Life-cycle Assessment for the Production of IonoSolv Dissolving Pulp Fiber

Master of Science in Petroleum Engineering

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Abstract

Lignocellulosic biomass is a competitive alternative to replace fossil fuels and to be utilized as feedstock for the sustainable and carbon-neutral generation of fuels, chemicals, and high added-value materials. To realize this potential, a cost-effective and low energy-demanded biomass pretreatment technology is highly required.

This thesis is mainly focused on the fractionation of lignocellulosic biomass using a protic ionic liquid following by a chlorine-free bleaching process to obtain dissolving pulp fiber (DPF) at industrial scale. The aim of this work is to achieve process improvements leading to an increase in the product's quality and to identify the environmental burdens in each step of the process. Firstly, the use of N,N-dimethylbutylammonium hydrogen sulfate as a low-cost ionic liquid for the fractionation of spruce softwood followed by alkaline hydrogen peroxide has been shown. Secondly, the concept of Life-cycle Assessment was defined to evaluate the environmental impacts of producing cellulose fiber. The complete pretreatment process, including synthesizing the ionic liquid, lignocellulose fractionation, and the bleaching stage were modeled together in Aspen Plus to obtain the mass and energy flows. The mass and energy flows were implemented to create detailed LCA inventories; the environmental impacts for each stage of the pretreatment were evaluated and compared to one another. Herein, the ReCiPe 2016 methodology was used to categorize LCI entries into 18 midpoints, and further, they were aggregated into 3 endpoints (damage) indicators. The fractionation step with the bleaching stage were shown to have higher environmental impacts than synthesizing the ionic liquid.

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Glossary

[BF_4]	tetrafluoroborate
[$C_nC_1$im]	alkylimidazolium
[C_4C_1im]	1-butyl-3-methylimidazolium
[DBNH]	1,5-diazabicyclo[4.3.0]non-5-ene
[DMBA]	N,N-dimethylbutylammonium
[Emim]	1-ethyl-3-methylimidazolium
[HSO_4]	hydrogen sulfate
[HBim]	1-n-Butylimidazolium
[HMIM]	1-methylimidazolium
[NTf_2]	bis(trifluoromethylsulfonyl)imide
[OAc]	acetate
[PF_6]	hexafluorophosphate
[SbF_6]	hexafluoroantimonate
[TEA]	triethylammonium
1,4-DCB	1,4-dichlorobenzene
AFEX	ammonia fiber expansion
AIL	aprotic ionic liquid
AIL	acid insoluble lignin
ALOP	agricultural occupation
ASL	acid soluble lignin
bara	bar absolute
barg	bar gauge
BOD	biological oxygen demand
CFC-11	trichlorofluoromethane
COD	chemical oxygen demand
DA	dilute acid
DALY	disability adjusted life years
d.b.	dry basis
DES	deep eutectic solvents
DF	dilution factor
DIBK	diisobutyl ketone
DOC	dissolved organic carbon
DP	degree of polymerization
DPF	dissolving pulp fiber
EC	elemental chlorine
ESI-MS	electrospray ionization - mass spectrometry

FDP	fossil depletion
FEP	freshwater eutrophication
FETPinf	freshwater ecotoxicity
GHG	greenhouse gas
GWP500	global warming potentials
HMF	hydroxymethylfurfural
HTPinf	Infinite time for human toxicity
IL	ionic liquid
IRP	ionizing radiation
LCA	life-cycle assessment
LCC	lignin-carbohydrate complexes
LCI	life-cycle inventory
MCC	microcrystalline cellulose
MDP	metal depletion
MEP	marine eutrophication
METPinf	marine ecotoxicity
MIBK	methyl isobutyl ketone
NC	nanocellulose
NLTP	natural land transformation
NMR	nuclear magnetic resonance
NMVOC	non-methane volatile organic compounds
NRTL	non-random two-liquid model
ODPInf	Infinite time for Ozone Depletion
PIL	protic ionic liquid
PMFP	particulate matter formation potential
PM_{10}	10 micrometers particulate matter
POFT	photochemical oxidant formation
RBatch	continuous batch reactor
SE	steam explosion
TAP500	terrestrial acidification potential
TCF	total-chlorine free
TGA	thermogravimetric analysis
TOC	total organic carbon
U235-eq	uranium^{235}
ULOP	urban land occupation
WDP	water depletion
wt%	weight percent
δ	chemical shift

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Introduction

In current times, most of the energy consumption for transportation sectors, manufacturing, and powering industry is provided from fossil feedstocks. Exploiting fossil feedstocks causes many environmental impacts such as land destruction, surface & groundwater contamination, and air pollution emission [1-3]. Carbon emissions from fossil fuels consumption result in global climate change and have many effects on human health [4]. It is almost undeniable that this human activity releases a significant amount of Green House Gases (GHG) which leads to an increase in land and oceans temperature and sea-level rise [5].

Therefore, a greener, environmentally friendly alternative is needed. Biomass is a key renewable feedstock expected to play an important role in energy supplying under strict emission regulations and renewable portfolio standards [6]. To enable biomass as an energy resource technical advancements need to proceed, and value chains need to be precisely evaluated in order to provide a competitive alternative.

Many types of biofuels and high added-value materials can be derived from plants. The method most commercially developed for producing bioethanol is from the plants that mainly contain sugar and starch [7]. However, the negative impacts of exploiting this kind of biomass, such as deforestation, have raised many concerns. On the other hand, lignocellulosic biomass is the most abundant type of plant that provides a more sustainable alternative that can be grown at a lower cost with fewer fertilizer inputs [8]. Besides biofuels, paper and fiber production can be achieved using woody feedstocks. Despite this, lignocellulose is highly resistant to chemical and biological processing. Therefore, an economic pretreatment method is required to commercialize the production of lignocellulosic biomass-derived fuels and materials [9]. The main industrial pretreatment methods use sulfate [10]. The sulfate process, which is also known as the Kraft process, exploits a solution of NaOH and sodium sulfide in which the pulp is cooked. Whilst the Kraft process is the most widely employed method for pretreatment, these plants have huge negative environmental impacts such as releasing odorous compounds, polluting the marine environment, etc. [11, 12].

Ionic liquids (ILs, a class of organic salts with melting points below 100°C [13]) based pretreatments are one of the most effective alternatives studied to date, and they offer many advantages especially those that use low-cost ionic liquids [14, 15]. This method has a large potential to be commercialized, thus there is a need for more details on its environmental impacts.

Cellulose pulp as a product of the pretreatment is one of the most interesting cellulosic materials mainly for producing viscose fibers; but it also can be used for the production of other materials like cellophane, rayon, cellulose acetate, cellulose ester and ethers, nitrocellulose, graft, and cross-linked cellulose derivatives [16, 17]. To have a pulp with high cellulose content and high brightness, a bleaching process is needed after the pretreatment.

Pulp bleaching is a process that enlightens the cellulose pulps or makes them brighter. It is meant to remove oxidable contents that cause the paper to brown from the wood pulp, *i.e.* lignin. Chemical pulp bleaching is done in many different ways using agents containing chlorine or oxygen and alkali extractions in several steps [18]. However, chlorine has significant environmental impacts - it can combine to form chemicals such as dioxins which leads to water contamination [19]. Hydrogen peroxide is a strong chlorine-free (TCF) environmentally friendly alternative which allows to bleach the pulp with the least pollution. However, bleaching DPF using hydrogen peroxide can cause a reduction in the degree of polymerization (DP), therefore the operating conditions should be optimized.

This project aims to address two different challenges: (1) process improvements for the production of dissolving pulp fiber; (2) identifying the environmental impacts in different stages of the IL pretreatment. A mixture of the low-cost IL [DMBA][HSO_4] with water (IL:water ratio = 80:20 wt%) will be used to deconstruct the softwood lignocellulosic feedstocks, recovering a cellulose-rich pulp. The performance of pretreatment will be evaluated using different temperatures and biomass loadings. As sustainability assessments, such as Life-Cycle Assessment (LCA), require the complete details of mass and energy flows, the full pretreatment process for obtaining DPF will be modeled. The ultimate goal is to find the pretreatment stage with the highest environmental impacts and comparing the LCA results with different technologies.

Part I of this thesis reviews existing literature around the topics of biomass, ionic liquids, pulp bleaching, and environmental impacts of biomass processing in order to identify gaps. Part II gives the experimental and simulation details for the results discussed in Part III to conclude the project.

Part I. Background

1. Ionic Liquid

1.1. General

Ionic Liquids (ILs) are salts that are present in the liquid state before they decompose or vaporize [20]. They usually contain an organic component and often melt at low temperatures (below 100°C). ILs have a huge variety of applications: performance additives in paints, capturing carbon dioxide from natural gas, etc. [21, 22]. Above all, ILs have strong potential to be used as solvents and electrolytes [23, 24]. They have negligible vapor pressure under ambient conditions which make them an ideal candidates for use as reaction solvents [25]. Other interesting properties of ILs are their low combustibility and high thermal stability [26, 27]. The thermal stability of ionic liquids is an important parameter for maximum operation temperature limits and their recyclability, and it makes them flexible for variety of applications. In addition, ILs are often used as Gas Chromatography Stationary Phases due to their dual nature retention selectivity that make them able to separate polar and nonpolar molecules [28, 29]. Ionic liquids can be either aprotic or protic in character. Aprotic ionic liquids (AILs) as the first generation of ILs can be formed by alkylation of an amine or phosphine or by anion metastasis reaction of another salt, typically halide; they also require complex synthetic strategies [30]. The following generation of the IL however, which is used in this thesis is comprised of a nitrogen-compound based cation and a sulfur oxyanion, considered protic ionic liquid (PIL). PILs have an acidic proton on the cation rather than an alkyl group for aprotic ionic liquids, some of which are displayed in Figure 1 [30, 31]. PILs are cheap and can be easily synthesized which is an advantageous property for lignocellulosic biomass processing [32].

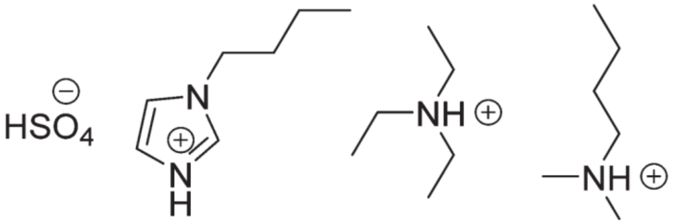

Figure 4: Common structures of some protic ionic liquid ions: the hydrogen sulfate anion, and the 1-butylimidazolium, [HBim]+, triethylammonium, [TEA]+, and N,N-dimethylbutylammonium, [DMBA]+, cations [31]

1.2. Physicochemical Properties

Most of the common ionic liquids melt at temperatures well below 100 °C, with some types, such as ones that contain formate anions, have melting points even lower than 0 °C [33]. Most ILs decompose before reaching their evaporation temperature, and the maximum decomposition temperatures of around 300 °C have been identified, e.g. 1,2-dimethyl-3-ethylimidazolium hexafluorophosphate [34]. Impurities have prominent effects on the melting point and decomposition temperature of ionic liquids [35]. However, having cation symmetry for ILs makes them have higher a melting point [36].

The viscosity of Ionic liquids is an important property for industrial applications. The viscosity of ILs is largely influenced by the nature of the anion and cation, however, their viscosities range is 10-1000 mPa·s at ambient temperature [30]. There are many impactful factors toward the viscosity, including van der Waals interactions, incorporation of certain functional groups, and branching of alkyl side changes [37-39]. Viscosity as well as the melting point is dependent on substitution symmetry and impurities. As an example, [BF_4] and [PF_6] ILs have high viscosities due to the high symmetry [40].

Just like phase transition points, the viscosity of ILs is sensitive to impurities. As it is reported in the literature, having a small fraction of impurities like chloride or water can significantly increase the viscosity up to 600% or decrease it by 50%, respectively [30]. viscosities of ILs show similar behavior as well as water by heating or cooling [30]. As a result of high viscosity, diffusivity is reduced in ionic liquids, expressed by small diffusion coefficients [41, 42]. In contrast to viscosity and melting point, the density of ionic liquids has been found to be independent of impurities and ranges from 0.9 to over 2.4 g cm^{-1} [30, 37].

The polarity of ionic liquids can assign their properties as solvents. The currently accepted definition of polarity is that it is the sum of all possible specific and non-specific intermolecular interactions between the solvent and any potential solute that do not lead to the chemical transformation of the solute [43]. The acidity of ILs is of paramount importance since different reactions require certain acidities for the highest efficiency. With the same cation, by determining the basicity of the anion or pK_a value, the relative acidity can be measured [44]. Plus, the Hammett (H_0) scale is a well-accepted method to measure acidity in non-aqueous solutions [45].

1.3. Stability

The type of ILs, based on chloroaluminates, are sensitive to air and moisture, and they need to be handled in inert atmosphere [30]. However, the next generation of ILs with anions such as $[NO_2]^-$, $[NO_3]^-$, and $[OAc]^-$ have better stability against moisture [46]. The following ionic liquids containing such as $[BF_4]^-$, $[PF_6]^-$, and $[SbF_6]^-$ on the other hand face hydrolysis in the presence of water, releasing corrosive HF and highly toxic compounds [40].

Generally, thermal stability of ionic liquids is measured through thermogravimetric analysis [47]. The T_{onset}[1] depends significantly on the experimental conditions and set up, and it has been reported for various ionic liquids in the literature [48, 49]. However, T_{onset} is often considerably higher than the temperature where the IL can be used in a process without significant loss [50]. $[C_nC_1im]Cl$ ILs have been reported to slowly decompose under isothermal conditions well below the T_{onset} [50]. Recently, triarylsulfonium ILs which are stable in inert atmosphere at 300 °C for 90 days have been found [51].

Whilst the determination of the thermal stability is widely done by TGA, this practice is only able to detect decomposition resulting in weight loss [52]. Therefore, the potentiometric acid-base titration is used to determine the long-term stability of imidazolium based ionic liquids [53]. According to the literature, $[C_4C_1im]$ and $[C_2C_1im]Cl$ degrade at temperatures as low as 140 °C while having a decomposition temperature of around 200 °C [53]. In addition, it was reported that $[C_4C_1im][PF_6]$ degrades twice as much as $[C_4C_1im]Cl$ at 140 °C while $[C_4C_1im][BF_4]$ shows a strong stability at this temperature [53]. Electrospray ionization mass spectrometry (ESI-MS) measurements have shown that the main decomposition pathways are the elimination of the sidechain, transalkylation and retroalkylation, by a nucleophilic attack from the anion [13]. Therefore, halogen containing ionic liquids such as $[PF_6]^-$ and $[BF_4]^-$ are more likely to experience degradation [54].

1.4. Protic Ionic Liquids

The cost of synthesizing ionic liquids always brings many concerns toward their commercialization. In general, many ILs require numerous steps to synthesis and purify due to their low volatility character and low melting points [55]. Recently, low-cost and more easily synthesized protic ILs have attracted lot of interest, especially for biomass processing purposes, such as pretreatment, to produce biofuels and high added-value materials [56-58]. PILs are synthesized through one step neutralization of a Brønsted acid

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[1] The intersection of the tangent at the steepest point of the thermogravimetric curve with the baseline weight

and a Brønsted base in dry or aqueous conditions, in which purification is not required [44]. A vast studies on the properties and applications of PILs can be found in the literature [44]. PILs have negligible vapour pressure in normal condition, and they are in equilibrium with their underlying acid and base, resulting in vapour pressures around 1 atm also at the time of boiling. Therefore, due to the non-negligible vapour pressure, the base or the acid of protic ionic liquids start boiling rather than decomposition under heating by reversing the proton transfer from the base back to the acid [36]. Moreover, the potential for varying the molar ratio of base and acid used for ionic liquid generation is another attractive property of PILs, enabling manipulation of their hydrogen-bonding capacity, reactivity potential, solvent features, and catalytic activity [44]. The electrochemical windows of PILs are narrower than those of corresponding APILs, yet PILs are promising electrolytes in many applications [59].

One of the prominent advantages of PILs over APILs is their lower cost, as protic ionic liquids can be synthesized based on inexpensive bases such as alkylamines and mineral acids [60]. Recently, it has been reported that PILs such as triethylammonium hydrogen sulfate $[TEA][HSO_4]$ and 1-methylimidazolium hydrogen sulfate $[HMIM][HSO_4]$ are significantly low-cost, including the externalities, compared to other conventional solvents like acetone and glycerol [61]. It has been estimated the production cost of $[TEA][HSO_4]$ at \$1.24/kg and $[HC_1im][HSO_4]$ is expected to cost \$2.96/kg [60]. As a result of the exothermic reactions involved in PIL synthesis, energy costs are largely reduced and excess heat can in some cases even be used for other processes [58]. The costs of PILs mainly come from the raw material costs, and, since mineral acids are typically inexpensive, depend mostly on the cost of the organic base involved [44]. Moreover, PILs have a less environmental impacts due to their simple synthesis which uses fewer organic solvents and results in smaller amount of waste than APIL synthesis [60].

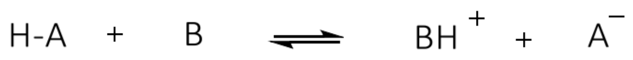


Figure 5: Protic ionic liquid formation from Brønsted acid base reaction

1.5. Toxicity

Many imidazolium ionic liquids, which were widely studied for their applicability in electrochemistry and biomass processing, are now known to be environmentally unfriendly [62]. Moreover, imidazole-derived ILs are now recognized to be either very expensive to synthesize or of limited stability [63]. The source of these solvents is mainly from petroleum-based feedstocks, resulting in quite high environmental impacts [64]. The toxicity of ILs to cells is highly dependent on the nature of the biological system. For this reason, an ionic liquid can be safe toward particular cells, but show high cytotoxicity for others [65]. According to the literature, in [$C_nC_1$im] ILs, longer alkyl chains result in higher toxicity likely because of high lipophilicity [66]. The contribution of hydroxyl or methoxy groups on the side chain decreases the toxicity [65]. In general, ionic liquids with fluorinated anions, such as [NTf_2], show higher toxicity in compared to chloride ILs [65].

The stability characteristics of ionic liquids have brought up many concerns about their accumulation in the environment [67]. Therefore, recent studies are mainly focused on the biocompatibility and biodegradability of ILs to make them more environmentally friendly [68, 69]. During the past few years, some research have examined the synthesis of bio-based ILs from renewable sources, such as amino acids, carbohydrates, or lignin [64, 70]. However, most of these ILs are not thermally stable for biomass processing and unlikely to be inexpensive [71].

Protic ionic liquids have been reported to have fewer environmental impacts than aprotic ones like those that are based on imidazolium and phosphonium [65, 72]. In addition, several alkylammonium ILs have been found to be biocompatible, and also it has been shown that it is possible to synthesize them from bio-based feedstocks [64, 73]. A study that analyzed PILs based on some particular amines and organic acids reported that these ILs are around 60 times more biodegradable than the APILs, and most PILs in the study fall into the category of “readily biodegradable” [72]. In a study on the mutagenic and carcinogenic effects of 16 PILs, 15 were found to be non-mutagenic or carcinogenic [74]. Furthermore, safe disposal of ionic liquids at industrial scale needs to be demonstrated next to their biocompatibility to make them a promising solvent [75].

2. Biomass Conversion

Biomass feedstocks are used to meet a variety of humans' needs, including generating electricity, heating homes, fueling homes, and production of chemicals & high added-value materials. The "biorefinery" concept is defined as a "facility that integrates biomass conversion processes and equipment to produce fuels, power, and chemicals from biomass" [76]. The conversion technologies for utilizing biomass embrace a wide range of approaches to separate biomass resources (wood, crops and their waste byproducts...) into their building blocks (carbohydrates, proteins, triglycerides…) which can be converted to high value-added materials, biofuels, and renewable p. Biorefineries and bioeconomy have important roles in meeting the Sustainable Development Goals (SDGs) [77].

The predominant biomass-derived products are biofuels (biodiesel, bioethanol, etc.) which can be obtained from different types of plants [78, 79]. Furthermore, some specific biomass resources named plant fibers such as cotton, hemp, and sisal are mainly used to produce natural fiber and textile. However, the production of biofuels, such as biodiesel from rapeseed or bioethanol from sugar beets can dramatically result in the release of nitrous oxide and land-use change that negates any CO_2 savings afforded from replacing petroleum [80, 81]. Moreover, natural fibers from some plants, such as cotton, can be highly expensive. Lignocellulose is more abundant, grown faster with greater ease, and requires low fertilizer requirements [82, 83].

Thus, the use of lignocellulosic biomass as a biorefinery feedstock is environmentally and socioeconomically preferential [84]. However, to change the structure of cellulosic biomass to make cellulose more available to further processes, a pretreatment step is necessary [85]. The main industrial methods to proceed with this are Kraft, ionoSolv, Organosolv, Ammonia Fiber Expansion processes [10, 14, 86, 87]. Other methods such as steam explosion (SE), concentrated & dilute acid, and hot water have been described in many literatures [88-91]. While the main goal of most pretreatment technologies is the isolation of a highly digestible cellulose pulp for enzymatic hydrolysis, several factors need to be taken into account for a successful industrial application. Therefore, there is still a need for R&D in cost-effective and optimized biorefining technologies, developing markets for new bio-based products, and pushing policymakers to consider long-term sustainability when developing bio-based value chains.

2.1. Lignocellulose

The most abundant biomass type is lignocellulosic biomass. It provides an alternative source for the production of sustainable energy and high-added-value materials. Lignocellulose is a complex material found in the cell walls of woody plants. It is mainly formed by polysaccharides (cellulose and hemicelluloses) and an aromatic polymer (lignin). Together, these three components account for ca. 90% of the dry weight of biomass. Figure 3 shows the structure of lignocellulose; linear cellulose fibres (light green) are surrounded by hemicellulose (dark green) which in turn is interconnected with lignin (brown). Lignocellulosic biomass contains up to 70% carbohydrates by weight, with the exact proportions depending on the biomass type, species, cell type and developmental stage. Lignocellulosic biomass can be split in three types, namely softwoods, hardwoods and grasses, which all differ not only in their carbohydrate content but also in the composition of their substructures lignin and hemicellulose (see Table 1).

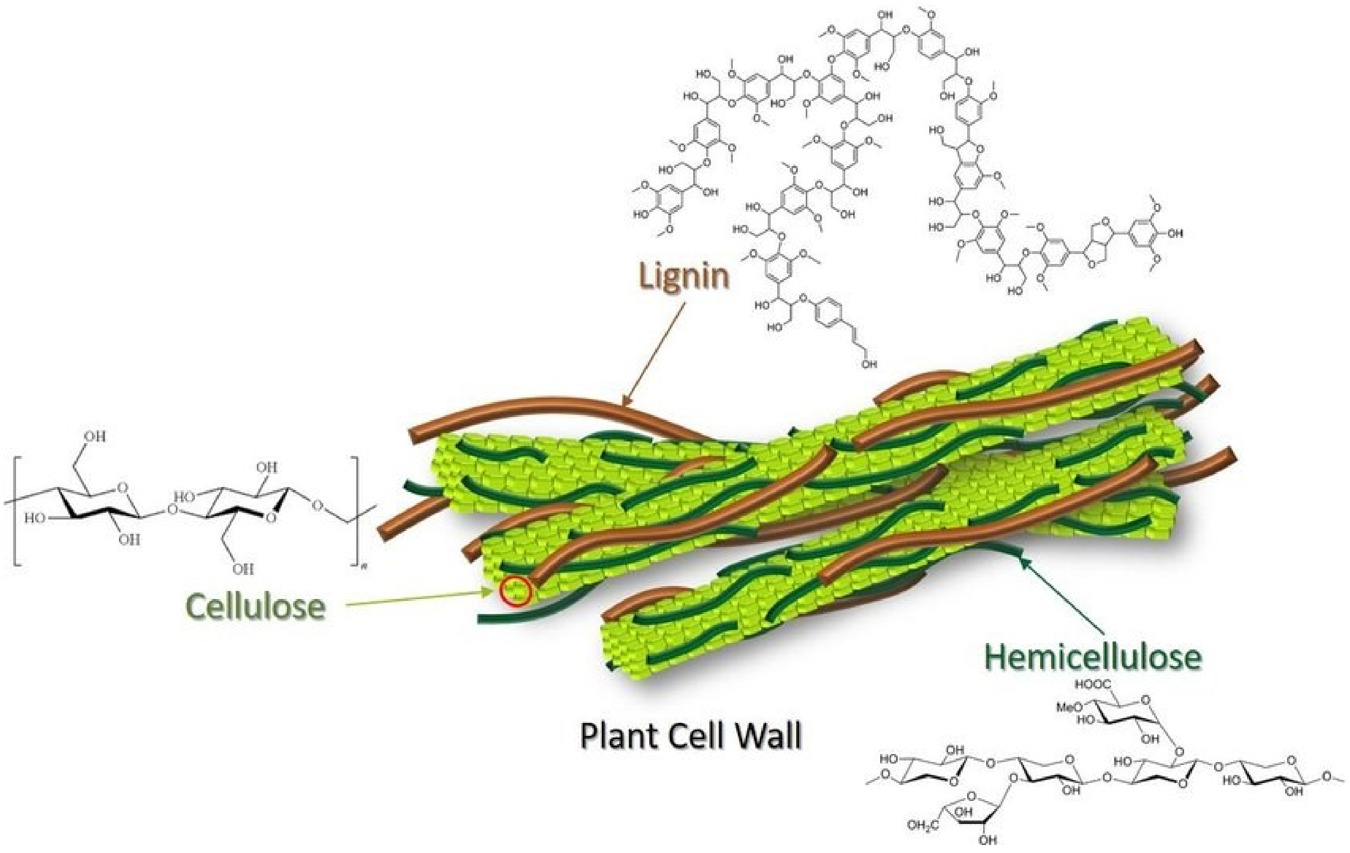


Figure 6: Structure of lignocellulosic biomass [92]

Table 3: Composition of different lignocellulosic substrates on a dry matter basis (wt%) [93, 94]

Plant Type	Cellulose	Hemicellulose	Lignin
Norway spruce (softwood)	26 – 42	9 – 30	8 – 29
Willow (hardwood)	20 – 25	45 – 50	20 – 25
Miscanthus (grass)	38 – 40	18 – 24	24 – 25

2.1.1. Cellulose

The biggest component of lignocellulose is cellulose, accounting up to 50% of its weight in dry basis [95]. Cellulose is a polymer made of repeating glucose molecules attached end to end [96]. The beta form of cellulose is formed by about 500 molecules of glucose flip-flopped connected (see Figure 3) [97]. This pattern allows for hydrogen bonding between two adjacent molecules of cellulose [98]. Two intramolecular hydrogen bonds between neighboring glucose units and one intermolecular hydrogen bond link the chains into flat sheets [99]. These sheets mostly interact with each other through van der Waals interactions which lead to a stabilization of the cellulose fibrils. While cellulose is water-insoluble, there are some solvents such as N-methylmorpholine-N-oxide, concentrated phosphoric acid, and a range of ionic liquids with or without mixing with organic solvents that are able to dissolve cellulose [100-103].

Cellulose itself represents an interesting material for variety of applications. Pulpwood is mainly being processed and bleached to produce dissolving pulp with high cellulose content (> 90%) [18]. Dissolving pulp, also known as dissolving cellulose, is primarily used to make cellulosic fibers and paper-quality pulps. There are many applications of dissolving pulp such as to produce rayon, cellophane, and cellulose acetate [104]. Nanocellulose (NC), a cellulosic material with a cellulose fibril width of up to 100 nm, has been shown to form aerogels used amongst others as oil sorbents [104]. Microcrystalline cellulose (MCC) is a pure partially depolymerized cellulose that is widely used as a filler or binder in tablets [105]. Alternatively, cellulose can be hydrolyzed to glucose which, in turn, can be converted into different bio-derived products such as ethanol, lactic acid, hydroxymethylfurfural (HMF), and gluconic acid [106-109].

Cellulosic fibers are the main feedstock of textile, chemical filters, and fiber-reinforcement composites industries [110, 111]. To obtain dissolving pulps, the pulp is chemically processed, pretreated, pressed, dried, and shredded to produce a dry cellulose compound [112, 113]. This is dissolved to create a solution and then forced through a spinneret – a device that resembles a showerhead – to produce strands [114]. These strands are then drawn – stretched – to produce long straight fibers [114]. After washing, these fibers are ready to be made into clothes and textiles [115].

As cellulosic fibers are used in the manufacturing process both reversible and irreversible changes, such as loss of swelling ability, reduction of wet-flexibility, etc., take place [116]. Thus, for many applications, the quality of cellulose fiber will be essential and a low-cost & optimized process to the product with the required purity and specifications will be necessary.

2.1.2. Hemicellulose

Hemicellulose is a copolymer which is constituted from linear and highly branched chains of C_5 (pentose) and C_6 (hexose) sugars such as xylose, arabinose, mannose, etc. [117, 118]. It usually makes up nearly 25 wt% of the dry biomass weight and has an average molecular weight of around 30,000 Da [93]. The backbone of hemicellulose is mainly made up of xylan (composed of xylose and arabinose), found in all lignocellulose types, while softwoods are typically rich in glucomannan (made up of mannose and glucose) [93]. Hemicellulose is an amorphous matrix material which is likely to attach covalently to cellulose fibrils [99]. Due to its non-crystallinity, it is more suspected of depolymerization in acidic environments [99]. However, as a result of the presence of lignin-carbohydrate complexes (LCC), hemicellulose forms covalent cross-links with lignin which makes the processing more difficult. Unlike cellulose, hemicellulose also contains functionalized groups, such as acetyl, resulting in lower thermal stability than both lignin and cellulose and enhancing the affinity of hemicellulose to lignin [95, 119, 120].

2.1.3. Lignin

Lignin is a phenolic polymer which fills the spaces in the cell wall between cellulose and hemicellulose [121]. Lignin approximately makes up to 30% of biomass weight and nearly 40% of its energy content [122]. Lignin is water-insoluble, thus adding to water resistance, and gives structural support to plant cells walls [123]. It is resistant to chemical and physical attack and thus acts as a shield for polysaccharides [124]. The integrated subunits in the lignin polymer are known as guaiacyl (G), syringyl (S), and p-hydroxyphenyl (H) subunits. These subunits are linked by a variety of C–O and C–C bonds, with around half of them are made up of the β-O-4’ ether bonds [125]. The main type of lignin found in softwood is guaiacyl and a small amount of p-hydroxyphenyl (H) residues, while hardwoods and grasses contain a large number of syringyl (S) and grasses contain all three [95, 126].

Both native and modified lignin adhering to the pulp is the major factor reducing biomass enzymatic hydrolyzability [127, 128]. This adds to the cost of biomass fractionation since higher enzyme loadings are required [84]. Thus, most chemical deconstruction methods aim to remove lignin. The potential of removing lignin from hydrolyzable cellulose fibers depends on the type of biomass and lignin solubility [127, 129]. It has been found that C–C crosslinks in softwoods are not easily hydrolyzed, and this makes the delignification process more challenging [130]. In contrast, making such cross-linkages in hardwoods due to the presence of (S) subunits is impossible, resulting in more readily delignification [95].

2.2. Deconstruction of Lignocellulose

Conversion of biomass into useful materials such as chemicals, fuels, and bio-products requires to separate cellulose, hemicellulose, and lignin apart from each other. The focus is on overcoming the structural and chemical barriers limiting carbohydrate release, namely lignin removal to increase the accessible surface area of cellulose while limiting the generation of inhibitory compounds [131, 132]. Pretreatment methods have been widely applied in pulp and paper industries, mainly for the delignification of cellulosic materials [112]. During the so-called Kraft process, a solution of caustic soda and sodium sulfide as the liquor are employed to process the biomass at 130-180 °C for several hours in which the pulpwood is cooked. In Kraft pulping, about 90% of wood lignin is solubilized to the cooking liquid. The remaining 10% chromophores group of lignin is mainly responsible for the dark color of the unbleached paper [133]. The Kraft process entails the treatment of wood chips with a hot mixture of water, sodium hydroxide (NaOH), and sodium sulfide (Na_2S), known as white liquor, which breaks the bonds that link lignin, hemicellulose, and cellulose [11]. The liquor is burnt afterward for energy generation and regeneration of the sulfide [100]. The Kraft process is not only used to remove lignin and/or hemicellulose but also to decrease the degree of polymerization and reduce the crystallinity of cellulosic components [10, 134-138]. The Kraft process alone accounts for over 80% of the chemical pulp produced in the USA [139]. This method has been used mainly for paper production, and it is optimized for high cellulose yield and fiber strength [95]. However, Kraft plants have huge negative environmental impacts such as releasing odorous compounds and polluting the marine environment [11, 12]. The most significant environmental impacts of pulp and paper manufacture result from the pulping and bleaching processes [140]. Spent chlorination and alkali extraction liquors from the bleaching of softwood Kraft pulp are mildly toxic to fish and other aquatic organisms [141, 142]. Moreover, In producing chemical pulp, the effluent rate represents 20-50 m^3/t of pulp, which contains up to 15 kg/t suspended solids [143].

There are many other different technologies for biomass pretreatment that can be categorized into three types: (1) physical; (2) biological; (3) chemical. Physical methods, such as mechanical milling, are significantly energy-demanded and lack enough efficiency for the lignin removal [144]. Mechanical milling increases the accessible surface area of cellulose and decreases cellulose crystallinity, resulting in increasing glucose digestibility; however, it does not seem economical due to the high energy required [145-147]. Other physical methods such as ultrasound and irradiation with microwave & γ-ray have been found out to also increase biomass digestibility when they are integrated with chemical methods [148, 149]. In biological methods, some microorganisms such as fungi and bacteria are employed to attack cellulose and/or degrade lignin [150]. These pretreatment methods offer some advantages of low energy required and operation in mild conditions. However, they require intensive space and process very slow, and thus cannot be commercialized [150]. Chemical methods that require also high thermal energy such as steam explosion (SE), dilute acid (DA), and ammonia fiber expansion (AFEX) are mainly used to increase sugar release rather than separating lignin [151-153]. SE pretreatment has some disadvantages, such as releasing inhibitory byproducts that limit yields and slow down hydrolysis [154]. DA method encounters not just the same issue of inhibitory generation but also has corrosion problems [155, 156]. In contrast, AFEX pretreatment releases negligible inhibitors, but it is ineffective for biomass with a high fraction of lignin [157].

Chemical pretreatments with the aim of biomass fractionation such as Organosolv, deep eutectic solvents (DES), and ionic liquid-based methods have gained much attention due to their additional value generation of lignin stream and lower enzyme loading [95, 100, 158, 159]. A highly interesting pretreatment method especially for softwood feedstock is the Organosolv process, in which biomass is treated with hot organic solvents (e.g. methanol, ethanol, or acetone) at 150–200 °C [160]. The main advantages of this method are the high degree of lignin removal around 60-95% and producing a high concentrated lignin stream with low molecular weight [161, 162]. However, Organosolv is not economically attractive due to the high cost of organic solvents, high-pressure equipment, and possible release of volatiles [150].

The first Ionic liquid-based pretreatment, known as the Dissolution process, is a promising approach to fractionate lignocellulose. Ionic liquid pretreatment offer several advantages over existing processes such as averting the emission of volatile organic or toxic compounds in the viscose process and having high thermal stability [163]. In this method, whole the biomass is dissolved in the IL, and the addition of anti-solvent allows re-precipitation of decrystallized cellulose which has high potential for enzymatic hydrolysis [32]. It is found out that IL pretreatment has the most effectiveness in the absence of water (<1%), therefore, drying the IL and the feedstock are highly cost and energy-demanded [14, 164]. There are number of ionic liquids which have been used to pretreat biomass in processes that are based on the dissolving and decrystallization of cellulose, such as 1-ethyl-3-methylimidazolium acetate ([Emim][OAc])], 1,5-diazabicyclo[4.3.0]non-5-ene acetate ([DBNH][OAc]), 1-butyl-3-methylimidazolium chloride ([C_4mim][Cl]), etc. [103, 165-169]. The most widely investigated IL for biorefining to date is [Emim][OAc], which has been found out to be significantly compatible with a variety of feedstocks [170]. Furthermore, it has been reported that it gives around 100% glucose yield within 24 h of hydrolysis, with nearly 65 and 85% removal of lignin and hemicellulose, respectively [84, 95]. However, [Emim][OAc] decomposes at low temperatures, around 100 °C, and it has raised much concern about its suitability for industrial-scale biomass processing [47]. In general, lignocellulose fractionation by APILs have some restrictions: high solvent cost, low recyclability, and sometimes due to changing the crystalline structure of cellulose, they cannot be applicable for producing a variety of final products [47, 171].

IonoSolv pretreatment, developed in 2010 by Brandt, Hallett *et al.*, is a lignocellulose fractionation technology that exploits protic ionic liquids such as triethylammonium hydrogen sulfate ([TEA][HSO_4]), 1-butylimidazolium hydrogen sulfate ([HBim][HSO_4]), and N,N-Dimethylbutylammonium hydrogen sulfate ([DMBA][HSO_4]) to extract lignin and hemicellulose from the biomass while leaving behind a cellulose-rich pulp [14, 172]. It can address many of the drawbacks of the dissolution process. In the IonoSolv process, the cellulose remains crystalline after pretreatment, and the majority of lignin is extracted from biomass [14, 31]. Water was found to have an important role, reducing IL viscosity which enhances lignin removal and acting as an anti-solvent for cellulose [173]. The low-cost PILs employed in the ionoSolv process could be synthesized at a cost of around $1 per kg, and they are also thermally stable [61]. Furthermore, the high delignification (>80%) and hemicellulose removal, resulting in suitable digestibility of the recovered cellulose-rich pulp [174]. Several types of feedstocks such as grasses, hardwoods, and softwoods have been reported to have glucose yields of 70-100% [175, 176]. The IL recovery is significantly high (>99%) and can be reused with minimal effect on the efficiency of fractionation [14]. Moreover, ionoSolv has a high potential for lignin valorization because it allows for lignin isolation as well as to tune its properties through optimizing residence time, temperature, pH and re-precipitation [159, 176].

2.3. Bleaching

Bleaching is the chemical processing of wood pulp to lighten its color, which leads to preparation for textile, paper, etc. The primary goal of bleaching is to remove the residual lignin from the pulp as selectively as possible. This purpose should be done without degrading cellulose, which would decrease the viscosity and strength [177]. The chlorine-based bleaching process exploits elemental chlorine (EC) agents to react selectively with the non-carbohydrate compounds and ruptures the lignin bonds [178]. The pulp chlorination bleaching process is not environmentally friendly; it produces many toxic compounds as organic halide compounds [179]. Total chlorine-free (TCF) is a more environmentally friendly alternative which will allow operating with the least pollution of the environment and will not cause the formation of any organochlorine matter to the pulp. Hydrogen peroxide is a strong bleaching agent for use in TCF sequences [180, 181]. Cellulose pulps which were treated and bleached using ionoSolv fractionation and TCF process (alkaline H_2O_2 oxidation treatment) are shown in Figure 4. M120 and M170 are *Miscanthus* after pretreatment at 120 °C for 6 hours and 170 °C for 45 minutes. BM120 and BM170 are the same pretreated pulps which were bleached by alkaline H_2O_2 oxidation treatment.

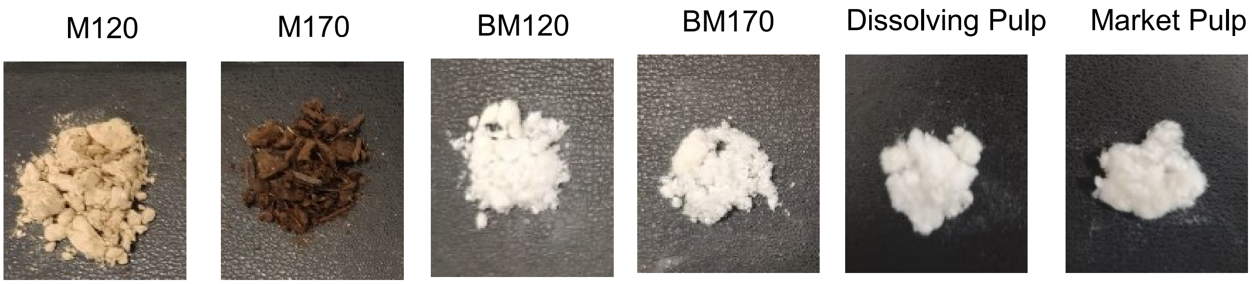


Figure 4: Cellulose pulps treated using ionoSolv fractionation and ionoSolv + alkaline H_2O_2 oxidation treatment, dissolving and market pulps

Due to a better understanding of the role of ions in the decomposition of peroxide, developments in the hydrogen peroxide bleaching process have been possible [182]. Bleaching pulps to high brightness with alkaline hydrogen peroxide requires: (1) the elimination of conjugated carbonyl groups in the lignin structure by perhydroxyl anion HOO^- ; (2) removal of lignin through degradation/dissolution by reaction with $HO^\cdot$ and O_2^- radicals [183]. The reactivity of $HO^\cdot$ and O_2^- radicals towards aromatic lignin (phenolic group) is only slightly higher than towards cellulose. Therefore, if H_2O_2 decomposes too fast and the concentrations of $HO^{\cdot}$ and O_2^- become too high, selectivity towards lignin is lost and cellulose degradation occurs as well as lignin degradation [183]. Furthermore, the selectivity of the reaction towards cellulose and lignin is dependent on lignin content because lignin is more reactive than cellulose [184]. Therefore, a pulp with lower lignin content has a higher potential of experiencing cellulose degradation. In general, perhydroxyl anion is the principal active species involved in the elimination of chromophores in the lignin structure. Reactions 1 and 2 show the hydrogen peroxide decomposition to perhydroxyl anion and its reaction with lignin [185].

$$H_2O_2 \ + \ OH^- \ \rightarrow \ HOO^- \ + \ H_2O \tag{1}$$

$$HOO^- \ + \ lignin \ \rightarrow \ lignin = O \ + \ OH^- \tag{2}$$

Transition metals can catalyze the wasteful hydrogen peroxide decomposition at a high rate, which causes cellulose degradation as previously discussed [186]. This is an important issue because it can decrease the degree of polymerization (DP) of the pulp. Certain transition metals (e.g. manganese, copper, and iron) contribute to the formation of hydroxyl radicals, and superoxide anion radicals. However, certain alkaline earth metals, such as magnesium sodium silicate, hinder hydrogen peroxide decomposition [187]. The concentration of active perhydroxyl ion increases with pH which must be adjusted and buffered at about 10.5 for best results [188]. In addition, transition metals activity can be a function of pH, which is usually controlled by sodium hydroxide [188, 189]. An increase in hydrogen peroxide dose until a maximum limit leads to higher pulp brightness as long as pretreatment and stabilization have been optimized.

2.4. Conclusion

To produce DPF with a viable quality, the residual lignin content of the pulp should be considered as an important factor. This necessitates a lignocellulose fractionation process with low operation cost and environmental impacts that can provide a product with consistent quality. Whilst ionoSolv process offers several advantages, such as high degree of delignification (>80%), the bleaching stage using hydrogen peroxide is still required to bleach down the pulp to a certain quality. Excessive use of chemical bleaching, H_2O_2, can result in cellulose degradation and significant DP reduction, thus lead to a decrease in the quality of the cellulose fiber. Therefore, the bleaching process requires more research to optimize the efficient amount of hydrogen peroxide.

2.5. Life-cycle Assessment

Sustainability assessment is being increasingly viewed as an important tool to aid in the shift towards sustainability. The overall goal is to analyze a technology from different perspectives. Life-cycle Assessment (LCA) is a very popular analysis for reporting potential environmental loads and resources consumed in each step of a product or service supply chain [190]. LCA comprises all environmental burdens of a product as a result of the raw materials consumption, energy, and chemical auxiliaries used in processing steps and waste treatment, as well as direct process emissions. Nowadays, this sort of assessment is accepted by all stakeholders as a guiding principle for both public policymaking and corporate strategies [191]. In this thesis, eighteen different midpoints were used, and then they were all aggregated to three endpoints.

2.5.1. Midpoint & Endpoint Indicators

Midpoints are defined as a point in the cause-effect chain (an environmental mechanism) of a specific impact category, prior to the endpoint, at which characterization factors can be estimated to represent the relative importance of emission or extraction in a Life-cycle Inventory (LCI) [192]. In midpoint approaches, the environmental relevance is generally presented in the form of qualitative relationships; however, in endpoint methods, there is no need to deal separately with the environmental relevance of the category indicators, since these indicators are considered more understandable to the decision-makers [192].

In this thesis, eighteen midpoints are used. **Global Warming Potentials (GWP500)** implies the amount of carbon dioxide that has the same cumulative climate change effect with 1 kg of the substance during, in this case, a 500-year time period [193]. **Infinite time for Ozone Depletion (ODPInf)** expresses the ozone depletion potential of 1 kg of a given compound, relative to the ozone depletion potential of 1 kg of CFC-11 [194]. **Ionizing radiation (IRP)** is linked to the collective dose resulting from the emission of a radionuclide, and it is reported in Uranium^{235} (U235-eq) [195]. **Infinite time for Human Toxicity (HTPinf)** is an indicator reported in 1,4-dichlorobenzene (1,4-DCB) that accounts for the toxicological impacts on human health in LCA that are related to chemical fate, human exposure, and toxicological effects [196]. **Particulate matter formation potential (PMFP)** expresses the human population intake of PM_{10} after the emission of a precursor, *i.e.* NH_3, NO_x, SO_2, and primary PM_{10} [197]. **Terrestrial Acidification Potential (TAP500)** implies the fate of a pollutant in the atmosphere and the soil expressed in kg SO_2-equivalents during a 500-year time period [198]. Environmental ecotoxicity Indicators such as **Terrestrial Ecotoxicity (TETPinf), Marine Ecotoxicity (METPinf), and Freshwater Ecotoxicity (FETPinf)** describe the fate, exposure, and the effects of toxic substances, such as heavy metals, on the environment [199]. Eutrophication indicators such as **Freshwater Eutrophication (FEP) and Marine Eutrophication (MEP)** express the build-up of a concentration of chemical nutrients in an ecosystem which leads to abnormal productivity. These indicators are reported in kg phosphorous/nitrogen-equivalent [200]. Resource depletion indicators such as **Water Depletion (WDP), Metal Depletion (MDP), and Fossil Depletion (FDP)** imply the equivalent resource consumption of a substance that is based on the Ecological Scarcity Method [201, 202]. **Photochemical Oxidant Formation (POFT)** refers to the photochemical ozone, also called ground-level ozone, which is formed by the reaction of volatile organic compounds and nitrogen oxides in the presence of heat and sunlight, and it is toxic to humans in high concentration. The impact category is expressed in kg NMVOC (non-methane volatile organic compounds) [203]. **Natural Land Transformation (NLTP)** represents the amount of natural land transformed in m^2. **Agricultural and Urban Land Occupation (ALOP and ULOP)** refer to the amount of natural land occupied, and they are measured as area time (m^2a) [204].

Further, all the midpoints were aggregated into three endpoint categories. **Human Health** endpoint expresses the Disability Adjusted Life Years (DALY) quantifying the impact of premature death or disability that climate change has on the population [205]. The **Ecosystems** indicator is local relative species loss in terrestrial, freshwater, and marine ecosystems, integrated over space and time (potentially disappeared fraction of species$\cdot m^2 \cdot$year or potentially disappeared fraction of species$\cdot m^3 \cdot$ year). These impacts are aggregated into one single unit (species.year) [205]. The unit for **Resources** endpoint is dollars ($), which represents the extra costs needed for future mineral and fossil resource extraction.

3. Research Gap and Objectives

As it was reviewed in the literature, IL-based pretreatment offers many advantages over the existing technologies as a cost-competitive route. The development of a route to produce DPF using low-cost ILs, such as [DMBA][HSO_4], requires an additional step, a bleaching process, in order to lighten the pulp and remove the residual lignin. Hydrogen peroxide is a strong chlorine-free agent that can bleach down the pulp to a certain quality in an environmentally friendly way. While there are many factors that can affect the product quality, the temperature of pretreatment and the biomass loading are investigated to find the optimal condition. To do this, different pretreatment conditions are selected to monitor the lignin removal which is a good measurement to identify the optimal condition.

The biomass feedstock selection is also highly important due to several chemical treatments. Softwoods are a fast-growing species known to possess longer fibers with a higher degree of polymerization than grasses and hardwoods, which is desirable for the preparation of fibers for textile applications. Here we are focusing on the use of Spruce, a type of softwood, as the selected feedstock. The main type of lignin found in softwood is guaiacyl and small amounts of p-hydroxyphenyl (H) residues. Softwood biomass is more recalcitrant and resistant to chemical pretreatment due to its high lignin content.

Another challenge is to identify the environmental impacts of all stages of DPF preparation. To do so, the full pretreatment process will be simulated, and a standardized sustainability assessment will be developed to find technological disadvantages, and identify environmental burdens. The experimental results would be used as inputs for ReCipe Life-cycle Assessment using openLCA software and ecoinvent database. These were new improvements for producing Dissolving Pulp Fiber using [DMBA][HSO_4] IL by ionoSolv process.

The main objectives of this project were therefore to:

- Optimize pretreatment process to obtain a pulp with the degree of delignification and high content of cellulose.
- Investigate the environmental burdens of each step involved in the production of ionoSolv dissolving pulp.

4. Thesis Outline

In Part I, the background of the research topics was introduced and the research goals outlined. Part II includes the experimental and simulation results, plus discussion chapters. Chapter 1 describes the experimental pretreatment of Spruce softwood which results are then used in the simulation of the bleaching process. The full process of production of DPF is modeled in Chapter II, which attempts to obtain the mass and energy flows to employ in the Life-cycle Assessment. The important research outcomes and summaries are then brought together in Part III, which concludes this MSc thesis.

Part II. Experimental Methods and Simulation

Chapter 1: Pretreatment and Bleaching

1.1. Materials & Methods (Pretreatment)

Spruce (softwood) biomass was air-dried, ground (Retsch AS200 cutting mill, 1 cm square mesh), and sieved (180 - 850 µm, 20 + 80 US mesh scale) prior to use. Starting materials for ionic liquid synthesis, H_2SO_4 (66.3% wt) and N,N-Dimethylbutylamine (99% wt) were purchased from Sigma Aldrich and used as received, unless stated otherwise. ^1H NMR spectra were registered on a Bruker 400 MHz spectrometer. Chemical shifts (δ) are reported in ppm, the DMSO signal at 2.500 (^1H dimension) and 39.520 (^{13}C dimension).

1.1.1. Synthesis of N,N-Dimethylbutylammonium hydrogen sulfate [DMBA][HSO_4] and its characterization

In order to prepare 700 g [DMBA] [HSO_4], N,N-Dimethylbutylamine (355 g, 3510 mmol) was cooled with an ice bath in a round-bottom flask. 519 g of H_2SO_4 (3510 mmol) was added dropwise while stirring. The solution was stirred for 2 hours and due to the exothermic reaction, an ice bath should be prepared during adding H_2SO_4. The mixture was characterized by ^1H NMR, ^{13}C NMR, and LR-MS [31].

^1H NMR: δ_H (400 MHz, DMSO-d_6)/ppm, 9.24 (s, 1H, N–H), 3.02 (dt, *J* = 12.9, 5.0 Hz, 2H, N–CH_2), 2.76 (d, *J* = 4.3 Hz, 6H, N–$(CH_3)_2$), 1.64–1.51 (m, 2H, N–CH_2–CH_2), 1.29 (h, *J* = 7.4 Hz, 2H, N–CH_2–CH_2–CH_2), 0.89 (t, *J* = 7.4 Hz, 3H, N–CH_2–CH_2–CH_2–CH_3).

^{13}C NMR δ_C (101 MHz, DMSO-d_6)/ppm: 56.62 (N–CH_2), 42.48 (N–CH_3), 25.82 (N–CH_2–CH_2), 19.40 (N–CH_2– CH_2–CH_2), 13.71 (N–CH_2–CH_2–CH_2–CH_3).

MS (Magnet FB^+) m/z: 102 ($[DMBA]^+$, 100%), (Magnet FB^-) m/z: 79 ($[HSO4]^-$, 100%).

The moisture content of IL was measured with a Karl-Fischer V20 volumetric Titrator (MettlerToledo). The titrator was calibrated before the experiment for obtaining accurate results. The final average value for the moisture content is 19.51% (wt).

Acid:base ratios were measured using a Mettler Toledo G20S compact titrator. Due to the importance of acid:base ratio for the pretreatment, this value is measured and if it is not 1:1, a correction must be applied. A titrator was calibrated with a standard solution, KHP (Potassium Hydrogen Phthalate. The final results gave an average acid:base ratio of 1:1.

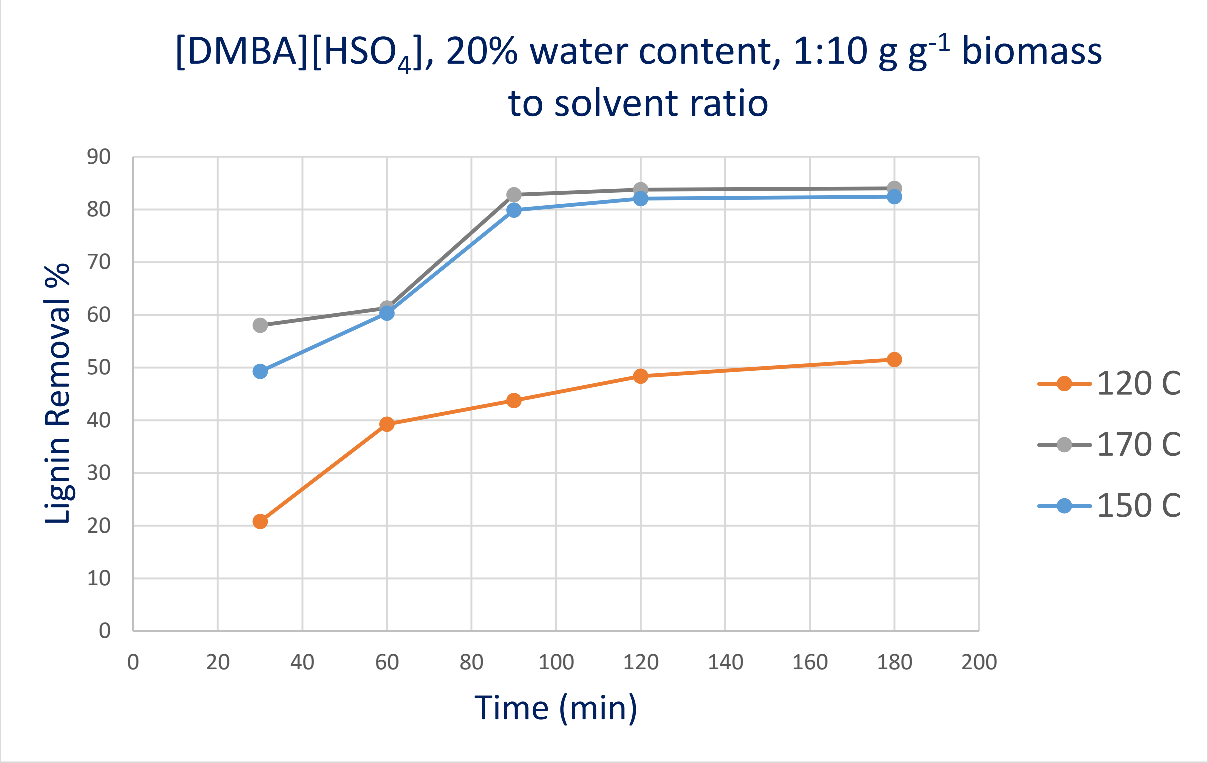
1.1.2. Ionic Liquid Pretreatment

The moisture content of [DMBA][HSO_4] was adjusted to 20 wt% prior to pretreatment considering the moisture content of the untreated biomass. The Spruce feedstock was pretreated as indicated by a scaled-up pretreatment methodology [206]. The pretreatment was carried out in a 1.5-L jacketed borosilicate glass pressure vessel which was equipped with a proportional relief valve set to 4.5 barg and a bursting disk (6 barg, with the most minimal rating of 5 barg at 120, 150, and 180 °C) with stirring. Reactions were completed in monoplicate, utilizing a procedure volume of 1 L. Stirring was performed using a 50 mm anchor agitator with flat blades set at a steady stirring rate of 100 rpm. Biomass loading of 20% was used with 1000 g of 80 wt% [DMBA][HSO4] and 200 g of biomass on a dry basis. Spruce was pretreated for 60 min, and the maximum recorded pressure at 120, 150, and 180 °C was at 3.70 bara.

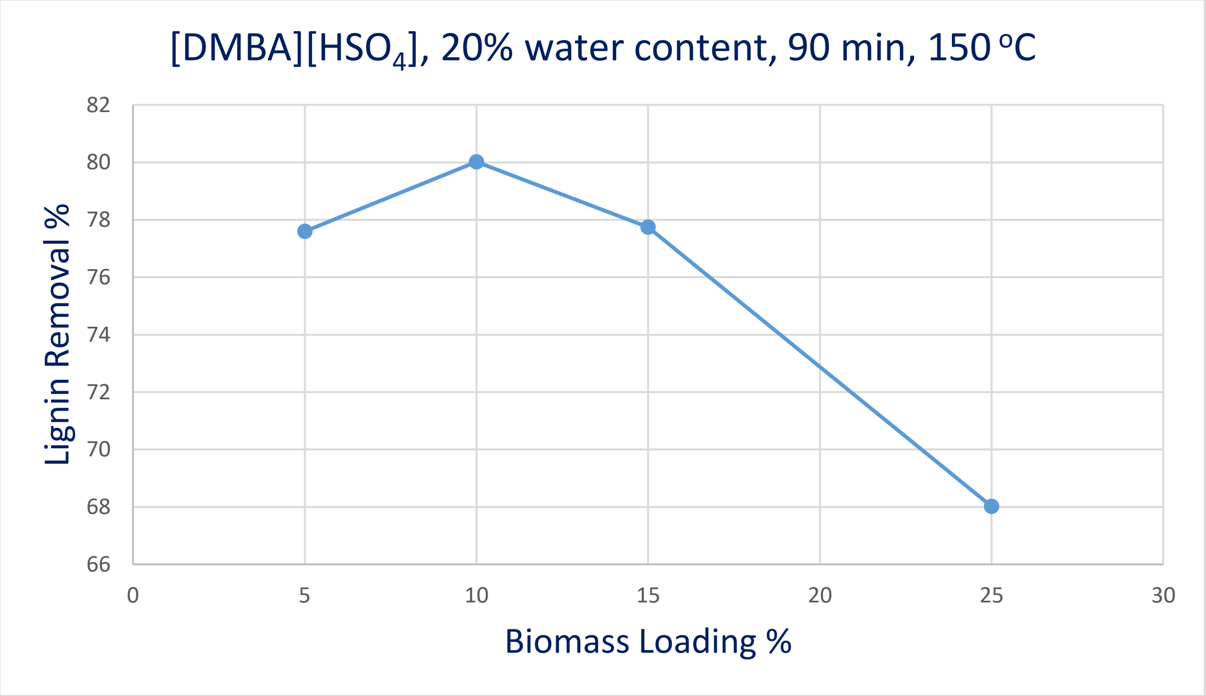
After cooling the reaction mixture, the vessel contents were emptied by washing with 1 L of absolute ethanol. The IL-biomass-ethanol slurry was moved to four 500 mL centrifuge tubes (Corning, USA), allowed to equilibrate for 1 h and centrifuged (Megastar 3.0, VWR, UK; 3000rpm, 50 min). The liquid phase was decanted and collected, while the pulp was washed 14 additional times with ethanol. Recovered IL and ethanol washes were combined, and ethanol was removed by rotary evaporation (by heating at 40 °C under reduced pressure) until complete ethanol removal was accomplished.

1.1.3. Pretreatment Results

After the pretreatment, the compositional analysis was carry out to measure the residual lignin content of pulp. According to the Graph 1, lignin removal is more than twice bigger at 170 and 150 ^{o}C than 120 ^{o}C. However, it has been found out that the delignification is almost stable after 90 minutes of the fractionation. Even though the lignin removal is higher at 170 ^{o}C To avoid the risk of cellulose degradation, 150 ^{o}C was selected as the optimal value for the pretreatment.



Graph 1: Pretreatment results using [DMBA][HSO₄], 20% water content, 1:10 g g^{-1} biomass to solvent ratio at 120, 150, and 170 ^{o}C



Graph 2: Pretreatment results using [DMBA][HSO₄], 20% water content, 90 min, 150 ^{o}C with 5, 10, 15, 25% of biomass loading

1.1.4. Compositional Analysis

According to the published procedure Determination of Structural Carbohydrates and Lignin in Biomass by the NREL, the compositional analysis was carried out on untreated extractives-free biomass feedstocks [207]. The extractives were removed from untreated biomass using ethanol before performing compositional analysis following NREL-TP-510-42619 [208]. The composition result of pretreated Spruce is shown in table 2. The results of CA was then used as inputs for the simulation and LCA inventories.

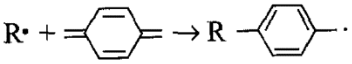
Table 4: Norway Spruce Sawdust composition after pretraetment, [DMBA][HSO4], 150 °C, 90 min (CA Resaults)

Compound	**Weight fraction %**
Glucose	65.1
Xylose	1.6
Mannose	3
ASL (acid insoluble lignin)	15.8
AIL (acid soluble lignin)	1.4
Ash	0.6
Total	87.5

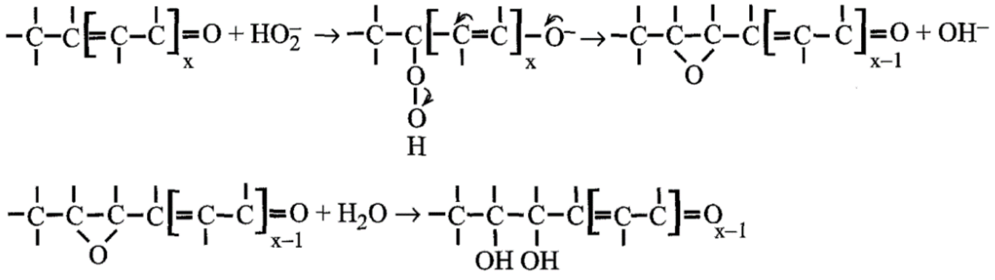
1.1.5. Bleaching Mechanism

The bleaching mechanism is started by the formation of HOO^-. This anion is believed to be the main agent for the elimination of chromophores. The model assumed that no side reaction is producing H_2O and oxygen leading to the wasteful decomposition of hydrogen peroxide (reaction 3). The reason is that NaOH and $MgSO_4$ are added to the solution for controlling the pH and reducing the activity of transition metals which catalyze this decomposition. It has found out that $HO\cdot$ or $HO_2\cdot$ demobilize the mobile electrons in the systems of conjugated double bonds present in chromophores leading to decolorize the compounds [209]. For instance, a quinoid chromophore can be converted to a benzenoid structure (reaction 4) [210]. It has been suggested that the perhydroxyl anion, as a nucleophile, might attack carbon-carbon double bonds present, preferably at the end carbonyl atom, in the chromophores of impurities (reaction 5) [211]. According to previous studies, H_2O_2 bleaching kinetic was modeled based on the "Differential Method" [212].

$$H_2O_2 \rightarrow \; H_2O + O_2 \tag{3}$$



(4)



(5)

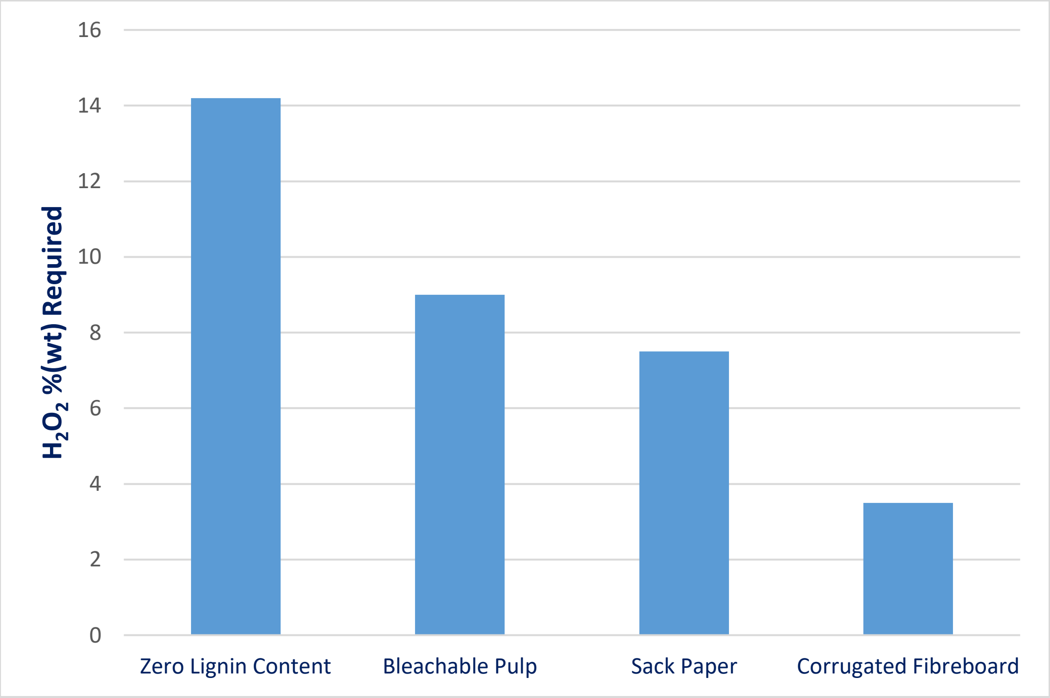
1.1.6. Bleaching Operation Condition

The bleaching process was assumed to be carried out at atmospheric pressure and 60 °C for 120 min under magnetic stirring. The pulp was treated with 10% Consistency, in a ratio of 1:10 (fiber mass/solution mass) in a continuous batch reactor (RBatch).

1.2. Results and Discussion

After synthesizing [DMBA][HSO_4], the water content was adjusted to 20 wt%. The acid-base ratio determination gave an average value equal to 1 and therefore did not require any correction. Different temperatures were investigated to monitor the lignin removal. 150 °C was the optimal temperature with 80% of lignin removal. Then different biomass loadings were tested and 10% of biomass to solvent ratio gave the highest degree of delignification. The compositional analysis of pretreated Spruce showed 25.3 wt% soluble/insoluble acid lignin included in the biomass.

The bleached pulp should have a certain kappa number to be applicable for different end products. For example, bleachable pulps, sack paper, and corrugated fiberboard require kappa numbers between 25-30, 45-50, and 60-110 respectively. According to Graph 1, 9, 7.5, and 3.5 wt% of H_2O_2 are approximated to prepare bleachable pulps, sack paper, and corrugated fiberboard from pretreated Spruce, respectively.



Graph 3: H_2O_2 amount required to obtain different pulp qualities from pretreated Spruce

Chapter 2: Process Design of DPF Production and LCA

2.1. Process Design of the IL Pretreatment

The developed process flowsheet was set up to solve the mass and energy balances. The latter requires thermodynamic properties of each compound, which, in contrast to petroleum-based compounds, are scarce in the case of biomass components and also ILs. Because the IL ([DMBA][HSO_4]) is a non-database component, it is modelled as pseudocomponent with its molecular mass, normal boiling point, density, vapour pressure, and critical properties specified. The critical properties (T_c, P_c, V_c), the normal boiling temperature (T_b), and the acentric factor (ω) were estimated based on the modified group contribution method proposed by Valderrama and Robles [213]. The estimated values are shown in Table 3.

Table 3: Critical properties values estimated using modified group contribution method

T_b (K)	650.29
T_c (K)	917.3996384
P_c (bar)	47.30563
V_c (cm^3/mol)	615.67
ω	0.743158

Additionally, data for estimating the energy variables were supplied for [DMBA][HSO_4]. Ahmadi *et al.* reported a simple group contribution correlation for the prediction of heat capacities of ionic liquids at different temperatures [214]. This correlation is a global temperature-dependent relation that uses temperature, molecular weight, and the number of atoms (such as carbon, hydrogen, oxygen, nitrogen, etc.) in the structure of the IL as input parameters. Enthalpy of vaporization at 298 K was estimated from a predictive rule given by Verevkin *et al.* and extended with Watson correlation for other temperatures [215, 216]. All the mentioned data were fitted to the Aspen Plus correlations using IK-CAPE Heat Capacity. Table 3 shows the correlations and coefficients value for estimating the heat capacities of [DMBA][HSO_4]. Equations 2 and 3 shows the correlations for estimating enthalpy of vaporization. The correlation of specific heat capacity and the fitted parameters estimated are shown in Table 4.

$$\Delta_{l}^{g}H_m(IL) = \sum n_i \Delta H_i \qquad (2)$$

$$\Delta H_{vap}(T_2) = \Delta H_{vap}(T_1)\left(\frac{1-\frac{T_2}{T_c}}{1-\frac{T_1}{T_c}}\right)^{a+b(1-{}^{T}/{}_{T_d})} \qquad (3)$$

$$C_P^{*} = C_1 + C_2T + C_3T^2 + C_4T^3 + C_5T^4 + C_6T^5 + C_7T^6 + C_8T^7 + C_9T^8 + C_{10}T^9 \qquad (4)$$

$$C_1 \le T \le C_{12}$$

Table 4: Estimated parameters for specific heat capacity and Enthalpy of [DMBA][HSO4]

$C_P^{IG}(kJ/kmol - K)$		$\Delta H_{vap}(kJ/mol - K)$	
C_1	187.2	$\Delta H_{vap}(T_1)$	127.5
C_2	0.3102	T_1 (K)	298
C_3	0.0002746	a	0.38
C_4	-1.359E-07	b	0
$C_5,\ldots,C_{10}$	0	T_{min} (K)	

The Spruce softwood was modeled as cellulose, hemicellulose, and lignin with the reported values of weight fractions equal to 45.3%, 27.3%, and 27.4%, respectively [94]. Kim *et al.* reported a proximate & ultimate analysis and calorific values for each biomass component which is shown in Table 5 [217]. Asides from the supplied data stated above, the remaining physical properties needed within the simulation were estimated by Aspen Plus inbuilt methods.

Table 5: Properties of each biomass component

	Cellulose	**Hemicellulose**	**Lignin**
Proximate analysis (wt.%, d.b.[a])			
Volatile matter	93.4	79.8	54.8
Fixed carbon	6.1	15.2	27.4
Ash	0.5	5.1	17.8
Ultimate analysis (wt.%, d.b.[a])			
C	43.0	41.9	51.6
H	6.4	6.0	4.3
N	0.0	0.0	0.0
O	50.1	47.0	26.3
Calorific value (MJ/kg, d.b.[a])	16.5	13.9	20.4

[a] Is on dry basis.

[redacted]

2.1.1. Process Description

The flowsheet depicted in Figure 5 includes ionic liquid pretreatment, washing, and solvent recovery. Four different colors green, purple, blue, and gray show the streams which are rich in lignocellulosic components, ionic liquid, water, and bleaching chemicals, respectively; black and red streams refer to mixed and waste compounds.

The modeled process starts with a stream of 6000 kg $_{\text{dry biomass}}$/h of softwood in ambient condition entering the process with stream BIOMASS in Figure 5. It is mixed with 310 kg/h of fresh [DMBA][HSO_4] (stream IL), recycle stream IL-RY, and stream W-RY which conclude in stream S1 consisting of 30163 kg/h [DMBA][HSO_4].

The recycled IL and water are at a temperature of around 120 °C, which results in a temperature of 119 °C in stream S1. Therefore, the thermal energy that is required in the heater H1 to reach the pretreatment temperature of 160 °C in the pretreatment reactor R1 is not significantly high. A solid load of 1:5 (biomass:solvent) is chosen. While the fresh IL has a water content of 20 wt%, the recycled IL and water introduce 12 and 99.9 wt% of water, respectively. Altogether, it results in water content during pretreatment of 20 wt%, which is determined as an optimal moisture content for lignocellulose fractionation.

During pretreatment in reactor R1, the wood is disintegrated for 60 minutes and exits the reactor in stream S4. The subsequent separation unit SP1 realizes a separation of the softwood from the liquid in which 90 wt% of lignin and hemicellulose are dissolved, whereas 95 wt% cellulose remains in the solid phase. After the filtration, the solid cellulose is then subjected to further washing with deionized water in units W1 and SP2. Washing is realized according to the concept of displacement washing [218].

The separation of dissolved lignin and hemicellulose from IL is realized in SP2. Further, lignin and hemicellulose are washed in units W2 and SP4 and leave as output in stream S13. The ionic liquid is separated from water through the evaporator E1 and then entered to shell & tube HE for heat exchanging with bleaching chemicals. The residual IL is separated from water in evaporator E2 and leaves the system as emission in stream S19.

The recovered water in stream S18 is employed again for washing stages and adjusting the water content of [DMBA][HSO_4] for the pretreatment. The cellulose-rich material in stream S15 is discharged with 84.5 wt% cellulose, 5 wt% hemicellulose, and 10.5 wt% lignin to the alkaline bleaching unit BL for removing the residual lignin. Hydrogen Peroxide (stream H_2O_2) as the bleaching chemical with 8.2 wt% concentration is discharged from the heat exchanger HE with the temperature of 50 °C and the rate of 2500 kg/hr of pure

H_2O_2. The bleaching process is carried out with 10% consistency at atmospheric pressure and 60 °C for 120 minutes.

Then, the bleaching liquor is removed from the pulp in SP5 and disposed in stream S26. Since the H_2O_2 amount was selected efficiently, there is the least amount of unreacted hydrogen peroxide, thus it cannot be recycled. Afterwards the bleached pulp is washed in W3, the final pulp will leave the process in stream DPF.

The process modeling of IL pretreatment provides the mass and energy flows data, which then were used as inputs for sustainability assessment. Due to the lack of data for the ionic liquid [DMBA][HSO4] in further assessment, detailed process models were developed by scaling-up the available experimental procedures.

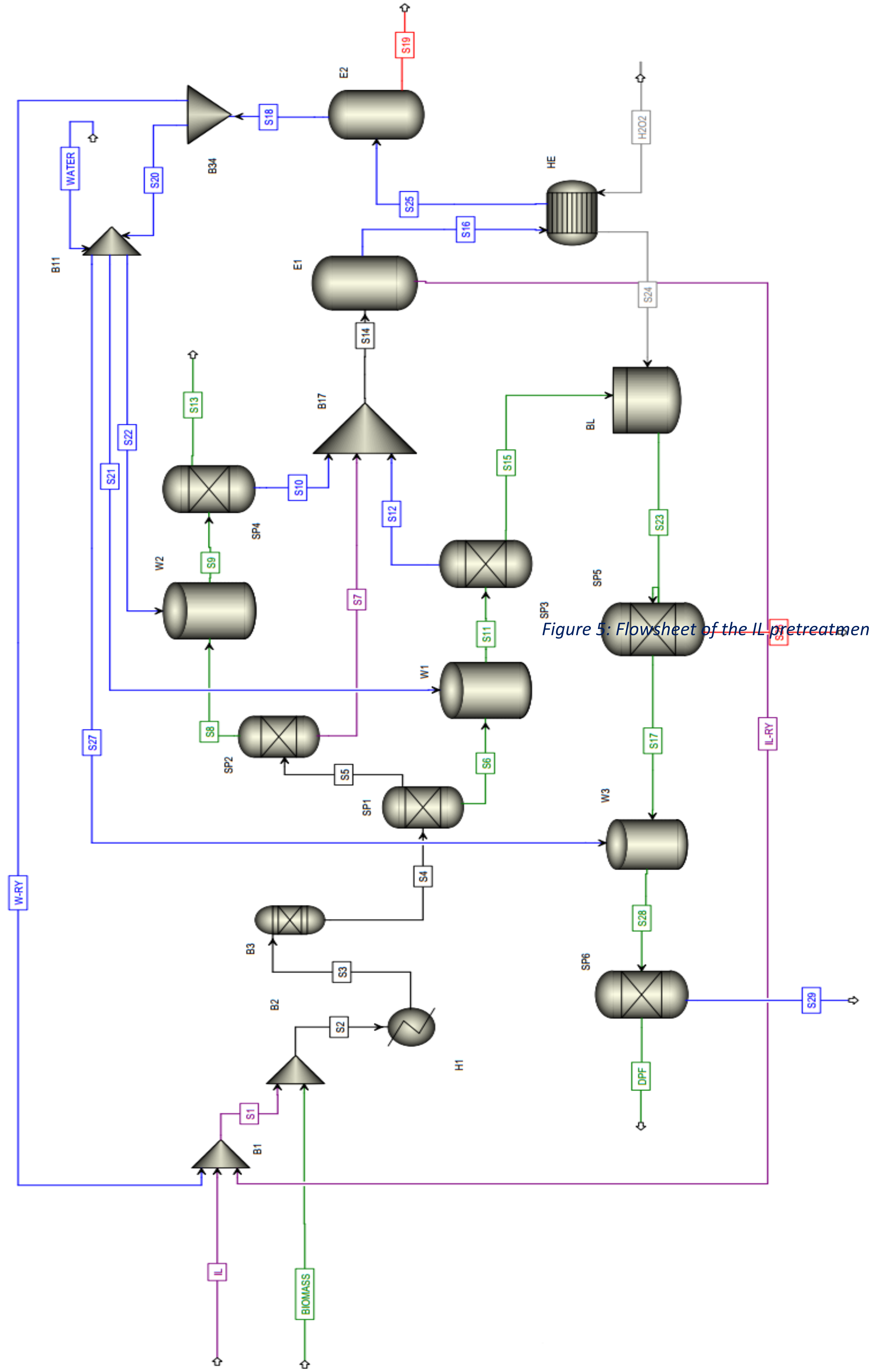


Figure 5: Flowsheet of the IL pretreatment and bleaching

2.1.2. Process Design of Protic Ionic Liquid Production

The ionic liquid [DMBA][HSO_4] is synthesized through the transfer of a proton from a Brønsted acid to a Brønsted base [44]. The base N,N-Dimethylbutylammonium is used in combination with sulfuric acid. The developed work by Chen *et al.* was used as the scaled-up manufacturing process in Figure 6 [60]. Equimolar amounts of DMBA and sulfuric acid are pumped and mixed with water at ambient temperature to produce an aqueous ionic liquid. Due to the nature of the reaction that produces high amount of heat, excess water is added to cool down the mixture and avoid thermal decomposition or formation of undesired by-products.

The ionic liquid leaves the reactor R1 and then is heated up to 107 °C in heater H1 to remove the excess water in flash tank FT. The recycled water is cooled down to ambient temperature and a 10% purge is implemented to avoid the accumulation of impurities. The discharge pressure of each pump is equal to 1.5 bar. Since the LCA data are available for sulfuric acid, but not for DMBA, detailed modeling of the production process of the base needed to be conducted as well.

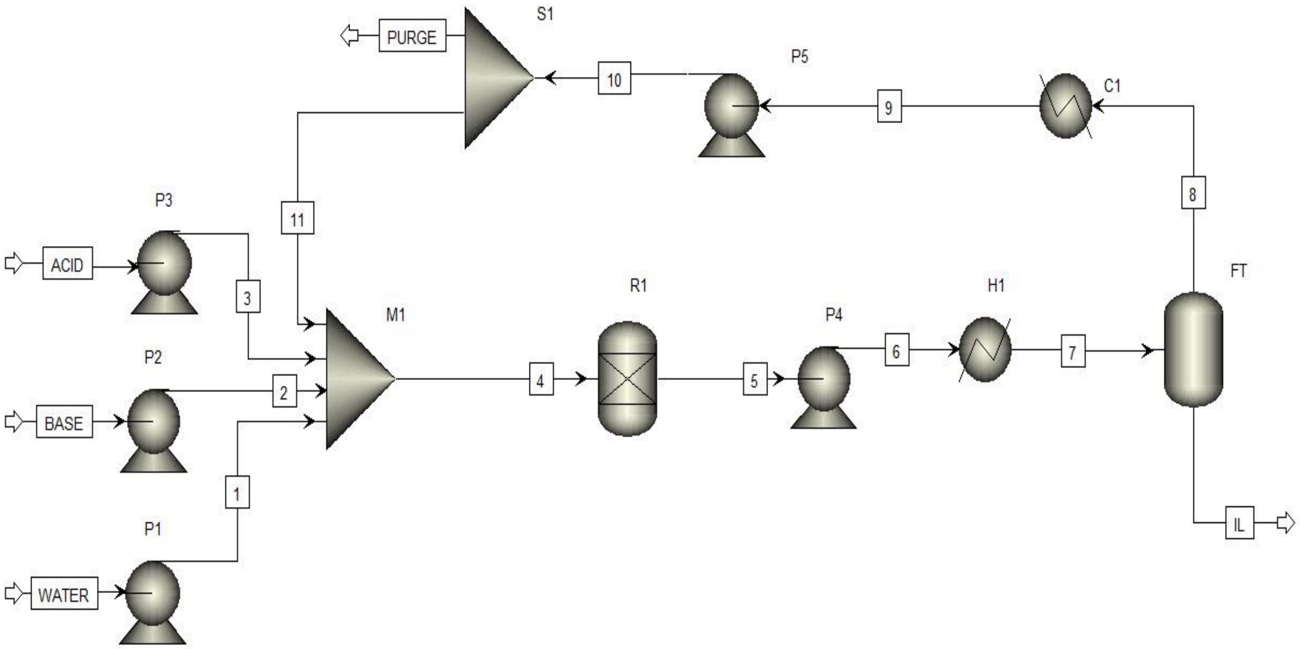


Figure 6: Flowsheet of the scaled-up manufacturing process of the [DMBA][HSO4] ionic liquid

2.1.3. Process Design of DMBA Production

N,N-Dimethylbutylammonium is a primary amine that is produced from biomass-derived aldehydes and ketones by reductive amination in aqueous ammonia over Ru/ZrO_2 catalyst [219]. Methyl isobutyl ketone (MIBK) is used as ketone with the combination of ammonia and ethanol which produce DMBA with a reaction yield of 73%. Moreover, MIBK is synthesized through a one-step low-pressure reaction of acetone and hydrogen over metal catalysis [220]. The flowsheet depicted in Figure 7 includes MIBK and DMBA production.

In the direct synthesis of MIBK, equimolar amounts of acetone and hydrogen are mixed and heated up to 200 °C in Heater H1. The reaction takes place in reactor R1 in the presence of a catalyst at atmospheric pressure. The reaction yield is 30.7% and has a by-product formation, Diisobutyl ketone (DIBK), which should be separated from MIBK for the further process. To realize this separation, the product stream 3 is cooled down to 100 °C and then enters to the separator S1. Moreover, in the separator S1, a substantial amount of acetone is separated and recycled back to the feed stream.

In the next step, MIBK is mixed with ammonia and ethanol for DMBA production. The reactants are mixed with the molar ratio of 1:13:2.5 (MIBK:ammonia:ethanol), then compressed and heated up to 1.2 MPa and 85 °C. The reaction takes place in reactor R2 without the formation of any by-products.

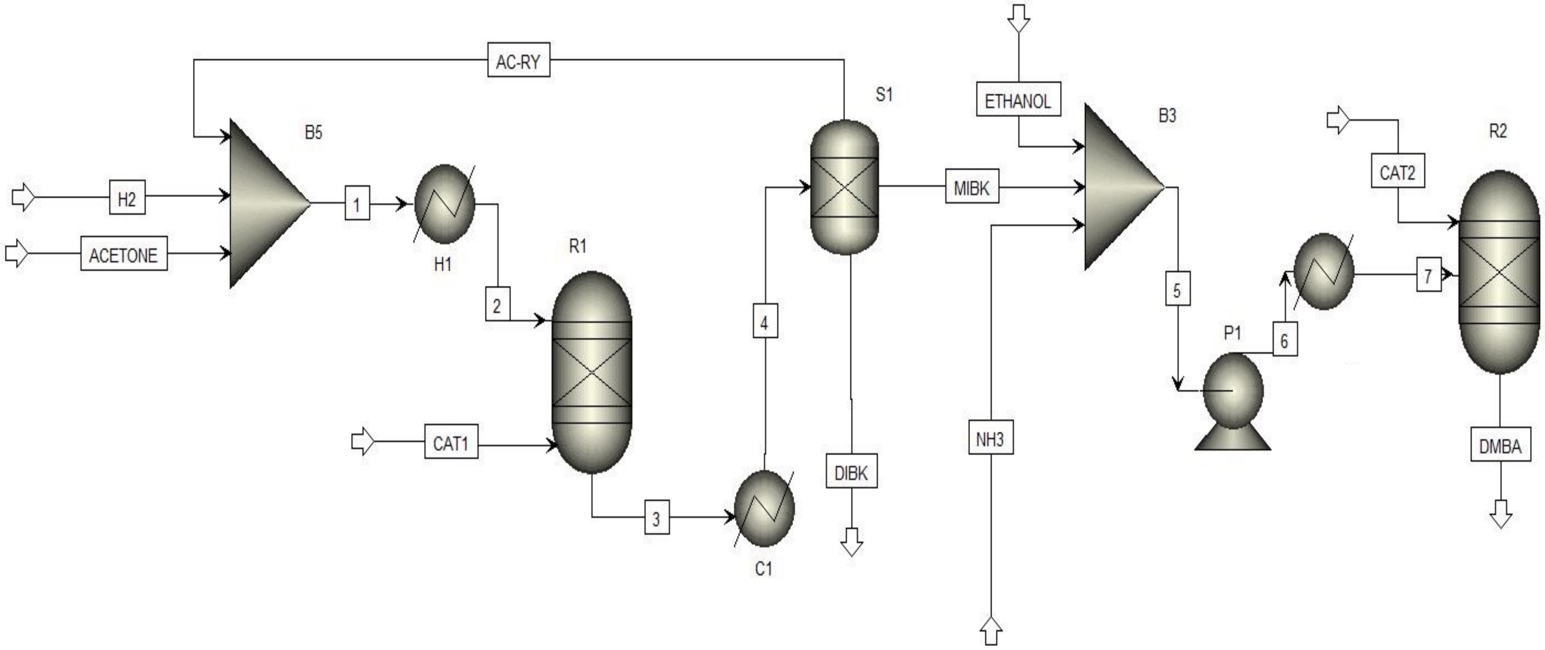


Figure 7: Flowsheet of the DMBA production

2.2. Environmental Assessment

The Life-cycle Assessment was conducted following the ISO 14040 framework using openLCA software and ecoinvent 3.5 database. The functional unit was defined as “1 kg of DPF with the lowest lignin content”. The environmental assessments were applied separately for DMBA production, synthesizing ionic liquid, and biomass pretreatment based on 20% biomass loading in the IL fractionation process. A cradle-to-gate scope was done that included the impacts of the raw material extraction to the final product.

The results about mass and energy flows from Aspen Plus were integrated with ecoinvent 3.5 database. To estimate air emissions, it was assumed that 90% mass of carbon in the waste stream is completely burned in waste treatment to produce CO_2. Furthermore, 4% of the cooling water and 0.2% of the raw materials were assumed to be vaporized or leaked into the atmosphere. For taking into account the water emissions, the chemical oxygen demand (COD) and the biological oxygen demand (BOD) were assumed be equivalent to the amount of oxygen needed to react with the amount of carbon remaining in the waste stream after treatment which is considered to be 10% of total carbon. The total organic carbon (TOC) and the dissolved organic carbon (DOC) were assumed to be equivalent to 10% of the total carbon in the waste stream.

A full list of the life Life-cycle Inventories (LCI) for the DMBA production, ionic liquid synthesize, and IL pretreatment are shown in Tables 6, 7, and 8. The LCI entries were converted into environmental impact using the ReCiPe 2016 approach [221]. All of the LCI entries were categorized into 18 midpoint indicators, including climate change, human toxicity, ozone depletion, water depletion, etc. Further, the midpoint indicators were combined into 3 endpoint (damage) categories: resources, human health, and ecosystem quality. The input and output flows for each inventory were set based on 1 kg production of cellulose fiber. The complete ReCiPe midpoint and endpoint results are given in Tables 9 and 10, respectively. The inventory prepared by Baaqel *et al.* for production of the [TEA][HSO_4] ionic liquid was used for the scaled-up manufacturing process [61]. Triethylamine (TEA) is a similar base with N,N-Dimethylbutylammonium with different molecular configurations (Figure 8). The synthesizing procedure for both ionic liquid is the same, and the inventory was set based on 1 kg production of cellulose fiber.

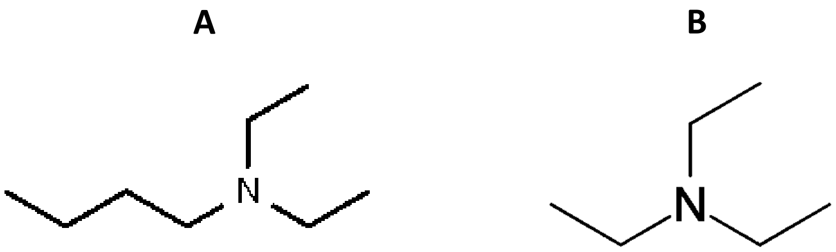


Figure 8: N,N-Dimethylbutylammonium (A), Triethylamine (B)

Table 6: DMBA inventory

Group	Inventory	Flow (per- kg DPF)	
Inputs from nature	Water, cooling, unspecified natural origin, RER	0.0014	m^3
	Water, river, RER	0.0007	m^3
	Water, well, in ground, RER	0.0007	m^3
Inputs from technosphere (materials)	acetone, liquid	0.098748	kg
	hydrogen, gaseous	0.005712	kg
	ammonia, liquid	0.135126	kg
	ethanol, without water, in 99.7% solution state, from ethylene	0.069711	kg
	heat, district or industrial, natural gas	355.6128	kJ
	metal catalyst for catalytic converter	10	mg
Emissions to air	Carbon dioxide, fossil	0.221595654	kg
	Acetone	0.000197	kg
	Ammonia	0.00027	kg
	Ethanol	0.000139	kg
	Hydrogen	1.14E-05	kg
	Water	0.0056	kg
Emissions to water	BOD5, Biological Oxygen Demand	0.026860079	kg
	COD, Chemical Oxygen Demand	0.026860079	kg
	DOC, Dissolved Organic Carbon	0.00671502	kg
	TOC, Total Organic Carbon	0.00671502	kg
Product	DMBA	0.0574	kg

Table 7: [DMBA][HSO4] inventory

Group	**Inventory**	**Flow** (per- kg DPF)	
Inputs from nature	Water, cooling, unspecified natural origin, RER	0.01855	m^3
	Water, river, RER	0.00927	m^3
	Water, well, in ground, RER	0.00927	m^3
Inputs from technosphere (materials)	N,N-Dimethylbutylammonium	0.0574	kg
	Chemical factory, organics, GLO	5×10^{-11}	p
	Tap water, RER	0.03467	kg
	Sulfuric acid, RER	0.0619	kg
	Heat, from steam, in chemical industry, RER	1.793	kJ
	heat, district or industrial, natural gas	16.141137	kJ
	Electricity, medium voltage, RER	0.000015	kWh
Emissions to air	N,N-Dimethylbutylammonium	1.28×10^{-4}	kg
	Sulfuric acid	0.000123	kg
	Water	4.2×10^{-7}	kg
Emissions to water	Water, RER	0.00884	kg
Outputs to technosphere	Wastewater, average, Europe without Switzerland	2.5×10^{-6}	kg
Product	[DMBA][HSO4]	0.113	kg

Table 8: IL pretreatment inventory

Group	**Inventory**	**Flow** (per- kg DPF)	
Inputs from nature	Water, cooling, unspecified natural origin, RER	0.3417	m^3
	Water, river, RER	0.0034	m^3
	Water, well, in ground, RER	0.0034	m^3
Inputs from technosphere (materials)	pulpwood, softwood, measured as solid wood under bark	0.003	m^3
	[DMBA][HSO4]	0.113	kg
	hydrogen peroxide, without water, in 50% solution state	1.214	kg
	heat, district or industrial, natural gas	5.776	MJ
Emissions to air	Hydrogen peroxide	0.002428	kg
	Water	13.668	kg
Emissions to water	Water, river	5.8519	kg
	Hydrogen peroxide	0.3992	kg
Product	Cellulose fiber	1	kg
	Lignin, in solution	0.6385	kg
	Hemicellulose, in solution	0.7817	kg

Table 9: LCA ReCiPe midpoint results, for 1 kg of DPF

Impact indicator	Unit	DMBA	[DMBA][HSO4]	IL pretreatment	Total
climate change - GWP500	kg CO_2 eq	0.647	0.0131	0.398	1.059
ozone depletion - ODPinf	kg CFC11 eq	1.03E-07	1.20E-09	4.44E-08	1.49E-07
ionizing radiation - IRP_HE	kg U235 eq	0.0383	0.0015	0.0186	5.85E-02
human toxicity - HTPinf	kg 1,4-DCB eq	4.643	1.002	4.381	10
particulate matter formation - PMFP	kg PM10 eq	0.00065	5.12E-05	0.00064	1.34E-03
terrestrial acidification - TAP500	kg SO_2 eq	0.00245	0.00012919	0.00137	3.95E-03
terrestrial ecotoxicity - TETPinf	kg 1,4-DCB eq	0.00057	0.00121	0.00241	0.004198
freshwater eutrophication - FEP	kg P eq	8.07372E-05	1.24859E-05	8.92E-5	0.000182
marine eutrophication - MEP	kg N eq	0.00034	1.92939E-05	0.00039	0.000749
marine ecotoxicity - METPinf	kg 1,4-DCB eq	6.44242	1.950829202	7.659	16.05225
freshwater ecotoxicity - FETPinf	kg 1,4-DCB eq	0.01185	0.004202233	0.01101	0.027062
water depletion - WDP	m^3	0.00222	0.018718981	0.00229	0.023229
metal depletion - MDP	kg Fe eq	0.02896	0.032755067	0.02486	0.086575
fossil depletion - FDP	kg oil eq	0.32941	0.004660022	0.15679	0.49086
photochemical oxidant formation - POFP	kg NMVOC	0.00157	6.01816E-05	0.00128	0.00291
natural land transformation - NLTP	m^2	0.0002	3.88147E-06	8.25E-5	0.000286
agricultural land occupation - ALOP	m^2a	0.01954	0.002524181	4.41982	4.441884
urban land occupation - ULOP	m^2a	0.03662	0.0107152	0.12719	0.174525

Table 10: LCA ReCiPe endpoint results, for 1 kg of DPF

Impact indicator	Unit	DMBA	[DMBA][HSO4]	IL pretreatment
Human Health	DALY	5.7E-06	7.57E-07	4.53E-06
Ecosystems	species.yr	1.755E-08	1.97E-09	6.62E-08
Resources	$	0.05088	0.000716	0.02394

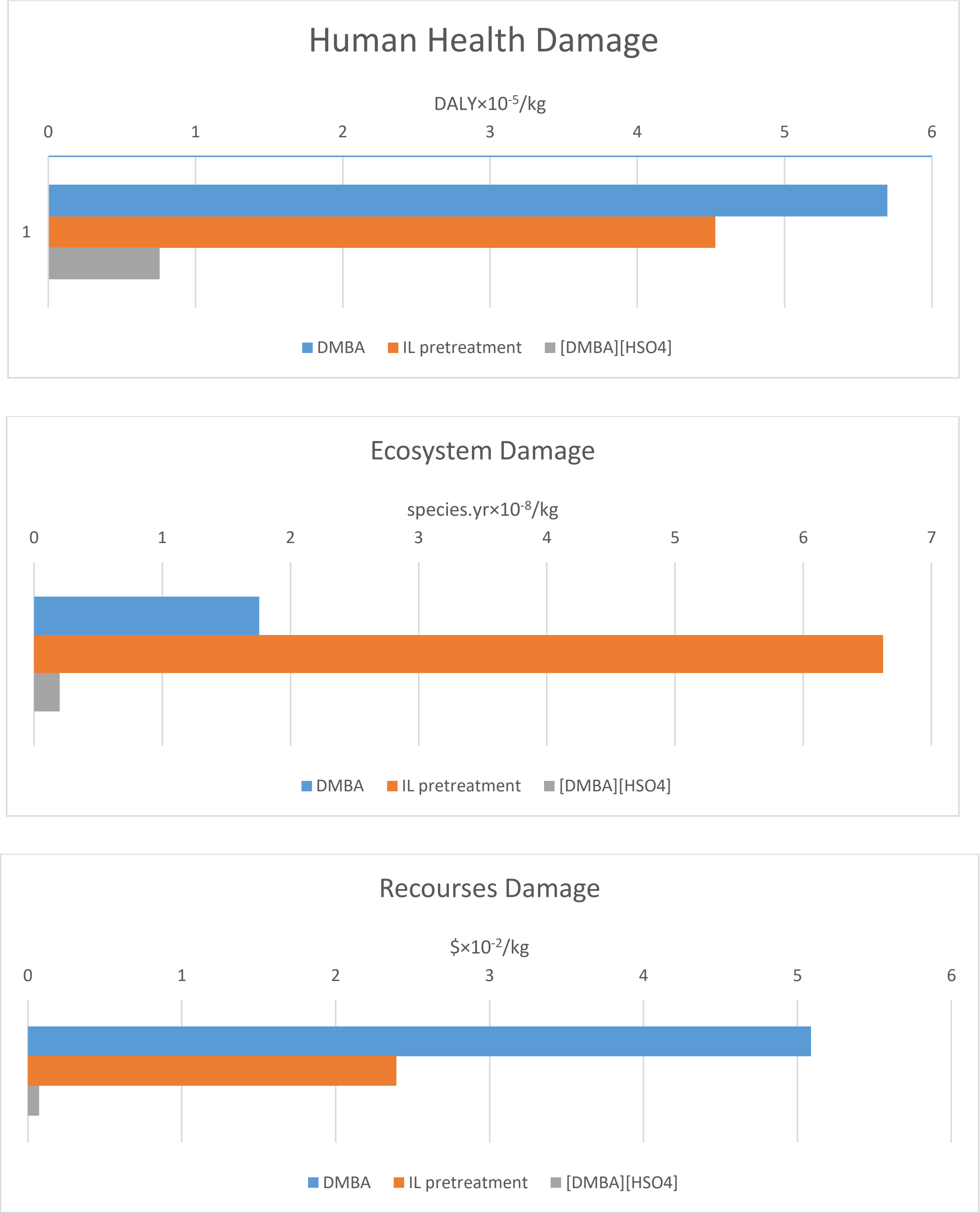
2.3. Results and Discussion (Midpoints & Endpoints)

The LCA results for all three endpoint impact categories: human health, ecosystem quality, and resources are presented in figure Graph 3. In the human health category, the impact of the IL pretreatment is 4.5 and 34 times higher than the DMBA and the [DMBA][HSO_4] synthesizing, respectively. The IL pretreatment requires many steps of biomass disintegration, hydrogen peroxide bleaching, separations, and all the washings, therefore generating more wastes and emissions. This is explained by the higher scores in all human health indicators, including climate change, ozone depletion, human toxicity, photochemical oxidant formation, particulate matter formation, and ionizing radiation. The high score in the climate change impact category for IL pretreatment is resulted from the high heat and electricity generation from coal, natural gas, and light oil which increase the CO_2 emission. The major contributor to ionizing radiation is the treatment of low-level radioactive wastes, tailing, and nuclear fuels. High emissions in ozone depletion are mainly caused by chlore-alkali electrolysis which is used in the production of hydrogen peroxide and the extraction of petroleum and natural gas. The treatment of spoil from hard coal and lignite mining for producing some raw materials results in emissions to water and groundwater as the main contribution to human toxicity impact. Moreover, the production of hydrogen peroxide and heat generation from hard coal are the main contributors to photochemical oxidant formation and particulate matter formation categories, respectively. In the DMBA synthesizing, ammonia production is the main factor influencing the climate change and particulate matter formation impact categories; petroleum & gas production has the most contribution to ozone depletion. Further, the impact of photochemical oxidant formation is linked to ethanol production in DMBA synthesizing process. In contrast, [DMBA][HSO_4] synthesizing has the lowest score in the human health impact category, because it does not require significant energy and has a simple process; treatment of sulfidic tailings coming from sulfuric acid production is the primary contributor which is detrimental to human health.

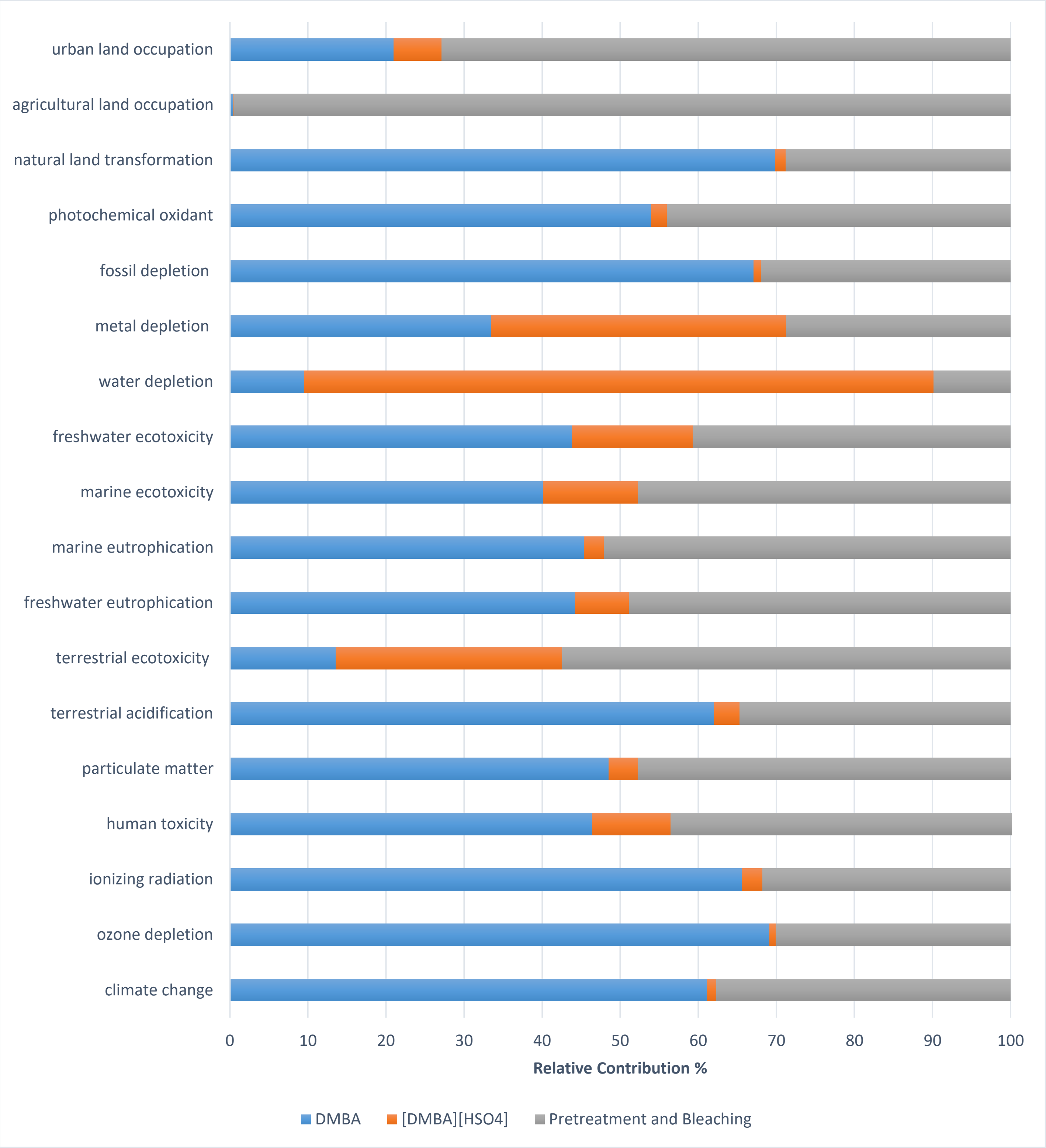
The impact of IL pretreatment on the ecosystem endpoint is more than six times higher than those of DMBA and [DMBA][HSO_4]. The reason behind this is the production and harvesting of softwood Spruce impacting the agricultural land occupation and natural land transformation categories; this deforestation is responsible for soil damage and loss of habitat for plants and animals. Furthermore, the large amount of heat that is necessary to be generated from hard coal, natural gas, and light oil for the process influences the impact categories such as terrestrial acidification and climate change. In DMBA synthesizing, the major impact on ecosystem is related to CO_2 emission to air.

Regarding resource depletion, IL pretreatment has higher scores than both DMBA and [DMBA][HSO_4], because the largest amount of fossil fuels are used during the pretreatment. The impact of IL pretreatment is 50% higher than DMBA, whereas the ionic liquids synthesizing require the lowest amount of fossil fuels if we consider the base production, DMBA, as an independent process. Production of the Brønsted bases makes up the largest impact on resources since they are derived from fossil resources.

Then the impact contribution analysis was carried out for the mid points to get more detailed information of the assessment. The DMBA production, pretreatment and the bleaching stages had the highest contribution to most of the midpoints. For the climate change category, the CO_2 resulted of ammonia and DMBA production had the highest impact. In the ozone depletion, the production of on-shore petroleum contributed the most. In the ionizing radiation, the treatment of low radioactive waste had the highest contribution resulted from the DMBA production. For the human toxicity, the treatment of spoil from mining contributed the most in the pretreatment and bleaching. In particulate matter and terrestrial acidification, DMBA and pretreatment had similar contribution which was because of the heat production during these processes. In terrestrial ecotoxicity, the treatment of solid waste from bleaching had the highest contribution. In freshwater eutrophication, ethanol production contributed the most for obtaining DMBA. In marine eutrophication, ammonia production had the highest contribution from DMBA production. In marine ecotoxicity, treatment of sulfidic tailing was the main contributor for pretreatment, bleaching, and DMBA subsystem. In water depletion, [DMBA][HSO_4] had the highest contribution for synthesizing. In metal depletion, zinc mine operation was the main factors for all subsystems. In fossil depletion and photochemical oxidant, the ethylene production needed for preparing ethanol in DMBA production contributed the most. In natural land transformation, the on-shore well production was the main factor of contribution. In agricultural land occupation, the pretreatment had almost all the contribution due to the softwood forestry and harvesting.



Graph 4: Endpoint environmental impacts for producing 1 kg cellulose fiber. Top: Human health; middle: ecosystem quality; bottom: resources

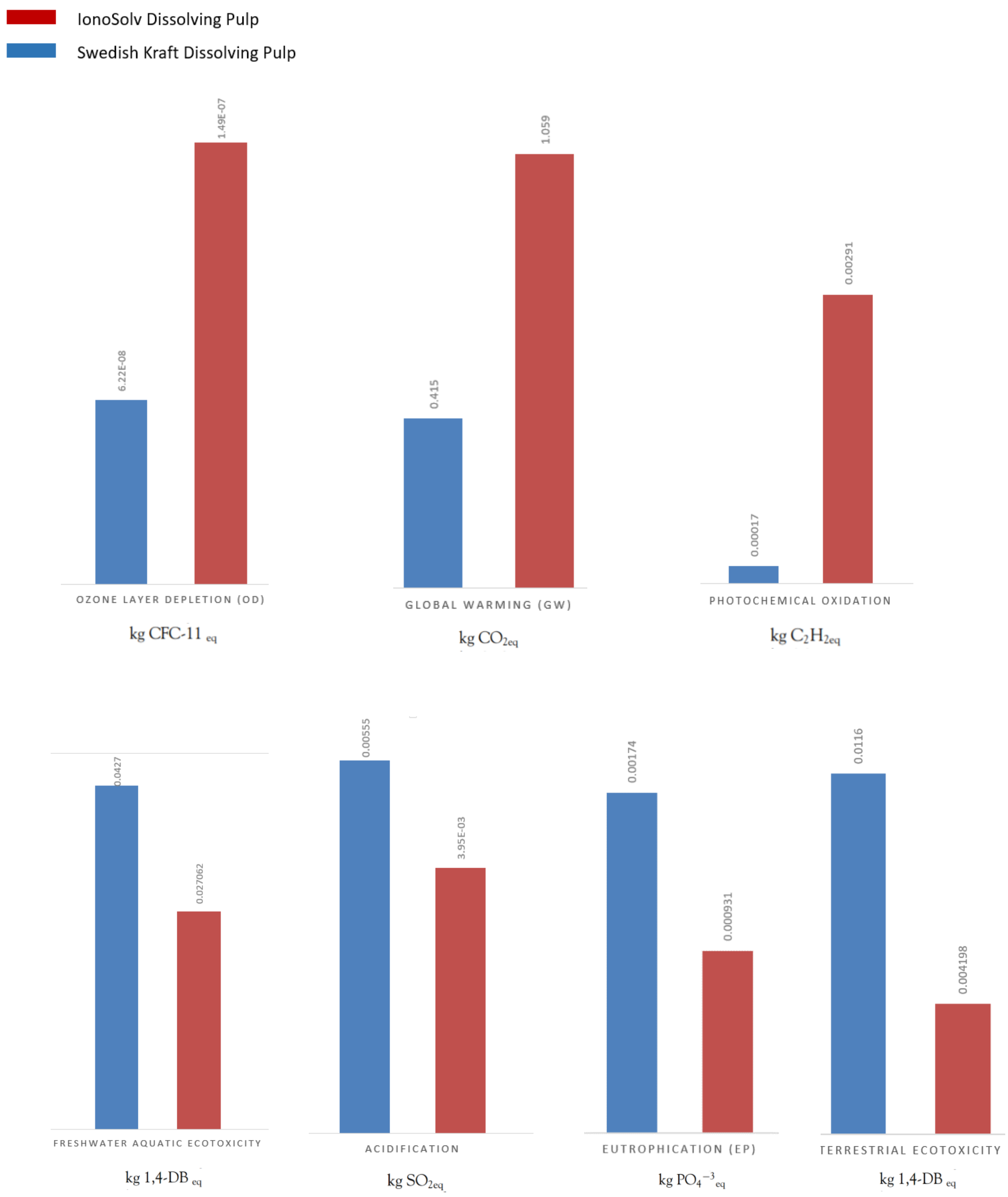


Graph 5: Midpoints impact contribution analysis for producing 1 kg cellulose fiber

2.4. Results and Discussion (ionoSolv vs. Swedish Biorefinery)

After obtaining the LCA results, the ionoSolv technology was compared to the Swedish biorefinery for producing 1 kg of bleached dissolving pulp. The life-cycle assessment was already done on the Swedish dissolving pulp mill Integrated biorefinery [222]. According to the study, the LCA was conducted at 7 midpoints, so that the comparison will be limited to the available results of Swedish Dissolving Pulp. The feedstock of the biorefinery was 80% spruce and 20% pinewood. Both technology employs the same bleaching stage, a total chlorine-free (TCF) bleaching process using hydrogen peroxide (H_2O_2), but with different pretreatment approach. The Swedish biorefinery exploits H_2SO_3 with NaOH as the pretreatment media to fractionate the lignocellulosic biomass. This process is named as Kraft process and accounts for more than 70% of dissolving pulp production worldwide, thus it can be good comparison to the proposed ionoSolv technology. However, the by-products of both technologies are completely different that can significantly influence the obtained results. Moreover, the LCIA prepared for the ionoSolv is based on laboratory processes that contain rough values of mass and energy flows. In contrast, the Swedish biorefinery has some heat integrating units and co-generation sections that substantially can reduce its midpoint results.

The midpoints that were suggested by the study are global warming, ozone layer depletion, photochemical oxidant, freshwater ecotoxicity, acidification, total eutrophication, and terrestrial ecotoxicity. According the Graph 6, the Swedish biorefinery has lower score in global warming, ozone layer depletion, and photochemical oxidant midpoint categories. IonoSolv dissolving pulp showed a really high score in photochemical oxidant category in compare to the Swedish biorefiney. This is mainly because of the high amount of nitrogen oxide emission coming from the DMBA production. The Swedish biorefinery has scores almost less than half of ionoSolv in Global warming and ozone layer depletion. On the other hand, ionoSolv has showed lower scores in freshwater ecotoxicity, acidification, total eutrophication, and terrestrial ecotoxicity categories. In freshwater ecotoxicity category, Swedish biorefinery releases many emissions due to NaOH production and H_2O_2. In acidification category, the cogeneration unit is the main responsible subsystem which releases SO_x substances. In eutrophication category, the Swedish biorefinery has higher COD emission to water than ionoSolv resulting in the higher score. In terrestrial ecotoxicity category, Swedish biorefinery had higher score due to its cogeneration units that releases emissions such as chromium and mercury to air. According to the report, the cogeneration unit in the Swedish biorfinery that mainly produces biogas significantly reduced the midpoint scores. These reductions are reported as 21, 19, 18, 16, 19, 2, and 18% for the ozone layer depletion, global warming, photochemical oxidant, freshwater ecotoxicity, acidification, total eutrophication, and terrestrial ecotoxicity, respectively. It can be found out that without cogeneration unit the midpoint scores for the global warming and ozone layer depletion would be closer to ionoSolv. In addition, for the other midpoints, the Swedish biorefinery would have even lower scores than ionoSolv without the cogeneration unit.



Graph 6: Midpoints for ionoSolv versus Swedish Kraft Biorefinery for producing 1 kg of bleached dissolving pulp

Part III. Conclusion

Key Findings

This MSc project optimized the ionoSolv pretreatment for obtaining Dissolving Pulp Fiber with high cellulose content. Further, the complete route to produce DPF, including synthesizing ionic liquid, pretreatment, and the bleaching stage was simulated with the aim of obtaining the mass and energy flows for use as the input for Life-cycle Assessment. In Chapter 1, it was shown that the optimal temperature for the lignocellulose fractionation is 150 ^{o}C for 80% lignin removal. Then the biomass loading was investigated, and 10% biomass to solvent ratio was selected as the optimal value. Moreover, it was shown that DMBA HSO_4 / water mixture could successfully pretreat Spruce softwood having final lignin content around 17 wt%. In the case of preparing a DPF as bleachable pulp, sack paper, or corrugated fiberboard, 9, 7.5, and 3.5 wt% of H_2O_2, respectively, are required for the bleaching stage. It should be pointed out that an excessive use of hydrogen peroxide could result in involving cellulose in the reactions, leading to its degradation.

In Chapter 2, all the steps to produce DPF were expanded into the process modeling. Due to the lack of data for DMBA precursor and [DMBA][HSO_4] IL in ecoinvent database, both synthesizing processes were modeled as well. The IL pretreatment was found to have more environmental impacts in all three endpoints, namely human health damage, ecosystem damage, and resource damage. The process of synthesizing ionic liquid alone holds the least environmental impacts because of the simplicity of the route and low energy required. By considering the DMBA production as part of synthesizing the ionic liquid, IL pretreatment with the bleaching stage has higher impacts, special on the ecosystem. This is resulted from harvesting the softwood that is almost inevitable in any process. In addition, the ionoSolve technology was compared to the Swedish biorefinery. The Swedish biorefinery showed lower scores than ionoSolv in some midpoints which was mainly due to the cogeneration unit.

Proposed Future Work

Since the bleaching process contains many other reactions and factors that are influential, there is still a need to find more details on transitional metals that can cause cellulose degradation. Furthermore, experimental process and scaled-up manufacturing process can give substantially different mass and energy flows. Life cycle analysis also can be expanded with lignin and hemicellulose valorization streams that can affect the LCA results. Moreover, a Techno-economic Assessment is required to estimate the DPF production cost.

Appendix

The lignin removal was calculated by Equation 5.

$$Lignin\ Removal = 1 - \frac{unreacted\ lignin}{original\ lignin} \tag{5}$$

The Kappa Number was calculated by Equation 6.

$$K = c \times l \tag{6}$$

$c \approx 6.57\ depends\ on\ wood\ type\ and\ process$
$l - \%\ lignin\ content$

The K values needed for different pulp qualities are shown in Table 12.

Table 11: Kappa Number of different pulp qualities

Type	K range	The selected K value in this project
Bleachable Pulps	25 – 30	27.5
Sack Paper	45 – 50	47.5
Corrugated Fibreboard	60 – 110	90

The concept of displacement washing used in the pretreatment modeling is explained in Figure 9. The pretreated biomass in stream A is washed by the deionized water (stream B), but some of the water leave the washing step with the washed, pretreated biomass in stream C. The number of times of displacement or dilution by the washing liquid is described by the dilution factor (DF) [218].

$$DF = \frac{m_B - m_C^{liquid}}{m_A^{biomass}} = \frac{m_D - m_A^{liquid}}{m_A^{biomass}} \tag{7}$$

A common value of DF = 2 was chosen here. Since the ionic liquid is to be removed in stream C after washing, the filtrate (stream D) contains the corresponding amount of IL.

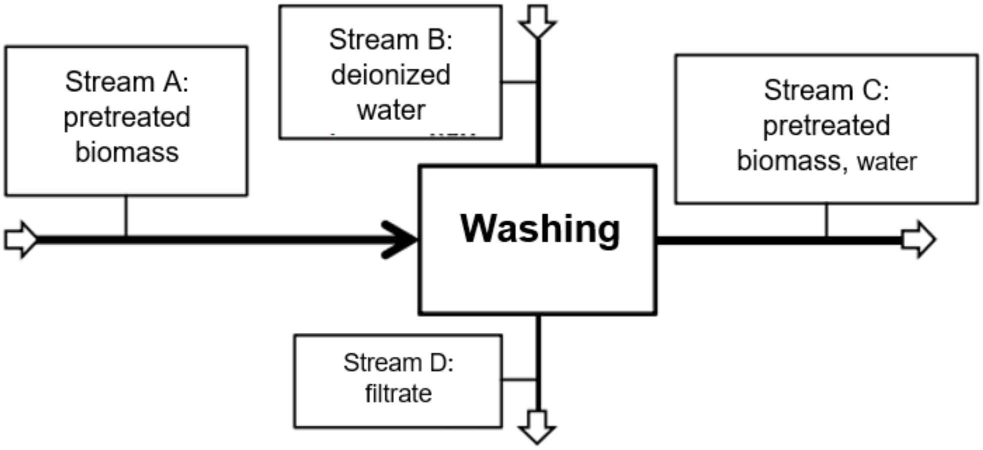


Figure 9: The block flow diagram of the washing of pretreated biomass. The pretreated biomass passes through the stage from stream A to C

The input and output flows of the pretreatment and bleaching modeling used in LCA are described in Table 13.

Table 12: The input and output flows for preparing DPF in Aspen Plus

Feed Flows (kg/hr)		**Price (\$/kg)**
[DMBA][HSO_4]	310	
Biomass	6000	
Water	14000	
H_2O_2	2500	
Product (kg/hr)		
DPF (zero lignin)	2059.425	0.45 [223]
Lignin (in solution)	1315	0.3 [223]
Hemicellulose (in solution)	1610	0.6 [223]
Emissions/Wastes (kg/hr)		
Water	12051.7	
[DMBA][HSO_4]	3.1	
H_2O_2	822.3	

Energy Consumption		
Heating Duties	5776.78 (KJ/hr.kg DPF)	
Cooling Duties	341.7 (kg of water/hr.kg DPF)	

The proxy data used in Life-cycle Inventories are shown in Table 14.

Table 13: Proxy data used in LCI

Data Category	Proxy Data	Proxy Method
Air emissions	Raw materials	0.2% by mass of inflows are assumed to be vaporized or leaked
	Cooling Water	4% by volume of total cooling water are assumed to be vaporized or leaked
	CO_2	90% by mass of carbon in waste stream is assumed to be completely burned in waste treatment to produce CO_2 as per the following complete combustion equation: $C_\alpha H_\beta O_\gamma + (\alpha + \frac{\beta}{4} - \frac{\gamma}{2}) O_2 \longrightarrow \alpha CO_2 + \frac{\beta}{2} H_2O$
Water emissions	COD	The chemical oxygen demand (COD) or total oxygen consumed is assumed to be equivalent to the amount of oxygen needed to react with the amount of carbon remaining in the waste stream after treatment which is assumed to be 10% of total carbon
	BOD	For worst case scenario, the biological oxygen demand (BOD) which is the oxygen consumed due to biological aerobic digestion by organisms is assumed to be equivalent to the amount of COD
	TOC	The total organic carbon (TOC) which is the total amount of carbon is assumed to be equivalent to 10% of the total carbon in the waste stream which is the amount of carbon remaining after treatment
	DOC	For waste case scenario, dissolved organic carbon (DOC) is assumed to be equivalent to TOC

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