissions to air	Dinitrogen monoxide	kg	5.11E-06
Emissions to air	Dioxin, 2,3,7,8 Tetrachlorodibenzo-p-	kg	6.89E-14

Emissions to air	Fluorine		kg	1.11E-07
Emissions to air	Formaldehyde		kg	2.89E-07
Emissions to air	Hydrocarbons, aliphatic, alkanes, unspecified		kg	2.02E-06
Emissions to air	Hydrocarbons, aliphatic, unsaturated		kg	6.89E-06
Emissions to air	Lead		kg	5.56E-08
Emissions to air	m-Xylene		kg	2.67E-07
Emissions to air	Magnesium		kg	8.00E-07
Emissions to air	Manganese		kg	3.78E-07
Emissions to air	Mercury		kg	6.67E-10
Emissions to air	Methane, biogenic		kg	2.67E-06
Emissions to air	Nickel		kg	1.33E-08
Emissions to air	Nitrogen oxides		kg	1.78E-04
Emissions to air	NMVOC, non-methane volatile organic compounds		kg	6.22E-06
Emissions to air	PAH, polyclic aromatic hydrocarbons		kg	2.47E-08
Emissions to air	Particulates, < 2.5 um		kg	1.11E-05
Emissions to air	Phenol, pentachloro-		kg	1.80E-11
Emissions to air	Phosphorus		kg	6.67E-07
Emissions to air	Potassium		kg	5.20E-05
Emissions to air	Sodium		kg	2.89E-06
Emissions to air	Sulfur dioxide		kg	5.56E-06
Emissions to air	Toluene		kg	6.67E-07
Emissions to air	Water/m3		m3	1.29E-04

Waste to treatment

Type	Name	Location	Unit	Value
Waste	Municipal solid waste	SE	kg	7.29E-06
Waste	Waste mineral oil	Europe without Switzerland	kg	7.29E-06
Waste	Wastewater, average	Europe without Switzerland	m3	1.75E-06
Waste	Wood ash mixture, pure	Europe without Switzerland	kg	1.176E-03

This dataset is a modified copy of the original "Heat, district or industrial, other than natural gas {SE}| heat and power co-generation, wood chips, 6667 kW, state-of-the-art 2014 | Conseq, U" from Ecoinvent 3.9.1 consequential. The original dataset had 0.117875 kg of wood chips as input to be incinerated, the main product delivered was 1MJ of Heat, electricity produced was listed in the inputs section with a value of -0,0925925925925927 kWh. The efficiencies to Heat and electricity are reported to be 0.45 and 0.15 respectively.

Appendix B: LCIA and Contribution analysis results

Table B1. *Impact assessment of unbleached pulp production from S1-Burn and S2-AF.*

Impact category	Unit	S1-Burn	S2-AF	Var% between S1-Burn and S2-AF
Climate change	kg CO_2 eq	2.34E-01	-5.63E-02	-515%
Ozone depletion	kg CFC 11 eq	4.29E-08	-2.27E-08	-289%
Ionising radiation	kBq U-235 eq	-2.00E-02	-2.29E-02	-13%
Photochemical ozone formation	kg NMVOC eq	2.18E-03	2.66E-03	18%
Particulate matter	disease inc.	3.22E-08	3.51E-08	8%
Human toxicity, non-cancer	CTUh	3.94E-09	1.56E-09	-153%
Human toxicity, cancer	CTUh	1.78E-10	6.18E-10	71%
Acidification	mol H^+ eq	2.10E-03	2.19E-03	4%
Eutrophication, freshwater	kg P eq	5.75E-05	1.64E-04	65%
Eutrophication, marine	kg N eq	7.57E-04	8.22E-04	8%
Eutrophication, terrestrial	mol N eq	9.04E-03	8.91E-03	-2%
Ecotoxicity, freshwater	CTUe	1.11E+01	5.18E+00	-114%
Land use	Pt	8.48E+01	1.72E+02	51%
Water use	m^3 depriv.	1.05E-01	3.69E-01	72%
Resource use, fossils	MJ	2.62E+00	5.16E+00	49%
Resource use, minerals and metals	kg Sb eq	4.06E-06	-6.44E-05	-106%

Table B2. *Contribution analysis, S1-Burn (Swedish + Finland scenario).*

Impact category	Unit	Total	Raw materials	Pulping and incineration	Energy
Climate change	kg CO_2 eq	2.34E-01	6.60E-02	1.91E-01	-2.33E-02
Ozone depletion	kg CFC 11 eq	4.29E-08	1.40E-08	3.21E-08	-3.21E-09
Ionising radiation	kBq U-235 eq	-2.00E-02	3.76E-03	5.83E-03	-2.96E-02
Photochemical ozone formation	kg NMVOC eq	1.41E-03	5.27E-04	2.00E-03	-1.13E-03
Particulate matter	disease inc.	1.88E-08	2.36E-09	3.50E-08	-1.85E-08
Human toxicity, non-cancer	CTUh	3.77E-09	9.69E-10	8.86E-09	-6.06E-09
Human toxicity, cancer	CTUh	1.65E-10	5.90E-11	2.84E-10	-1.78E-10

Acidification	mol H+ eq	1.45E-03	2.78E-04	2.61E-03	-1.44E-03
Eutrophication, freshwater	kg P eq	5.75E-05	1.27E-05	8.17E-05	-3.69E-05
Eutrophication, marine	kg N eq	4.58E-04	1.06E-04	7.45E-04	-3.93E-04
Eutrophication, terrestrial	mol N eq	5.76E-03	1.11E-03	1.11E-02	-6.40E-03
Ecotoxicity, freshwater	CTUe	1.04E+01	7.40E-01	2.41E+01	-1.44E+01
Land use	Pt	8.48E+01	1.53E+02	-1.78E+01	-5.09E+01
Water use	m³ depriv.	1.05E-01	3.84E-03	1.16E-01	-1.45E-02
Resource use, fossils	MJ	2.62E+00	9.03E-01	1.96E+00	-2.44E-01
Resource use, minerals and metals	kg Sb eq	4.06E-06	-3.84E-07	6.43E-06	-1.99E-06

Table B3. *Contribution analysis, S1-Burn (European scenario).*

Impact category	Unit	Total	Raw materials	Pulping and incineration	Energy
Climate change	kg CO₂ eq	1.91E-01	-8.92E-01	1.91E-01	-8.92E-01
Ozone depletion	kg CFC 11 eq	3.21E-08	2.08E-08	3.21E-08	2.08E-08
Ionising radiation	kBq U-235 eq	5.83E-03	-6.87E-03	5.83E-03	-6.87E-03
Photochemical ozone formation	kg NMVOC eq	2.00E-03	-2.74E-03	2.00E-03	-2.74E-03
Particulate matter	disease inc.	3.50E-08	-1.91E-08	3.50E-08	-1.91E-08
Human toxicity, non-cancer	CTUh	8.86E-09	-1.50E-08	8.86E-09	-1.50E-08
Human toxicity, cancer	CTUh	2.84E-10	-2.59E-10	2.84E-10	-2.59E-10
Acidification	mol H+ eq	2.61E-03	-7.55E-03	2.61E-03	-7.55E-03
Eutrophication, freshwater	kg P eq	8.17E-05	-1.43E-03	8.17E-05	-1.43E-03
Eutrophication, marine	kg N eq	7.45E-04	-1.20E-03	7.45E-04	-1.20E-03
Eutrophication, terrestrial	mol N eq	1.11E-02	-1.15E-02	1.11E-02	-1.15E-02
Ecotoxicity, freshwater	CTUe	2.41E+01	-1.92E+01	2.41E+01	-1.92E+01
Land use	Pt	-1.78E+01	-3.25E+01	-1.78E+01	-3.25E+01
Water use	m³ depriv.	1.16E-01	-1.45E-01	1.16E-01	-1.45E-01
Resource use, fossils	MJ	1.96E+00	-8.70E+00	1.96E+00	-8.70E+00
Resource use, minerals and metals	kg Sb eq	6.43E-06	3.25E-06	6.43E-06	3.25E-06

Table B4. *Contribution analysis, birch wood to unbleached pulp and hydrocarbons (S2-HC Swedish + Finland scenario).*

Impact category	Unit	Total	Raw materials	Pulping and incineration	Chemicals	Catalysts	Avoided products	Energy	Avoided CO$_2$
Climate change	kg CO$_2$ eq	1.53E-01	8.72E-02	1.91E-01	9.58E-02	1.39E-03	-4.97E-02	-2.35E-02	-1.50E-01
Ozone depletion	kg CFC 11 eq	5.97E-08	1.85E-08	3.22E-08	2.14E-08	1.03E-10	-9.23E-09	-3.23E-09	0.00E+00
Ionising radiation	kBq U-235 eq	-2.04E-02	4.97E-03	5.84E-03	1.04E-03	-4.28E-05	-2.39E-03	-2.98E-02	0.00E+00
Photochemical ozone formation	kg NMVOC eq	2.44E-03	6.96E-04	2.79E-03	3.44E-04	3.95E-06	-2.60E-04	-1.13E-03	0.00E+00
Particulate matter	disease inc.	3.72E-08	3.12E-09	4.85E-08	6.91E-09	8.11E-11	-2.82E-09	-1.87E-08	0.00E+00
Human toxicity, non-cancer	CTUh	5.92E-09	1.28E-09	9.07E-09	1.73E-09	1.17E-10	-1.77E-10	-6.10E-09	0.00E+00
Human toxicity, cancer	CTUh	2.31E-10	7.79E-11	2.98E-10	3.45E-11	3.44E-12	-3.57E-12	-1.79E-10	0.00E+00
Acidification	mol H$^+$ eq	2.73E-03	3.68E-04	3.27E-03	7.81E-04	1.06E-05	-2.47E-04	-1.45E-03	0.00E+00
Eutrophication, freshwater	kg P eq	7.61E-05	1.68E-05	8.17E-05	1.44E-05	1.10E-06	-7.78E-07	-3.71E-05	0.00E+00
Eutrophication, marine	kg N eq	9.72E-04	1.40E-04	1.05E-03	2.22E-04	1.50E-06	-4.29E-05	-3.96E-04	0.00E+00
Eutrophication, terrestrial	mol N eq	1.17E-02	1.46E-03	1.44E-02	2.70E-03	2.51E-05	-4.68E-04	-6.44E-03	0.00E+00
Ecotoxicity, freshwater	CTUe	1.42E+01	9.77E-01	2.49E+01	2.81E+00	4.25E-01	-3.24E-01	-1.45E+01	0.00E+00
Land use	Pt	1.36E+02	2.03E+02	-1.78E+01	2.30E+00	2.13E-02	-6.97E-02	-5.13E+01	0.00E+00
Water use	m^3 depriv.	1.81E-01	5.07E-03	1.32E-01	5.97E-02	1.64E-03	-2.90E-03	-1.46E-02	0.00E+00
Resource use, fossils	MJ	1.66E+00	1.19E+00	1.96E+00	2.36E+00	1.46E-02	-3.62E+00	-2.46E-01	0.00E+00
Resource use, minerals and metals	kg Sb eq	5.52E-06	-5.07E-07	6.43E-06	1.53E-06	7.63E-08	-1.74E-09	-2.01E-06	0.00E+00

Table B5. *Contribution analysis, birch wood to unbleached pulp and hydrocarbons (S2-HC European scenario).*

| Impact category	Unit	Total	Raw materials	Pulping and incineration	Chemicals	Catalysts	Avoided products	Energy	Avoided CO_2
Climate change	kg CO_2 eq	-7.21E-01	8.72E-02	1.91E-01	9.58E-02	1.39E-03	-4.97E-02	-8.97E-01	-1.50E-01
Ozone depletion	kg CFC 11 eq	8.39E-08	1.85E-08	3.22E-08	2.14E-08	1.03E-10	-9.23E-09	2.09E-08	0.00E+00
Ionising radiation	kBq U-235 eq	2.44E-03	4.97E-03	5.84E-03	1.04E-03	-4.28E-05	-2.39E-03	-6.97E-03	0.00E+00
Photochemical ozone formation	kg NMVOC eq	8.09E-04	6.96E-04	2.79E-03	3.44E-04	3.95E-06	-2.60E-04	-2.76E-03	0.00E+00
Particulate matter	disease inc.	3.66E-08	3.12E-09	4.85E-08	6.91E-09	8.11E-11	-2.82E-09	-1.93E-08	0.00E+00
Human toxicity, non-cancer	CTUh	-3.04E-09	1.28E-09	9.07E-09	1.73E-09	1.17E-10	-1.77E-10	-1.51E-08	0.00E+00
Human toxicity, cancer	CTUh	1.49E-10	7.79E-11	2.98E-10	3.45E-11	3.44E-12	-3.57E-12	-2.61E-10	0.00E+00
Acidification	mol H^+ eq	-3.42E-03	3.68E-04	3.27E-03	7.81E-04	1.06E-05	-2.47E-04	-7.60E-03	0.00E+00
Eutrophication, freshwater	kg P eq	-1.33E-03	1.68E-05	8.17E-05	1.44E-05	1.10E-06	-7.78E-07	-1.44E-03	0.00E+00
Eutrophication, marine	kg N eq	1.60E-04	1.40E-04	1.05E-03	2.22E-04	1.50E-06	-4.29E-05	-1.21E-03	0.00E+00
Eutrophication, terrestrial	mol N eq	6.50E-03	1.46E-03	1.44E-02	2.70E-03	2.51E-05	-4.68E-04	-1.16E-02	0.00E+00
Ecotoxicity, freshwater	CTUe	9.41E+00	9.77E-01	2.49E+01	2.81E+00	4.25E-01	-3.24E-01	-1.93E+01	0.00E+00
Land use	Pt	1.54E+02	2.03E+02	-1.78E+01	2.30E+00	2.13E-02	-6.97E-02	-3.27E+01	0.00E+00
Water use	m^3 depriv.	4.90E-02	5.07E-03	1.32E-01	5.97E-02	1.64E-03	-2.90E-03	-1.46E-01	0.00E+00
Resource use, fossils	MJ	-6.85E+00	1.19E+00	1.96E+00	2.36E+00	1.46E-02	-3.62E+00	-8.75E+00	0.00E+00
Resource use, minerals and metals	kg Sb eq	1.08E-05	-5.07E-07	6.43E-06	1.53E-06	7.63E-08	-1.74E-09	3.27E-06	0.00E+00
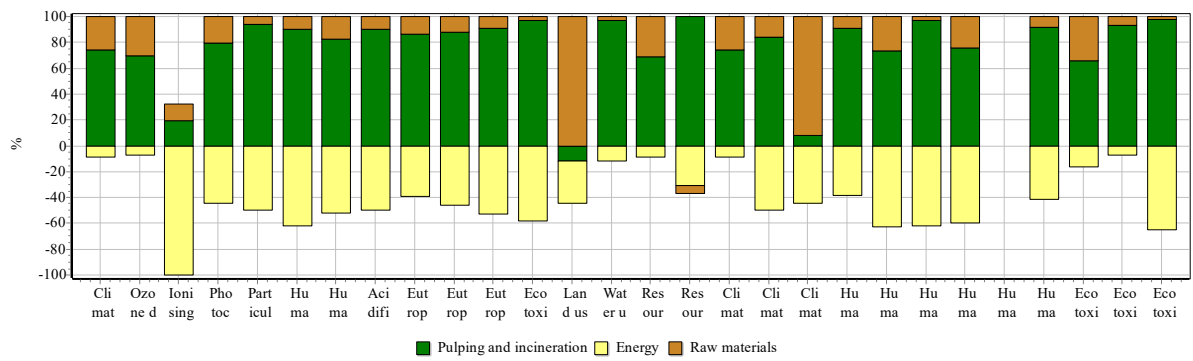
Figure B1: Contribution analysis outcome, S1-Burn, Swedish and Finland mix.
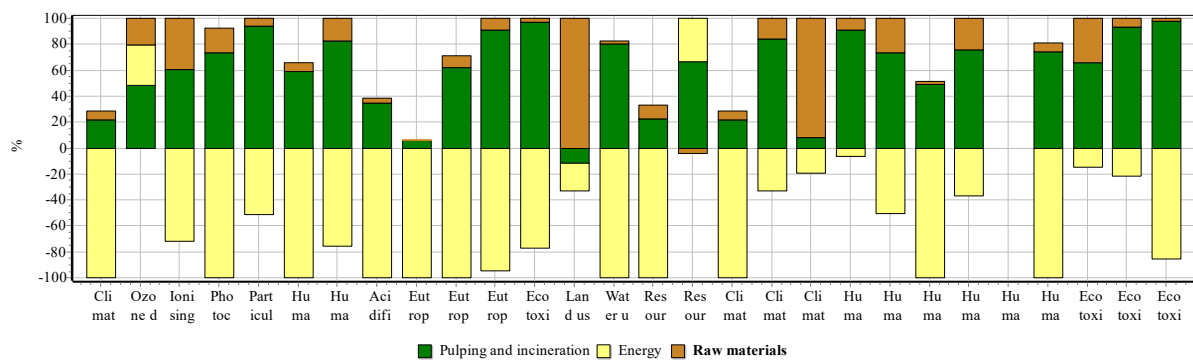

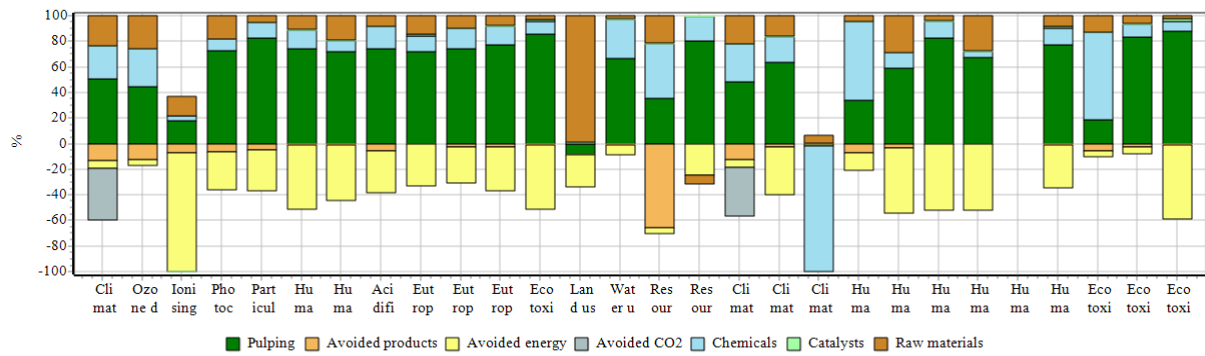**Figure B2:** Contribution analysis outcome, S1-Burn, average European mix.

Figure B3: Contribution analysis outcome, S2-HC Swedish and Finland mix.
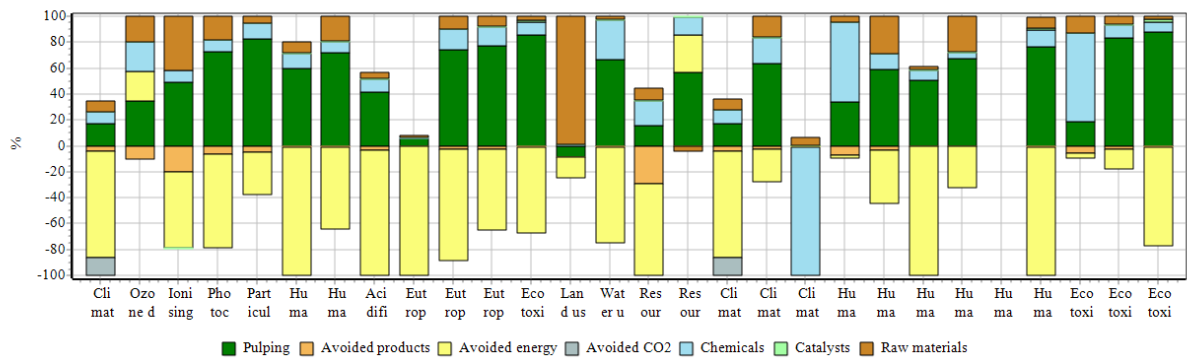
Figure B4: Contribution analysis outcome, S2-HC average European mix.

APPENDIX C: Sensitivity analysis results

Table C1. *Sensitivity analysis comparing incineration in recovery boiler and in a co-generation plant.*

Impact category	Unit	S1-Burn	S1-BL	Var%
Climate change	kg CO_2 eq	2.34E-01	2.52E-01	-8%
Ozone depletion	kg CFC 11 eq	4.29E-08	4.51E-08	-5%
Ionising radiation	kBq U-235 eq	-2.00E-02	2.38E-03	112%
Photochemical ozone formation	kg NMVOC eq	2.18E-03	2.89E-03	-33%
Particulate matter	disease inc.	3.22E-08	4.40E-08	-36%
Human toxicity, non-cancer	CTUh	3.94E-09	7.90E-09	-101%
Human toxicity, cancer	CTUh	1.78E-10	2.96E-10	-67%
Acidification	mol H^+ eq	2.10E-03	3.01E-03	-43%
Eutrophication, freshwater	kg P eq	5.75E-05	8.20E-05	-43%
Eutrophication, marine	kg N eq	7.57E-04	1.01E-03	-33%
Eutrophication, terrestrial	mol N eq	9.04E-03	1.31E-02	-45%
Ecotoxicity, freshwater	CTUe	1.11E+01	2.02E+01	-83%
Land use	Pt	8.48E+01	1.17E+02	-38%
Water use	m^3 depriv.	1.05E-01	1.16E-01	-10%
Resource use, fossils	MJ	2.62E+00	2.88E+00	-10%
Resource use, minerals and metals	kg Sb eq	4.06E-06	5.95E-06	-47%

Impact category	Unit	S2-HC	S2-HC-BL	Var%
Climate change	kg CO_2 eq	1.53E-01	1.71E-01	12%
Ozone depletion	kg CFC 11 eq	5.97E-08	6.19E-08	4%
Ionising radiation	kBq U-235 eq	-2.04E-02	2.11E-03	110%
Photochemical ozone formation	kg NMVOC eq	2.44E-03	3.16E-03	29%
Particulate matter	disease inc.	3.72E-08	4.90E-08	32%
Human toxicity, non-cancer	CTUh	5.92E-09	9.91E-09	68%
Human toxicity, cancer	CTUh	2.31E-10	3.50E-10	52%
Acidification	mol H^+ eq	2.73E-03	3.65E-03	34%

Eutrophication, freshwater	kg P eq	7.61E-05	1.01E-04	32%
Eutrophication, marine	kg N eq	9.72E-04	1.22E-03	26%
Eutrophication, terrestrial	mol N eq	1.17E-02	1.57E-02	35%
Ecotoxicity, freshwater	CTUe	1.42E+01	2.35E+01	65%
Land use	Pt	1.36E+02	1.68E+02	24%
Water use	m³ depriv.	1.81E-01	1.91E-01	6%
Resource use, fossils	MJ	1.66E+00	1.92E+00	16%
Resource use, minerals and metals	kg Sb eq	5.52E-06	7.42E-06	34%

Table C2. *Sensitivity analysis comparing Northern context to average European context.*

S1-Burn				
Impact category	**Unit**	**Swedish + Finland scenario**	**European scenario**	**Var%**
Climate change	kg CO₂ eq	2.34E-01	-6.34E-01	-371%
Ozone depletion	kg CFC 11 eq	4.29E-08	6.69E-08	56%
Ionising radiation	kBq U-235 eq	-2.00E-02	2.73E-03	114%
Photochemical ozone formation	kg NMVOC eq	2.18E-03	5.62E-04	-74%
Particulate matter	disease inc.	3.22E-08	3.16E-08	-2%
Human toxicity, non-cancer	CTUh	3.94E-09	-4.96E-09	-226%
Human toxicity, cancer	CTUh	1.78E-10	9.65E-11	-46%
Acidification	mol H⁺ eq	2.10E-03	-4.01E-03	-291%
Eutrophication, freshwater	kg P eq	5.75E-05	-1.34E-03	-2426%
Eutrophication, marine	kg N eq	7.57E-04	-4.96E-05	-107%
Eutrophication, terrestrial	mol N eq	9.04E-03	3.91E-03	-57%
Ecotoxicity, freshwater	CTUe	1.11E+01	6.28E+00	-43%
Land use	Pt	8.48E+01	1.03E+02	22%
Water use	m³ depriv.	1.05E-01	-2.54E-02	-124%
Resource use, fossils	MJ	2.62E+00	-5.83E+00	-323%
Resource use, minerals and metals	kg Sb eq	4.06E-06	9.30E-06	129%

S2-HC

Impact category	Unit	Swedish + Finland scenario	European scenario	Var%
Climate change	kg CO_2 eq	1.53E-01	-7.21E-01	-572%
Ozone depletion	kg CFC 11 eq	5.97E-08	8.39E-08	40%
Ionising radiation	kBq U-235 eq	-2.04E-02	2.44E-03	112%
Photochemical ozone formation	kg NMVOC eq	2.44E-03	8.09E-04	-67%
Particulate matter	disease inc.	3.72E-08	3.66E-08	-2%
Human toxicity, non-cancer	CTUh	5.92E-09	-3.04E-09	-151%
Human toxicity, cancer	CTUh	2.31E-10	1.49E-10	-35%
Acidification	mol H^+ eq	2.73E-03	-3.42E-03	-225%
Eutrophication, freshwater	kg P eq	7.61E-05	-1.33E-03	-1844%
Eutrophication, marine	kg N eq	9.72E-04	1.60E-04	-84%
Eutrophication, terrestrial	mol N eq	1.17E-02	6.50E-03	-44%
Ecotoxicity, freshwater	CTUe	1.42E+01	9.41E+00	-34%
Land use	Pt	1.36E+02	1.54E+02	14%
Water use	m^3 depriv.	1.81E-01	4.90E-02	-73%
Resource use, fossils	MJ	1.66E+00	-6.85E+00	-513%
Resource use, minerals and metals	kg Sb eq	5.52E-06	1.08E-05	96%

Table C3. *Sensitivity analysis when the hydrocarbons Yield decrease by 10%.*

		S2-HC		
Impact category	**Unit**	**Proposed Scenario**	**Lower Yield scenario**	**Var%**
Climate change	kg CO_2 eq	1.53E-01	1.72E-01	13%
Ozone depletion	kg CFC 11 eq	5.97E-08	6.00E-08	1%
Ionising radiation	kBq U-235 eq	-2.04E-02	-2.03E-02	0%
Photochemical ozone formation	kg NMVOC eq	2.44E-03	2.46E-03	1%
Particulate matter	disease inc.	3.72E-08	3.74E-08	1%
Human toxicity, non-cancer	CTUh	5.92E-09	5.93E-09	0%
Human toxicity, cancer	CTUh	2.31E-10	2.31E-10	0%
Acidification	mol H^+ eq	2.73E-03	2.75E-03	1%
Eutrophication, freshwater	kg P eq	7.61E-05	7.61E-05	0%
Eutrophication, marine	kg N eq	9.72E-04	9.76E-04	0%
Eutrophication, terrestrial	mol N eq	1.17E-02	1.17E-02	0%
Ecotoxicity, freshwater	CTUe	1.42E+01	1.42E+01	0%
Land use	Pt	1.36E+02	1.36E+02	0%
Water use	m^3 depriv.	1.81E-01	1.81E-01	0%
Resource use, fossils	MJ	1.66E+00	1.99E+00	20%
Resource use, minerals and metals	kg Sb eq	5.52E-06	5.52E-06	0%

Table C4. *Sensitivity analysis when upgrading hemicellulose in an independent facility.*

		S2-HC		
Impact category	**Unit**	**Integrated pulp mill scenario**	**Independent plant scenario**	**Var%**
Climate change	kg CO_2 eq	1.53E-01	1.51E-01	-1%
Ozone depletion	kg CFC 11 eq	5.97E-08	6.34E-08	6%
Ionising radiation	kBq U-235 eq	-2.04E-02	-1.71E-02	16%
Photochemical ozone formation	kg NMVOC eq	2.44E-03	4.52E-03	85%
Particulate matter	disease inc.	3.72E-08	7.15E-08	92%
Human toxicity, non-cancer	CTUh	5.92E-09	1.53E-08	159%
Human toxicity, cancer	CTUh	2.31E-10	4.79E-10	107%
Acidification	mol H^+ eq	2.73E-03	5.37E-03	97%
Eutrophication, freshwater	kg P eq	7.61E-05	1.27E-04	68%
Eutrophication, marine	kg N eq	9.72E-04	1.71E-03	75%
Eutrophication, terrestrial	mol N eq	1.17E-02	2.39E-02	105%
Ecotoxicity, freshwater	CTUe	1.42E+01	4.05E+01	185%
Land use	Pt	1.36E+02	2.37E+02	74%
Water use	m^3 depriv.	1.81E-01	1.84E-01	2%
Resource use, fossils	MJ	1.66E+00	6.02E-01	-64%
Resource use, minerals and metals	kg Sb eq	5.52E-06	2.71E-07	-95%

Table C5. *Sensitivity analysis comparing the different scenarios using ReCiPe 2016 (Midpoint), H.*

Impact category	Unit	S1-Burn	S2-HC	Var% between S1-Burn and S2-HC
Global warming	kg CO2 eq	2.33E-01	1.52E-01	-35%
Stratospheric ozone depletion	kg CFC11 eq	8.92E-08	2.93E-07	228%
Ionizing radiation	kBq Co-60 eq	-2.62E-02	-2.90E-02	-10%
Ozone formation, Human health	kg NOx eq	1.95E-03	2.12E-03	9%
Fine particulate matter formation	kg PM2.5 eq	5.38E-04	5.99E-04	11%
Ozone formation, Terrestrial ecosystems	kg NOx eq	1.98E-03	2.16E-03	9%
Terrestrial acidification	kg SO2 eq	1.19E-03	1.59E-03	34%
Freshwater eutrophication	kg P eq	5.01E-04	5.42E-04	8%
Marine eutrophication	kg N eq	1.96E-06	4.36E-05	2123%
Terrestrial ecotoxicity	kg 1,4-DCB	1.16E+00	1.49E+00	29%
Freshwater ecotoxicity	kg 1,4-DCB	1.79E-04	2.49E-05	-86%
Marine ecotoxicity	kg 1,4-DCB	1.62E-03	1.79E-03	10%
Human carcinogenic toxicity	kg 1,4-DCB	1.05E-02	1.30E-02	23%
Human non-carcinogenic toxicity	kg 1,4-DCB	2.04E-01	2.48E-01	22%
Land use	m2a crop eq	7.58E-01	1.21E+00	59%
Mineral resource scarcity	kg Cu eq	6.15E-04	8.28E-04	35%
Fossil resource scarcity	kg oil eq	7.48E-02	5.61E-02	-25%
Water consumption	m3	8.10E-04	3.41E-03	321%

Nomenclature

Cp,g	=	GasSpecific heat capacity
Cp,l	=	Liquid Specific heat capacity
m_{sm}	=	Mass of starting material
ΔH_{vap}	=	Standard heat of vaporization
$\Delta H°f$	=	Standard heat of formation

Acronymous:

ADP-fossil	=	Abiotic resource depletion potential – fossil resources
ADP-min&met	=	Abiotic resource depletion potential – minerals and metals
BPH	=	Bleached grade Pulp from Hardwood
BPS	=	Bleached grade Pulp from Softwood
CSF	=	Constant scaling factor
DGP	=	Dissolving Grade Pulp
EF	=	Environmental Footprint
FI	=	Country Code for Finland
FU	=	Functional Unit
GC-MS/FID	=	Gas chromatography-Mass spectrospcopy/Flame Ionization detector
GHG	=	Green House Gasses
GWP	=	Global Warming Potential
HDO	=	Hydro-DeOxygenation
HMU	=	Hydrgen Manufacturing Unit
LCA	=	Life-Cycle Assessment
aLCA	=	attributional Life-Cycle Assessment
cLCA	=	consequential Life-Cycle Assessment
LCI	=	Life-Cycle Inventory
LCIA	=	Life Cycle Impact Assessment
MSR	=	Methane Steam Reforming
MW	=	Molecular weight
PHL	=	Pre-hydrolysis liquor

RER	=	Regional code for European
RoW	=	Regional code for "Rest of World)
S1-BL	=	First scenario, incineration of PHL in the recovery boiler
S1-Burn	=	First scenario, incineration of PHL in the co-generation facility
S2-HC-BL	=	Second scenario, incineration of hemicellulose residues in the recovery boiler
S2-HC	=	Second scenario, incineration of hemicellulose residues in the co-generation facility
SE	=	Country code for Sweden
SQP	=	Soil Quality Potential
TRS	=	Total reduced sulfur
USP	=	Unbleached Sulfate Pulp
UP	=	Unit Process
UPH	=	Unbleached grade Pulp from Hardwood
UPS	=	Unbleached grade Pulp from Softwood
WDP	=	Water Depletion Potential
WGS	=	Water-Gas Shift

Bibliographical references

1. Bajpai P. *Biermann's Handbook of Pulp and Paper, Volume 1, Third edition.* Chapter 2 – Wood and Fiber Fundamentals, (2018). P.46.

2. Bajpai P. *Biermann's Handbook of Pulp and Paper, Volume 1, Third edition.* Chapter 12 – Pulping Fundamentals, (2018). P.331.

3. Bajpai P. *Biermann's Handbook of Pulp and Paper, Volume 1, Third edition.* Chapter 14 – Production of Dissolving Grade Pulp, (2018). P.375.

4. Balkissoon, S., Andrew, J. & Sithole, B. (2023) Dissolving wood pulp production: a review. *Biomass Conv. Bioref.* **13**, 16607–16642.

5. D. D. S. Argyropoulos, C. Crestini, C. Dahlstrand, E. Furusjö, C. Gioia, K. Jedvert, G. Henriksson, C. Hulteberg, M. Lawoko, C. Pierrou, J. S. M. Samec, E. Subbotina, H. Wallmo, M. Wimby (2023), *ChemSusChem* , **16**, e202300492.

6. Capello C., Fischer U., Hungerbühler K. (2007) What is a green solvent? A comprehensive framework for the environmental assessment of solvents. *Green Chem.*, **9**, 927-934.

7. Damiani M, Sinkko T, Caldeira C, Tosches D, Robuchon M, Sala S, (2023). Critical review of methods and models for biodiversity impact assessment and their applicability in the LCA context. *Environmental Impact Assessment Review*, **101**, 107134.

8. Furlan F, Filho R, Pinto F, Costa C, Cruz A, Giordano Ra, Giordano Ro (2013) Bioelectricity versus bioethanol from sugarcane bagasse: is it worth being flexible? *Biotechnol Biofuels* **6**, 142.

9. Lebedeva D. and Samec J.S.M. (2023). Hydrocarbons from kraft pulp pre-hydrolysis liquors in two steps using heterogeneous catalysis. *Sustainable Energy Fuels*,**7**, 3637-3643.

10. Marson A, Samec J.S.M., Manzardo A, (2023). Consequential life cycle assessment of kraft lignin recovery with chemical recycling. *Sci Total Environ*, **882**, 163660.

11. *Perry's Chemical Engineering Handbook, 8th edition.* Don W. Green and Robert H. Perry. McGraw-Hill Professional Pub (2007). P. 2-174, 2-176. P. 2-186, 2-195.

12. Vakkilainen E. (2005). *Kraft recovery boilers – Principles and practice.* Valopaino Oy. P. 2-7.

13. Witthayolankowit, K.; Marson, A.; Baddigam, K. R.; Lebedeva, D.; Shaikh, M.; Kane, A.; Gupta, D.; Wide, M. I.; Mathew, A. P.; Kubička, D.; Manzardo, A.; Samec, J. S. M. Valorization of Beetle Infected Spruce to Produce Textile Fibers and Biofuels: Environmental Sustainability Evaluated by Life Cycle Assessment. *Chemical Engineering Journal*, **470**, 144179.

14. Witthayolankowit, K.; Ramazanova L.; Baddigam, K. R.; Marson, A.; Apostolopoulou-Kalkavoura V.; Lebedeva D.; Muangmeesri S.; Wide M.; Kubička, D.; Håkansson H.; Mathew, A. P.; Manzardo, A.; Samec, J. S. M. (2024). Valorization of Tops and Branches to Textile Fibers and Biofuel: Value Chain Explored Experimentally; Environmental Sustainability Evaluated by Life Cycle Assessment. *ACS Sustainable Chem. Eng.*, **12**, 1, 526–533.

15. Zampori, L. and Pant, R., Suggestions for updating the Product Environmental Footprint (PEF) method, EUR 29682 EN, Publications Office of the European Union, Luxembourg, 2019.

Websites references

1. Cameo Chemicals, Dioxane chemical Datasheet.
   https://cameochemicals.noaa.gov/chemical/617 (last access: 10/02/2024)

2. Cameo Chemicals, Ethyl acetate chemical Datasheet.
   https://cameochemicals.noaa.gov/chemical/665 (last access: 10/02/2024)

3. Energimyndigheten, https://www.energimyndigheten.se/, (last access 10/02/2024)

4. NIST Chemistry WebBook, https://webbook.nist.gov/chemistry/ (last access 13/02/2024)

Acknowledgements

Dasha, Shida, Andrea, Prof. Joseph, Dear, Pop, William, Lala, Lena and Manolis

You got to take the helm and chart your own course! Stick to it, no matter the squalls! And when the time comes, you'll get the chance to really test the cut of your sails and show what you're made of!

- *Treasure Planet* (2002)