



Review Paper


Removal of wood extractives as pulp (pre-)treatment: a technological review



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Abstract

Wood extractives usually do not exceed five percent of dry wood mass but can be a serious issue for pulping as well as for the pulp itself. They cause contamination and damages to process equipment and negatively influence pulp quality. This paper addresses not only the extractives-related problems but also different solutions for these issues. It is an extensive review of different technologies for removing wood extractives, starting with methods prior to pulping. Several wood yard operations like debarking, knot separation, and wood seasoning are known to significantly decreasing the amount of wood extractives. Biological treatment has also been proven as a feasible method for reducing the extractives content before pulping, but quite hard to handle. During pulping, the extractives reduction efficiency depends on the pulping method. Mechanical pulping removes the accessory compounds of wood just slightly, but chemical pulping, on the other hand, removes them to a large extent. Organosolv pulping even allows almost complete removal of wood extractives. The residual extractives content can be significantly reduced by pulp bleaching. Nevertheless, different extraction-based methods have been developed for removing wood extractives before pulping or bleaching. They range from organic-solvent-based extractions to novel processes like supercritical fluid extractions, ionic liquids extractions, microwave technology, and ultrasonic-assisted extraction. Although these methods deliver promising results and allow utilization of wood extractives in most cases, they suffer from many drawbacks towards an economically viable industrial-scale design, concluding that further research has to be done on these topics.

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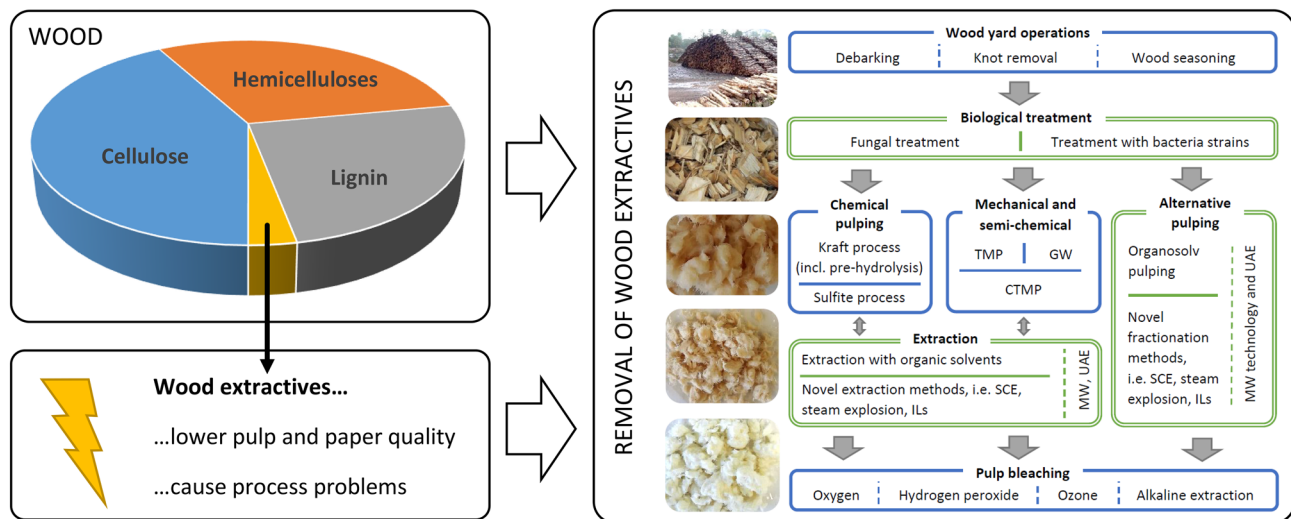
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Graphical abstract



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Abbreviations

ASE	Accelerated solvent extraction
COD	Chemical oxygen demand
CTMP	Chemi-thermomechanical pulp
CTO	Crude tall oil
D (bleaching)	Chlorine dioxide (bleaching)
E (bleaching)	Alkaline extraction (bleaching)
ECF (bleaching)	Elemental chlorine-free (bleaching)
EDTA	Ethylenediaminetetraacetic acid
FT-IR	Fourier-transform infrared spectroscopy
FT-NIR	Fourier-transform near-infrared spectroscopy
FT-RAMAN	Fourier-transform RAMAN spectroscopy
GC	Gas chromatography
GWP	Groundwood pulp
HPLC	High-performance liquid chromatography
HW	Hardwood
ILs	Ionic liquids
MW	Microwave
O (bleaching)	Oxygen (bleaching)
P (bleaching)	Hydrogen peroxide (bleaching)
PHWE	Pressurized hot-water extraction
RMP	Refined mechanical pulp
SC-CO ₂	Supercritical extraction with carbon dioxide
SCE	Supercritical extraction
SD	Standard deviation
SW	Softwood

TCF (bleaching)	Totally chlorine-free (bleaching)
TDS	Total dissolved solids
TMP	Thermomechanical pulp
UEA	Ultrasonic-assisted extraction
VOC	Volatile organic compounds
Z (bleaching)	Ozone (bleaching)

1 General introduction

Wood has been used from prehistory on and therefore rated among the oldest materials of humanity. In the beginning, wood was just used as fuel wood for simple cooking and heating purposes. Over time, wood has become more important as a building material, and since the industrial revolution, wood has also been intensively used for different industrial purposes [1, 2]. Nowadays, there is still a broad range of wood usages even in highly developed countries—from the initial use as fuel wood, i.e., wood pellets, through to high-performance materials for various applications, like wood polymer composites (WPC) as a special structural material, xylose as base chemical and lignin as biopolymer [3–6]. One important application is wood pulp—used for paper and cardboard—with a global production of 184 million tons in 2017, excluding recovered paper [7].

For producing paper, wood must be defibered, which is known as pulping. Unfortunately, this defibration is quite challenging because of the complex structure of wood with the lignin matrix. Therefore mechanical (including thermomechanical and semi-chemical) or chemical

methods are applied [8, 9]. In mechanical pulping, on the one hand, the grinding and refining processes increase the temperature, which leads to softening the lignin and breaking the bonds between the fibers. On the other hand, chemical pulping achieves defibration by removing the two cellulose-fiber-surrounding components, lignin, and hemicelluloses [10]. Besides these three main components, wood also contains many organic compounds. Since those organic compounds can be extracted with organic solvents or hot water, they are called accessory compounds or extractives [11]. Björklund Jansson and Nilvebrant [12] define wood extractives as the chemical compounds that are extractable from wood with various neutral solvents. With this definition, the accessory components of wood can be clearly differentiated from the major structural components (cellulose, hemicelluloses, and lignin), because neutral solvents, in general, do not dissolve any of the main wood components. Cellulose can only be dissolved by special solvents that break the intermolecular hydrogen bridge bonds [13, 14]. Hemicelluloses must be hydrolysed under acidic (sulfite pulping) or alkaline (Kraft pulping) conditions. Apart from novel methods, in conventional pulping lignin has to be cleaved and dissolved under alkaline conditions (Kraft pulping), or sulfonated first (sulfite process) to make it soluble [15].

Although wood extractives usually do not exceed five percent of dry wood mass on average (heartwood and sapwood)—except some tropical and subtropical woods, which contain significantly higher amounts of extractives (up to 20 wt% based on dry wood)—they can be a serious issue for pulping as well as for the pulp itself. Therefore, the removal of these wood extractives should be considered as pulp (pre-)treatment—not only for avoiding any problems during pulping but also for ensuring satisfying pulp quality [11, 16, 17].

After a short introduction to wood extractives, including an overview on analytical basics, this paper describes the effects of wood extractives on pulp and paper quality and production. The removal of wood extractives as solution for these problems is addressed in the main part of this paper later on. Beginning with wood yard operations and biological treatment, this paper is an extensive review

of different technologies for removing wood extractives, from conventional pulping and bleaching processes through different organic-solvent-based extractions to several promising novel methods, including the utilization of extracted wood extractives.

2 Introduction to wood extractives

The so-called wood extractives or accessory compounds are a mixture of many low- and high-molecular-weight compounds that can be extracted from wood with hot water and organic solvents [11, 12, 18]. In living trees, wood extractives play different important roles, which is a reason for the complex extractive's composition. They protect living trees against biotic attacks like insects and fungi, and play an important role for the metabolism of trees (particularly the parenchyma resin which is described later on) [11, 12, 19–21].

2.1 Content and classification

The extractives content of wood, as well as the exact extractives composition, depends on various factors. On the one hand, the extractives vary not only between the two groups, softwoods (Gymnospermae, SW) and hardwoods (Angiospermae, HW) but also among species and even single trees, as shown by Ekeberg et al. [22]. On the other hand, there are differences in the accessory component's content depending on the location inside the tree and the growth conditions like the geographical site, age, and cutting season [11, 21, 23, 24]. Thus, universal statements about the extractives content in woods are almost impossible.

Table 1 clearly shows the broad range of extractives contents published by different authors. Besides different genera and species, the determined extractives content is also influenced by several other factors, i.e., the sampling locations inside the tree, which are often not included in literature (like in the references of Table 1). One significant variable is the extraction itself because different solvents with different polarities result in different contents

Table 1 Extractives content of different economically attractive genera obtained by various experimental works

Wood Class	Genus	Extractives content in wt% on a dry matter basis			Samples	References
		Range	Mean	SD		
HW	Beech	1.0–1.6	1.3	0.2	3	[25–27]
HW	Eucalyptus	1.4–2.5	2.2	0.5	4	[28–31]
SW	Douglas fir	1.1–3.9	2.2	1.2	3	[31–33]
SW	Pine	1.0–3.4	2.2	0.9	4	[34–37]
SW	Spruce	1.0–4.9	3.0	1.4	4	[2, 38–40]

and compositions of determined accessory compounds [41]. Two wood-related factors important for pulping, since they can easily be influenced, are listed by Nisula [21]: tree age and the part of the tree. Older trees contain more extractives than younger ones; especially, the extractives content of heartwood is higher in older trees than in younger ones [23, 42–44]. Experiments of Miranda et al. [45], Morais and Pereira [46], and Tasooji et al. [47] showed that heartwood, in general, contains significantly more extractives than the surrounding sapwood. Other parts like knots (the part of the branches inside the stem) or the bark contain even more and different accessory compounds [48–50]. Björklund Jansson and Nilvebrant [12] categorized the different wood extractives depending on the chemical composition and structure into aliphatic compounds, terpenes, and phenols (presented in Table 2), since many important properties, like dissolution behavior and volatility, are similar within each of these groups.

The aliphatic compounds and the terpenes can be grouped to the so-called resin or pitch, including terpenes, resin acids, fatty acids and esters, various alcohols, hydrocarbons, and other neutral compounds [51]. There are significant differences in the resin composition depending on the location of the resin inside the wood, inside parenchyma cells, or in resin canals. Parenchyma resin, located in the parenchyma cells, serves as a reserve nutrient and therefore contains mainly fatty acids [52]. In growing trees, fatty acids mainly occur as esters (as fats when esterified with glycerol in the form of mono-, di- and triglycerides, as waxes when esterified with fatty alcohols, and as steryl esters when esterified with sterols) [12]. When cells die during the transition from sapwood to the inner heartwood or when the tree is felled, esters are enzymatically hydrolyzed into free fatty acids [21, 51]. The fatty acids in wood have lengths of 16–24 carbon atoms, with the unsaturated fatty acids oleic, linoleic, and linolenic acid (each with 18 carbon atoms) as the main components [12]. On the other hand, the resin inside resin canals, canal resin, or oleoresin differs from the parenchyma resin in its composition. Oleoresin mainly consists of terpenoids, mainly resin acids, dissolved in terpenes to ensure flowability. The function of canal resin is to seal wounds of the tree

through evaporation of the volatile terpenes leaving the solid resin acids (called rosin) as a hydrophobic mechanical seal back on the tree surface [53]. Although wood does not contain phenol, compounds with one or more phenol units occur in wood as structural phenolic components (i.e., lignin) and non-structural ones [54]. The non-structural phenolic components are the phenolic extractives, one major group of wood extractives. They are essential for the durability of wood since they protect the tree from different biotic attacks [20]. Björklund Jansson and Nilvebrant [12] grouped the many different phenolic extractives to lignans, stilbenes, flavonoids, tannins, and tropolones.

Since extractives are, as already mentioned, the accessory compounds of wood that can be extracted with hot water or organic solvents, they can also be categorized with their dissolution behavior. Depending on the solvent, they can be divided into hydrophilic and lipophilic extractives, which are also presented in Table 2 [55].

The classification of wood extractives based on their dissolution behavior rates among the most used categorization strategies, but this method also has problems. Both lipophilicity and hydrophilicity are just parameters—depending on various factors—not states [56, 57]. The polarity of solvents also depends on many parameters and is rather a spectrum than just two absolute conditions “polar” and “non-polar” [58]. Therefore, the classification of the accessory compounds based on their dissolution behavior is just an approximate simplification. However, it provides an opportunity for predicting dissolution behaviors and choosing the proper solvent(s) or mixture(s) for the extraction of the desired accessory compound(s), rather polar solvents for hydrophilic extractives, and rather non-polar solvents for lipophilic extractives. For comparing determined extractives contents, a more reproducible way to group wood extractives is the classification depending on the solvent itself, i.e. (hot-)water extractives, acetone extractives, or cyclohexane extractives [59, 60].

2.2 Determination and analysis

Wood can be analyzed for extractives directly with different spectroscopy methods. This fast and non-destructive

Table 2 Classification of wood extractives based on their dissolution behavior, chemical composition, and structure (adapted from ref. [12])

Lipophilic extractives		Hydrophilic extr
Aliphatic compounds	Terpenes	Phenols
Free fatty acids	Sterols	Lignans
Esterified fatty acids (i.e., mono-, di-, triglycerides, waxes, steryl esters)	Mono-, sesqui- and diterpenes	Stilbenes
Fatty alcohols	Terpenoids	Flavonoids
Hydrocarbons		Tannins
		Tropolones

measurement allows classifying and comparing wood species and wood treatments in terms of different wood compounds, i.e., certain extractives. Wagner et al. [61] successfully applied Fourier-transform RAMAN spectroscopy (FT-RAMAN), Fourier-transform infrared spectroscopy (FT-IR), and Fourier-transform near-infrared spectroscopy (FT-NIR) for this purpose. Similar qualitative analyses were carried out by Schnabel et al. [62] with FT-NIR for larch wood. However, spectroscopy methods are still not the right choice for quantifying wood extractives and require further research [61–63].

The two standards T204 [59] and NREL/TP-510–42,619 [60] describe how to determine the extractives content quantitatively. Wood shall be extracted with one or more solvents (depending on the desired group(s) of extractives). These solvents shall be evaporated afterward so that the residue can be weighed for calculating the extractives content. Even though the evaporation shall be done under vacuum and low temperature, the volatile components, particularly (mono)terpenes, are mostly also evaporated and therefore usually not included in the extract weight [59, 60]. Due to their volatility, terpenes, in general, do not play an essential role for pulps anyway. Thus, neglecting their contribution to the extractives content is mainly accepted, especially when analyzing woods for (developing) pulping (methods) [12].

However, wood extractives can be quantified directly out of the extract without evaporating the solvent first with several chromatographic methods like gas chromatography (GC), high-performance liquid chromatography (HPLC), size-exclusion chromatography, supercritical fluid chromatography, and thin-layer chromatography [64]. GC is the most widely used technique for analyzing the accessory compounds of wood with high selectivity and sensitivity [65, 66], even though the derivatization prior to the actual measurement includes some time-consuming steps [67]. Nisula [21], for example, successfully quantified wood extractives in her extensive work with long- and short-column gas chromatography; resin acids, fatty acids, sterols, diterpenoids, juvabionones, lignans, stilbenes, and flavonoids with long-column GC, the bigger sterol esters, triacylglycerols, and oligolignans with short-column GC. Poljanšek et al. [68], on the other hand, has recommended HPLC as the method of choice for analyzing particularly phenolic wood compounds. For lipophilic extractives, the resolution of HPLC is unfortunately not high enough to separate some individual wood extractives, particularly sterols and fatty acids [21].

Although the content of lipophilic extractives in wood is in general significantly lower than the hydrophilic one [69, 70], methods for analyzing lipophilic extractives are more important in pulp and paper manufacture since they cause many problems like sticky deposits [55, 71].

2.3 Effects on pulp and paper quality and production

The accessory compounds are extracted from wood in the papermaking process to a certain amount. Particularly lipophilic extractives such as fatty acids and resin acids tend to agglomerate in the process water forming so-called pitch deposits [9, 72]. In Kraft pulping, the alkaline conditions enable saponification of the glycerol esters to soluble soaps. On the contrary, other lipophilic extractives like sterols and sterol esters cannot be saponified and still form hydrophobic deposits [73]. The ratio of unsaponifiable to saponifiable components is, therefore, an important indicator of pitch formation in Kraft pulping. A higher ratio (for example, silver birch, which has one of the highest ratios among pulpwood species) indicates pitch problems [74] because the deposits stick to process equipment, causing contamination and piping blockages [75]. Pitch also sticks to different parts of the papermaking machines and stains the felts and canvas, even leading to major failures like web breaks of the machine [76]. Hence, pitch deposition originating from wood extractives is responsible for reduced production levels, higher operating costs, and higher equipment maintenance costs of papermaking processes [77]. In Kraft pulp mills, economic losses due to pitch problems are assumed to account for 1–2% of sales [78].

Once pitch deposits become released from the equipment, they contaminate the pulp in the form of dark spots, specks, and streaks, lowering the quality of the final product [79, 80]. Additionally to dark spots, specks, and streaks, extractives are considered to have a negative influence on the color and bleachability of pulps [81, 82]. Also, the oxidation products of some accessory compounds, particularly polyphenols, lead to the darkening of wood and pulp when exposed to sunlight and oxygen [82]. Pereira et al. [20] highlighted stilbenoids as the phenolic compounds that darken wood in the presence of sunlight, bringing up some problems when producing paper. Wei et al. [83] isolated the phenolic extractives of locust wood and observed color changes also when exposed to heat. However, chromophores as the UV/VIS absorbing groups responsible for the color of wood cannot be attributed exclusively to phenolic wood extractives [84]. They also originate from lignin to a large extent and sometimes even from organometallic extractive complexes [84, 85]. Especially heat- and light-induced color changes of wood and pulp result from complex reactions of hemicelluloses, lignin, and extractives [85].

Besides the negative impact on color and bleachability, wood extractives are also responsible for the odor of the pulp [86]. Ghadiriasli et al. [87] identified various volatile organic compounds (VOC), including terpenes

and degradation products from fatty acids and lignin, as odor-active compounds in oak wood, while Schreiner et al. [88] stated more precisely that fatty acid degradation products represent about two third of all the odor-active compounds in pine wood. Among all fatty acid degradation products, aldehydes play an essential role as odor-active compounds because their odor threshold is very low, and their smell is generally considered highly unpleasant [12, 89]. Aldehydes are not part of the original wood extractives but formed through an auto-oxidation of unsaturated fatty acids, called lipid oxidation, catalyzed by enzymes and heavy metal ions in wood [90, 91]. Although different aldehydes are formed through these lipid oxidation processes, hexanal as a linoleic acid oxidation product accounts for most of the aldehydes content [90]. Today's solution to deal with the odor from lipid oxidation in pulp and paper is using chelating agents like ethylenediaminetetraacetic acid (EDTA) to inhibit the catalyzing effect of heavy metal ions [12, 90]. However, EDTA is considered a risk for the aquatic ecosystem because it influences the heavy metals bioavailability and remobilization processes in the environment [92, 93]. Munn et al. [93] even concluded in the European Union's risk assessment report about EDTA that there is a need for limiting the environmental risks of EDTA. However, in conventional wastewater treatment plants, sufficient degradation of EDTA cannot be achieved [92]. EDTA containing process waters must therefore undergo special treatment before releasing them into the environment, leading to higher process costs [94, 95].

Environmental legislation has led to higher wastewater treatment requirements and, consequently, multiple reuses of process waters in the papermaking industry. This system closure decreases the wastewater treatment costs and creates new challenges due to the accumulation of wood extractives in process waters [67]. Naicker and Sithole [96] observed increasing extractives concentration and chemical oxygen demand (COD) of the process water with decreasing fresh water consumption in their experiments. Other issues with system closure are corrosivity and toxicity of process waters, mainly due to wood extractives, and more precisely because of phenolic compounds together with resin acids [12, 97]. Krilov and Gref [98] explained some corrosion effects with the ability of some phenolic wood extractives to form iron chelates. More specifically, Hazlewood et al. [99] stated that the phenolic catechols together with resin acids highly increase the corrosivity of black liquor from the Kraft process. On the contrary, other wood extractives like palmitic acid (a saturated fatty acid) were found to decrease corrosivity [99]. Similar findings were published by Singh and Anaya [100], who even found significant differences between some HW and SW species when pulping them with the Kraft process. Besides corrosivity, toxicity is

another important effect of wood extractives. This must be taken into account for treating the contaminated waste streams of the papermaking process, especially because there is increased focus on biotechnological processes for generating by-products out of waste streams like sludge [101] or fines [102]. Also, for conventional treatment of pulp mill sludge, wood extractives shall be removed by hydrothermal treatment, for example, to enhance anaerobic digestibility [103]. The accessory compounds of wood should thus be removed already during or even prior to pulping to avoid any further treatment in the papermaking process.

3 Removal of wood extractives during wood yard operations

Regardless of any subsequent pulp pre-treatment or the pulping itself, there are several opportunities for removing wood extractives at the wood yard in advance. The main tasks of wood yards include debarking the logs, chipping them (except groundwood pulping), screening the chips, and storing the wood [104]. The following sections explain the possible influences of these process steps on the wood extractives content.

3.1 Removal of bark and knots

Log debarking is, in general, the first process step at wood yards. It removes the dirt on the logs' outside and ensures that the resulting pulp is free of any bark [10]. On the other hand, it is also an efficient method for reducing the accessory compounds of the used raw material since the content of both lipophilic and hydrophilic extractives is usually very high in the bark. Among different species, wood extractives account for 20–40% of the dry matter of bark [23]. The experiments of Arisandi et al. [105] showed that eucalyptus bark contains not only more extractives than sapwood or heartwood but also more of every analyzed group of lipophilic extractives. Salem et al. [106] confirmed the findings with SW, showing that particularly fir and spruce bark contains up to 3 times as much lipophilic extractives than the wood itself. Balaban and Uçar [107] compared the content of the accessory compounds of oak wood with the one of the corresponding bark using different polar and non-polar solvents. All the bark extracts contained more extractives than the wood ones did [107]. The high extractives content of bark would negatively influence pulp quality and pulping; including extended cooking times and increased bleaching chemical consumption. Wood debarking prior to pulping has therefore become a well-established process. Nowadays, relatively low-cost

drum debarkers are among the most used technologies, reaching final bark contents below 1% [104].

Also, in debarked wood, the accessory compounds are not evenly distributed. For example, the inner heartwood is richer in both lipophilic and hydrophilic wood extractives than the outer sapwood [108, 109]. The starting points of branches inside the stem referred to as knots, contain even more extractives than all the surrounding stemwood [50]. Pohjamo et al. [110] reported significantly larger quantities of the phenolic flavonoids in knots than in the stem of the same trees. Other hydrophilic compounds like lignans can account for even 20% of the mass of the knots [111]. Willför et al. [112] analyzed knots for lipophilic wood extractives and found large amounts from 4.5 wt% up to 32 wt%. Besides the higher extractives content, knots also differ in the mechanical properties from wood since they are much denser and contain shorter and stiffer fibers. As so-called reaction wood, they have to withstand higher mechanical stress [21]. They are not fully cooked in chemical pulping and therefore leave the digester as large and dark impurities. Subsequent pressure screens remove the knots (called knotting) from the pulp stream [113]. However, the high extractives content of knots can negatively influence the entire pulp and paper manufacturing process, as already explained. Removing knots even before pulping should thus be considered. When chipping the logs, knots mainly result in over-thick chips because they are adamant and rigid [114]. Based on this finding and the fact that knots are denser than stemwood, Eckerman and Holmbom [115] developed a method for separating knots from the oversized chip fraction. This method, called “ChipSep”, relies on the phenomenon that dried knots are heavier than water, whereas dried stemwood, is lighter than water, provided that the dry matter content of the dried knots and stemwood is at least 85% (advantageously at least 87%), according to the patent of Eckerman and Holmbom [115]. Hence, knots containing wood sinks in water while knots-free wood rises towards the water surface [115].

3.2 Wood storage and biological treatment

Besides debarking and chipping, one primary purpose of a wood yard is wood storage. Delivered logs and cut wood chips are stored to ensure continuous supply of the subsequent pulping processes and compensate for any fluctuations in raw material supply [104]. Moreover, wood storage is even recommended to decrease the extractives content of the wood. During this wood seasoning, the accessory compounds of wood are reduced through volatilization, oxidative processes, and enzymatic hydrolysis in tree cells and by microorganisms [116]. In fact, the content of wood extractives starts to decrease immediately after felling

the trees and continues during storage, in the shape of chips and even entire logs, as shown in the experiments of Gutiérrez et al. [117] and Silverio et al. [80]. The reaction rate of all the chemical and biochemical reactions occurring during storage is highly dependent on environmental conditions, i.e., temperature, UV irradiation, wind, rain, and storage conditions like ventilation, protection with covers and the duration of storage [23]. The main reactions include oxidation of wood resin, hydrolysis of glycerides and other esters, loss of volatile components, and microbial degradation [12]. Logs and particularly wood chips require well-suited storage conditions.

Otherwise, chip deterioration and wood decay due to sap stain and a fungal attack occur [104]. Ramnath et al. [118] even found variations in bacterial and fungal communities on frozen stored wood chips. They showed that storing the chips at $-20\text{ }^{\circ}\text{C}$ had similar effects on the decrease of lipophilic wood extractives than seasoning does. During six months of storage, 25–44% reduction of lipophilic extractives was observed [118].

To summarize, wood seasoning can be applied as a strategy for reducing wood extractives without a significant decrease in the quality of the wood, but wood might be attacked by microorganisms, resulting in chip deterioration and mass losses of cellulose and hemicelluloses [16]. Seasoning offers no control over the microbial species growing on wood chips, leading to unpredictable wood effects, like loss of brightness or strength. Nevertheless, methods for controlled seasoning have been developed using microorganisms that effectively remove extractives without causing discoloration or strength loss [119]. This biological treatment method includes different bacteria strains and fungi, such as white-rot fungi, and is referred to as biopulping. The employed microorganisms can also digest lignin to a certain extent [120, 121]. Dorado et al. [122] proved white-rot fungi to decrease the amount of accessory wood compounds successfully. Their experiments removed up to 51% of resin acids and up to 87% of free fatty acids from pine wood within two weeks, while total loss of wood mass was below 12% [122]. Similar findings were published by Thao et al. [123], who removed up to 89% of fatty acids and fatty alcohols and 79% of free sterols from acacia wood within 30 days by means of a white-rot fungus. Košíková et al. [124] investigated four yeast strains concerning their wood extractives removal behavior. They could decrease the extractives content up to 63% and the fatty and resin acids up to 78% within four weeks. Experiments on bacterial strains done by Burnes et al. [125] and Kallioinen et al. [126] showed that the total wood extractives content can be bacterially decreased up to 41% (the lipophilic extractives even up to 67%) within two weeks without any visible discoloration of the wood. However, the experiments about biopulping mentioned

above showed that microbiological treatment has to be carried out in a bioreactor under controlled conditions and takes quite long (several weeks) compared to mechanical or chemical pulping (minutes to hours).

4 Extractives' removal through conventional pulping

The two conventional technological principles to produce paper pulp out of wood are mechanical and chemical processes, differing in the yields (80–95% at mechanical pulping comparing to 45–55% at chemical pulping), properties, and economic potential [8].

The defibration during pulping leads to exposure of the resin channels, making oleoresin accessible for dissolution and chemical reactions. On the one hand, this can lead to pitch problems at mechanical pulping, but on the other hand, it enables deresination in chemical pulping [12]. The parenchyma resin, on the contrary, is more difficult to remove because the pulping liquors must diffuse into the parenchyma cells, dissolve the resin or form soap micelles with the sterols and esters and diffuse out again afterwards. This process is enhanced by breaking the cell walls through chemical or mechanical pulping [21].

4.1 Mechanical and semi-chemical pulping

Mechanical pulping can be divided into two main categories, depending on the defibering method; groundwood pulp (GWP) obtained by grinding processes and refined mechanical pulp (RMP) produced with refining processes [8]. In semi-chemical pulping processes, the wood undergoes mild chemical treatment preceded by a mechanical refining step [2]. The most important refining process is thermomechanical pulping (TMP). Before refining, the wood chips are heated with steam (to 100–130 °C) to soften the lignin [10, 127]. The thermal treatment can also be combined with a chemical treatment to produce chemithermomechanical pulp (CTMP), representing the transition from mechanical to chemical pulps [2, 128].

Except for CTMP, the mechanical pulp contains most of the original lignin and still many accessory compounds [82]. However, the high temperatures of the defibering processes lead to partial degradation of cellulose and hemicelluloses. The resulting saccharides are then dissolved in the process water. Increased temperatures (above approximately 160 °C) at the TMP process even enhance these mechanisms, as shown by the work of Schneider et al. [129]. Besides saccharides, also extractives are liberated to a certain amount and released into the process water afterwards. These extracted accessory compounds do not only include hydrophilic extractives but

also lipophilic extractives like fatty and resin acids [130]. Resin acids and phenolic compounds contribute the most to the toxicity of mechanical pulping process waters [12].

4.2 Chemical pulping

Compared to mechanical pulping, in chemical pulping, lignin is rather removed by degradation and dissolution than just softened. Depending on the chemicals used for cooking the wood chips, there are mainly two types of processes: the sulfite process and the sulfate or Kraft process as the dominant pulping process [131]. Johansson et al. [132] stated as early as 1987 that most of the world's chemical pulp is produced by the Kraft process because of several advantages, including versatility in dealing with different raw materials and efficient recovery of cooking chemicals. Sixta et al. [9] defined Kraft pulping 2006 still the dominating chemical pulping process with almost 90% of the produced pulp worldwide, although sulfite pulping has accounted for approximately 70% of the world's dissolving pulp production [9]. Especially for dissolving pulp, wood extractives are important disruptive factors since they decrease the reactivity of cellulose with carbon disulfide when producing viscose out of dissolving pulp [133]. The accessory compounds of wood are usually mainly removed through chemical pulping but lead to increased consumption of cooking chemicals since they compete with lignin and hinder its removal [81].

The pH-flexible sulfite process uses aqueous sulfur dioxide and a base for cooking the wood chips. The dominating sulfite process in Europe is the acid magnesium bisulfite process [10]. While hemicelluloses are removed directly through hydrolysis during a cooking process called digestion, lignin must be sulfonated by the bisulfite ions to make it soluble in the cooking liquor [15]. In addition to hemicelluloses and lignin, most of the accessory compounds of wood are also removed through sulfite pulping. Unfortunately, some extractives participate in the sulfonation reactions, competing with lignin and increasing cooking liquor consumption [81]. Nevertheless, Rodrigues et al. [133] removed with the acid sulfite process nearly 85 wt% (based on initial dry wood) of acetone-soluble wood extractives, leaving mainly just extractives consisting of fatty acids and sterols in the unbleached pulp [133]. Nevertheless, Sixta et al. [9] listed the extractives content of sulfite pulp and Kraft pulp for both spruce and beech wood, showing that the sulfate process even removed about twice as much extractives as the sulfite one, independent of the wood class (SW/HW). Duan et al. [134] published similar findings and attributed them to the alkaline conditions of the Kraft process, which promote saponification and subsequent extractives removal.

In Kraft pulping, lignin is depolymerized by cooking wood chips with an alkaline cooking liquor consisting of caustic soda and sodium sulfide. The resulting phenolic fragments are then dissolved into the cooking liquor [135]. For producing dissolving pulp, hemicelluloses have to be removed from wood by prehydrolysis prior to pulping. The prehydrolysis can be done with diluted acid (acid-prehydrolysis) or just hot water, called autohydrolysis because wood typically releases acetic acid through autohydrolysis [136]. Although autohydrolysis is technically a hot-water extraction, Da Silva Morais et al. [137] and Li et al. [138] found an increased extractive content, especially at more severe prehydrolysis conditions. Da Silva Morais et al. [137] explained that phenomenon with the partial degradation of some macromolecules (mainly hemicelluloses) at high prehydrolysis temperatures. Therefore, the macromolecules are mobilized, meaning that the degradation products can easily be extracted in the case of subsequent extractions. When determining the extractives content gravimetrically by evaporating the solvent from the extract, the degradation products are then distorting the extractives content. As already mentioned, experiments showed, that the sulfate process removes about twice as many extractives as the sulfite one due to saponification. The alkaline black liquor converts resin and fatty acids into soluble sodium soaps [12]. However, Dunlop-Jones et al. [139] published that in typical Kraft pulping, only half of the potentially saponifiable wood resin was saponified in the digester. Moreover, Shin et al. [140] found sterols, sterol esters, and fatty acids as the main compounds in residual Kraft pulp extractives. Therefore, there is a need to further eliminate the remaining accessory wood compounds through pulp bleaching, for example, removing the unsaturated fatty acids by oxygen delignification [140].

4.3 Pulp bleaching

Extended cooking for removing color in pulp originating from lignin, extractives and other colored impurities would significantly decrease pulp quality due to enhanced cellulose degradation [141]. Thus, pulp bleaching has been developed, which is defined by Sixta et al. [141] as a chemical process for removing the color sources in pulps, has been introduced. To quantify the results of these bleaching processes, brightness has been established as an indication of the pulp's whiteness [10]. Starting with chlorine as the main bleaching agent, in the 1980s, so-called elemental chlorine-free (ECF) bleaching processes have been developed to substitute chlorine with chlorine dioxide (D). The recent development is the totally chlorine-free (TCF) bleaching process, applying oxygen (O), hydrogen peroxide (P) and/or ozone (Z) as bleaching agents, and an alkaline extraction stage (E) [141]. Since mechanical pulp

aims to minimize mass loss, lignin of mechanical pulps is rather just brightened than removed compared to chemical pulps. This so-called lignin-preserving bleaching is accomplished commercially, primarily with hydrogen peroxide and/or sodium dithionate [142].

Alkaline hydrogen peroxide bleaching as lignin-preserving bleaching method decreases the lipophilic extractives content of TMP just slightly [143]. Ekman and Holmbom [144] examined alkaline peroxide bleaching of mechanical pulps with spruce groundwood. Hydrophilic extractives were oxidized almost wholly, whereas resin acids were just partly oxidized and fatty acids even unaffected [144]. As already mentioned, chemical pulping typically eliminates far more wood extractives than mechanical pulping, showed by Rodrigues et al. [133], with a removal rate of 85 wt% (based on initial dry wood) acetone-soluble wood extractives through the acid sulfite process. With subsequent E–O–P bleaching, they removed further 11 wt%, leaving just four wt% of the initial extractives in the bleached pulp, mainly consisting of fatty acids and sterols [133]. España Orozco et al. [145] achieved comparable results with oxygen-reinforced alkaline extraction of mixed HW sulfite pulp, followed by Z and P bleaching. They decreased the gravimetric acetone extract of pulp by 68% through the TCF bleaching sequence, with oxygen-reinforced alkaline extraction as the most effective stage, leaving mainly just sterols and sterol esters in the pulp. For lipophilic extractives (determined by GC–FID), the highest drop was observed after Z bleaching (–38%). Freire et al. [146] and Gutiérrez et al. [147] compared different bleaching sequences with eucalyptus Kraft pulp. They observed that unsaturated sterols and fatty acids were extensively degraded during D and Z bleaching but only partially degraded during O and P bleaching. The wood extractives removed during bleaching are not only degraded and oxidized but also dissolved to a certain extent into bleaching and washing liquids, as shown through analysis of pitch deposits in bleaching stages by Del Rio et al. [75] and evaluation of precipitated extractives on bleached Kraft pulp by Koljonen et al. [148]. For avoiding such problems during bleaching, the extractives content can be reduced by extractions before bleaching or even before pulping which is explained in the following chapter.

5 Alternative methods for pulping and removing extractives

Currently, high-purity cellulose fibers are commercially produced from wood with the sulfite or the Kraft process. These pulping methods are considered cellulose-first strategies since fractionation of biomass usually targets high-quality cellulose. The resulting lignin has different

properties than the native one (i.e., it is less reactive) and is mainly burned for energy recovery instead of using as a by-product [149]. The approach for using all the components of the biomass feedstock as products are so-called lignocellulose biorefineries. Besides pulping, lignocellulose biorefineries also include separation and purification processes, which contrasts the increased revenue streams with the high capital and operating costs of up to 20–50% of the total capital and operating costs of biorefineries [150]. However, there is growing interest in organosolv pulping processes using organic solvents instead of inorganic pulping liquors. The recovery of satisfying by-products is easier than in the Kraft process [151].

5.1 Organosolv pulping and extraction with organic solvents

Kleinert and Tayenthal [152] successfully carried out experiments as early as 1931 for fractionating different woods with aqueous ethanol. This so-called organosolv pulping uses—as already mentioned—organic solvents. It is a two-stage process where hydrolysis degrades hemicelluloses, and lignin is dissolved into the organic solvent to a certain extent depending on the pulping conditions [153]. Johansson et al. [132] showed that the organosolv process has considerable potential in terms of delignification selectivity. Compared to pulps produced through conventional pulping, organosolv SW pulps can have higher yields at equal kappa numbers, which indicates the lignin content of the pulp [132]. Good delignification of the organosolv process was also proved by the experiments of Botello et al. [28] and Kirci and Akgül [154]. They concluded that organosolv pulping could be a suitable alternative for producing dissolving pulps with very high cellulose contents. Moreover, organosolv pulps can have better optical and strength properties than conventional Kraft pulp [155].

Another advantage of the organosolv process is the effective removal of extractives from wood. As already described, the accessory compounds of wood can be extracted with (aqueous solutions of) organic solvents. This is even considered as the method of choice for the exclusive extraction of accessory wood compounds. The two most commonly used standards, T204 [59] and NREL/TP-510-42,619 [60], for quantitatively determining the wood extractives content, are based on a mild extraction with organic solvents through a Soxhlet apparatus. According to the standards, the wood shall be extracted with organic solvents at ambient pressure and low temperatures (below the solvent's boiling point) for a long period (up to 24 h). The extraction works automatically in a closed loop with a boiler on the bottom, a condenser on the top, and the extraction thimble with a siphon as well as

a vapor bypass in the middle. There are many siphon cycles within the entire extraction period, with fresh solvent for each cycle [59, 60]. The long period for complete extraction can be compensated with high pressures. National Renewable Energy Laboratory [60] describes a method to use a speed extractor with high pressures, which allows quantitatively extracting the wood in a few minutes. This method is called accelerated solvent extraction (ASE). Table 3 compares the ASE with the traditional Soxhlet extraction, as well as different solvents.

Vek et al. [156] showed that with the same solvent(s), ASE yields comparable amounts of extractives but takes just 10–20% of the time of Soxhlet extraction. The reason for the difference in extraction time is that Soxhlet extraction is carried out under atmospheric pressure and temperatures between 7 °C and 10 °C below the boiling point of the solvent compared to temperatures above the boiling point and pressures higher than 100 bar at the speed extraction [158, 160]. The solvent itself, on the contrary, can have a significant influence on the determined extractives content. It can be seen in Table 3 that solely extracting with non-polar solvents like Cyclohexane is not appropriate for quantitatively removing wood extractives. Non-polar solvents mainly extract lipophilic accessory compounds of wood, which are less in amount than the hydrophilic ones, as already mentioned. To enhance the quantitative removal of wood extractives, non-polar solvents should be mixed with miscible polar solvents, or a subsequent extraction with a polar solvent should be added [69, 156, 159]. Moodley [157] and Schwanninger and Hinterstoisser [160] could increase the amount of extracted material up to 150% with a hot-water extraction in addition to the organic solvent extraction step. On the other hand, one must be aware of autohydrolysis occurring during hot-water extraction, dissolving considerable amounts of wood compounds that are not wood extractives by definition, i.e., hemicellulose degradation products [161]. Krogell et al. [162] and Song et al. [163] removed considerable amounts of hemicelluloses from the wood meal by pressurized hot-water extraction (PHWE) within 20 min. Increasing the wood particle size significantly decreased the amount of total dissolved solids (TDS) [162, 163]. The influencing factor particle size was also investigated by Bertaud et al. [158] at extractions of coarse-crushed wood and groundwood with acetone and cyclohexane and significantly influenced the extraction behavior. A lower particle size led to sharply higher amounts of extracted wood extractives [158]. In terms of process design for an industrial application of organic solvent extraction for removing wood extractives, different extraction methods and conditions should thus be compared using the actual wood particle size of the process later on. Thurbide and Hughes [164] carried out

Table 3 Lab scale extractions of groundwood with different methods and solvents

Wood genus	Extraction 1			Extraction 2			Amount of extracted extractives in wt%	Reference
	Method	Solvent(s)	Time in min	Method	Solvent(s)	Time in min		
Beech ¹	Soxhlet	Cyclohexane	240	–	–	–	1.0	[156]
Beech ¹	Soxhlet	Cyclohexane	240	Soxhlet	Methanol	360	5.7	[156]
Beech ¹	ASE	Cyclohexane	15	–	–	–	1.0	[156]
Beech ¹	ASE	Cyclohexane	15	ASE	Methanol	15	5.3	[156]
Eucalyptus ²	Soxhlet	Acetone	240–300	–	–	–	3.1	[157]
Eucalyptus ²	Hot-water	Water	180	–	–	–	4.6	[157]
Eucalyptus ²	Hot-water	Water	180	Soxhlet	Acetone	240–300	5.2	[157]
Eucalyptus ²	Hot-water	Water	180	Soxhlet	Ethanol/Toluene (1/2)	240–300	6.7	[157]
Eucalyptus ³	Soxhlet	Acetone	240–300	–	–	–	2.2	[157]
Eucalyptus ³	Hot-water	Water	180	–	–	–	4.8	[157]
Eucalyptus ³	Hot-water	Water	180	Soxhlet	Acetone	240–300	5.4	[157]
Eucalyptus ³	Hot-water	Water	180	Soxhlet	Ethanol/Toluene (1/2)	240–300	5.4	[157]
Fir ⁴	Soxhlet	Acetone	360	Soxhlet	Acetone/Cyclohexane (1/9)	480	4.9	[158]
Fir ⁴	ASE	n-Hexane	20	ASE	Acetone/Water (95/5)	20	5.9	[158]
Pine ⁵	Soxhlet	Acetone	360	Soxhlet	Acetone/Cyclohexane (1/9)	480	5.7	[158]
Pine ⁵	ASE	n-Hexane	20	ASE	Acetone/Water (95/5)	20	9.5	[158]
Pine ⁶	Soxhlet	Cyclohexane	360	–	–	–	4.1	[159]
Pine ⁶	Soxhlet	Cyclohexane	360	Soxhlet	EtOH	360	4.8	[159]
Pine ⁶	Soxhlet	Acetone	480	–	–	–	4.6	[159]
Pine ⁶	Soxhlet	Cyclohexane/EtOH (2:1 v/v)	360	–	–	–	4.6	[159]
Pine ⁶	Soxhlet	Cyclohexane/EtOH (2:1 v/v)	360	Soxhlet	EtOH	360	4.8	[159]
Spruce ⁷	Soxhlet	Acetone	360	Soxhlet	Acetone/Cyclohexane (1/9)	480	4.8	[158]
Spruce ⁷	ASE	n-Hexane	20	ASE	Acetone/Water (95/5)	20	6.9	[158]
Spruce ⁷	Soxhlet	Benzene/EtOH (2:1 v/v) + EtOH (abs.) + EtOH (95 vol%)	540	–	–	–	2.3	[160]
Spruce ⁷	Soxhlet	Benzene/EtOH (2:1 v/v) + EtOH (abs.) + EtOH (95 vol%)	540	Hot-water	Water	180	4.2	[160]

Description: The amount of extracted wood extractives in wt% is based on initial dry wood

¹Fagus sylvatica L.; ²Eucalyptus grandis; ³Eucalyptus nitens; ⁴Abies alba; ⁵Pinus pinaster; ⁶Pinus nigra; ⁷Picea abies

experiments comparing Soxhlet extraction and ASE with TMP instead of wood meal as the standards T204 [59] and NREL/TP-510–42,619 [60] require. The obtained extractives content was quite similar, meaning that even at industrial wood particle sizes like TMP, long extraction times can be compensated by high temperatures and pressures and vice versa [164].

Soxhlet extraction is just a lab-scale method because of the long extraction period and the high energy demand for recycling the vast amount of organic solvent needed. Nevertheless, organic solvent extraction, in general, would technically be an interesting technology for removing wood extractives as pulp (pre-)treatment as well as for pulping itself. Shin et al. [165], for example, could

significantly decrease the chromophore groups of aspen Kraft pulp just by extracting the pulp with organic solvents to remove residual extractives. Baptista et al. [166] extracted wood with organic solvents even prior to Kraft cooking. The results showed better bleachability and less chlorine dioxide consumption to reach the same brightness levels when bleaching the pulp [166].

Despite all the advantages of extracting wood with organic solvents and aqueous solutions of organic solvents, like good pulp properties and superior capabilities of removing lignin as well as extractives (depending on the process conditions), it is unfortunately not an economic pulp (pre-)treatment method [167]. Notably, organic solvent recycling has a significant impact on the energy consumption of the process, as it remains one of the main challenges towards an economically viable design [168, 169].

5.2 Novel extraction and fractionation methods

In the organosolv process, as already mentioned, not only the accessory compounds of wood are extracted, but also lignin and hemicelluloses by breaking down the internal bonds. The lignin obtained as a by-product of this process is characterized by high purity and quality [170]. On the other hand, organic solvents are associated with flammability, volatility, toxicity, environmental hazards, and increased costs [171, 172]. Thus, extensive research has been done to develop various (pre-)treatment processes with different methods and solvents, particularly environmentally friendly or green solvents [172, 173].

One alternative method with green solvents is supercritical extraction (SCE), more precisely, the extraction with supercritical fluids. The advantages of using supercritical fluids are the low viscosity, high diffusivity, high dissolving power, and low surface tension, leading to higher solvent mass transfer when penetrating cell wall layers. Typical SCE solvents are water, carbon dioxide, and mixtures with organic co-solvents [171]. Supercritical extraction with carbon dioxide (SC-CO₂) has become an established technology since CO₂ is non-toxic, non-flammable, and recyclable. Furthermore, carbon dioxide is considered non-polar and dissolves lipophilic compounds, i.e., resin and fatty acids [158]. Another alternative process is steam explosion, which is technically the treatment of wood through hot steam under pressure with a subsequent pressure drop to atmospheric pressure. This leads to the destruction of cell wall layers and easier solubilization of wood compounds [174]. Table 4 compares different supercritical extractions and steam explosion treatments with Soxhlet as the reference method for quantitatively extracting the accessory wood compounds.

As it can be seen in Table 4, supercritical extraction and steam explosion can yield significantly more extractives than a Soxhlet extraction. Still, one should be aware that SCE and especially steam explosion degrades hemicelluloses to a certain extent [170]. This means that the extractives content gravimetrically determined by evaporating the solvent from the extract can incorrectly be too high because the evaporation residue contains extractives and hemicellulose degradation products. Nevertheless, Demirbaş [175], for example, extracted four times more extractives and ten times more amount of fatty acids with SCE than the Soxhlet extractions. The big advantage of steam explosion is the lower capital costs and the higher energy efficiency, which makes it suitable for lab-scale and commercialized applications from an economical point of view [176]. Despite the benefits of SC-CO₂ as low solvent costs and low temperatures, the exceptionally high pressure of up to several hundred bars is a barrier for upscaling this process to an industrial scale [177].

One relatively new approach to overcome the disadvantages of using volatile organic solvents, or applying high pressures for SCE or steam explosion, for example, are ionic liquids (ILs) which are also considered to have lower environmental impacts [178]. ILs are salts and therefore composed of anions and cations. The properties resulting from this composition are thermal stability, remarkable solvating ability, nonvolatility, and near-zero vapor pressure [179]. Especially in biorefineries, ILs were proven to be an effective solvent for fractionating wood and even dissolving entire wood particulates after an autohydrolysis step, as shown by Deb et al. [180]. On the other hand, Papa et al. [181] could extract significant amounts of the terpene α -pinene from pine wood applying IL treatment, and Kilulya et al. [182] demonstrated the removal of lipophilic wood extractives from dissolving pulp with ILs in amounts comparable to other extraction technologies. Additionally, ILs exhibit favorable behavior when producing food supplements or drugs out of wood, i.e., antioxidants. Pinkert et al. [183] successfully applied food-additive-derived ILs for extracting wood lignin without dissolving or degrading cellulose. However, the drawback was the requirement of recycling the ILs more than 100 times for an economically feasible process [183]. The reason are high costs for ILs due to synthesis, purification, and downstream processing procedures, which are currently the limiting factors for using ILs at a large scale [179]. Other disadvantages of ILs are poor biodegradability and biocompatibility, and usually, fossil resources are needed to produce ILs [184]. In 2007, Fukaya et al. [185] developed so-called "Bio-ILs" completely derived from biomaterials to overcome these problems. However, Yiin et al. [184] concludes that further research has to be done on Bio-ILs, because studies are still limited in 2021.

Table 4 Groundwood extraction results of SCE and steam explosion compared to Soxhlet extraction

Wood genus	Extraction 1					Extraction 2					Amount of extractives in wt%	Reference
	Method	Solvent(s)	Temp. in °C	Pressure in bar	Time in min	Method	Solvent(s)	Temp. in °C	Pressure in bar	Time in min		
Fir ¹	Soxhlet	Acetone	N/A	N/A	360	Soxhlet	Acetone/ Cyclohexane (1/9)	N/A	N/A	480	4.9	[158]
Fir ¹	SCE	CO ₂	60	200	90	-	-	-	-	-	4.8	[158]
Fir ¹	SCE	CO ₂	60	300	90	-	-	-	-	-	5.7	[158]
Spruce ²	Soxhlet	Acetone	N/A	N/A	360	Soxhlet	Acetone/ Cyclohexane (1/9)	N/A	N/A	480	4.8	[158]
Spruce ²	SCE	CO ₂	60	200	90	-	-	-	-	-	6.0	[158]
Spruce ²	SCE	CO ₂	60	300	90	-	-	-	-	-	5.8	[158]
Pine ³	Soxhlet	Acetone	N/A	N/A	360	Soxhlet	Acetone/ Cyclohexane (1/9)	N/A	N/A	480	5.7	[158]
Pine ³	SCE	CO ₂	60	200	90	-	-	-	-	-	7.4	[158]
Pine ³	SCE	CO ₂	60	300	90	-	-	-	-	-	8.5	[158]
Juniper ⁴	SCE	CO ₂ /EtOH (8/2 v/v)	120	250	60	-	-	-	-	-	3.2	[174]
Juniper ⁴	Soxhlet	EtOH/Water (95/5)	N/A	N/A	240	SCE	CO ₂ /EtOH (8/2 v/v)	120	250	60	4.1	[174]
Juniper ⁴	Steam explosion	Water	235	32	3	SCE	CO ₂ /EtOH (8/2 v/v)	120	250	60	5.9	[174]
Beech ⁵	Soxhlet	Acetone	N/A	N/A	1080	-	-	-	-	-	2.5	[175]
Beech ⁵	SCE	Acetone	240	60–65	30	-	-	-	-	-	9.6	[175]

Description: The amount of extracted wood extractives in wt% is based on initial dry wood

¹Abies alba; ²Picea abies; ³Pinus pinaster; ⁴Juniperus communis L.; ⁵Fagus orientalis

One of the drawbacks of all the treatment methods mentioned above is the heat transfer resistance limiting the process efficiency. Microwave (MW) technology, which has received increased attention in recent years, can overcome this limitation because MWs penetrate materials and deliver energy throughout the material volume. Therefore, this so-called in-core volumetric heating generates heat directly inside the volume instead of heat transfer through conduction and convection when conventionally heating from outside [186]. The advantages are enhancement of reaction rate, reduction of the reaction time, increased product yield, and less formation of by-products, provided that the solvent and/or the biomass are high-microwave-absorption materials [187]. For example, Xu et al. [188] proved MW technology as an efficient method by liquefying about 75% of the initial wood in methanol at 180 °C in just 15 min. However, applying microwave extraction can lead to local overheating since composition, geometry, and size affect microwave power distribution, making it challenging to up-scaling the process [171].

Another novel method applying high-energy radiation is ultrasonic-assisted extraction (UEA) [189]. The principle behind UAE is disrupting the solid structure with ultrasonic waves [190]. In detail, the ultrasonic waves degrade cell walls and rupture bonds between lignin, hemicelluloses, and cellulose [171]. He et al. [191] proved the ultrasound-induced mechanical damage of wood structure in his work and observed a significant reduction of wood extractives. Wang et al. [192] could increase the extraction efficiency even by factor 2.6 when extracting hemicellulosic and phenolic compounds from bamboo wood with water. Similar findings were published by Sillero et al. [193], who successfully increased the extraction of phenolic wood extractives from different HW species with intensified UEA. Although UEA has been successfully proved as an effective extraction method, much more research has to be carried out for using UEA in large industrial-scale processes, i.e., optimization in terms of ultrasound power input and frequency [189].

6 Utilization of wood extractives

When applying extractive methods as pulp (pre-)treatment, the accessory compounds of wood cannot only be removed but also isolated as side products since they have many interesting properties.

Wood extractives play an essential role in protecting living trees against fungal attacks and other pests like insects [19]. Especially phenolic extractives and resin acids act as natural fungicides of trees [12, 194]. The extract of *Delonix regia* (also known as flame tree or flamboyant) in the study of Salem et al. [195] showed inhibition of fungal growth

and antioxidant activity. Additionally, the extract exhibited antibacterial behavior against different bacterial strains, i.e., *Escherichia coli*, suggesting the usage to control plant and human pathogens [195]. Hosseini Hashemi and Jahan Latibari [196] found that walnut-heartwood-extractives-coated poplar wood had significantly less mass loss after exposing it to white-rot fungus than untreated poplar wood. Belt [197] observed pine knot extract to have a significant antifungal character, but suggested more study before approving pine extractives as preservative chemicals. However, wood extractives have enormous potential in wood protection because they have many different antimicrobial properties, are renewable, and are less eco-toxic than chemical biocides [198].

Pine extractives have been used by humans for hundreds of years for paintings and coatings, particularly for caulking seams of wooden ships [199]. Since distilling wood extractives, the two resulting products, turpentine and rosin, have served as important platform chemicals. Today, the overwhelming predominance of petroleum-based chemicals has led to much less usage of wood extractives than their potential would be. Nevertheless, the rising demand for renewable materials and chemicals increases interest in wood extractives [200].

Currently, wood extractives resulting from thermomechanical pulping are wasted because today's approaches for managing them with additives during pulping do not allow efficient recovery [201]. In Kraft pulping of SW, on the other hand, the volatile accessory compounds of wood can be isolated, yielding approximately 10 kg/ton of pulp. These volatile extractives mainly consist of monoterpenes and are distilled for removing impurities. The resulting fraction is called turpentine, with the major constituent α -pinene. Turpentine is mainly used for producing chemicals, fragrances, and flavors. The non-volatile accessory compounds of wood, mainly soaps of resin acids and fatty acids, are separated from the cooking liquor after the Kraft cooking process. The addition of sulfuric acid liberates the free fatty acids, giving crude tall oil (CTO) with a yield of up to 50 kg/ton of pulp [202]. The CTO production in 2018 was about 2.5 million metric tons worldwide. From that amount, globally, two million metric tons were refined, while the rest was used for heat and power generation [203]. The distillation products of CTO are 30–50% pitch, 30–50% fatty acids, and 15–35% resin acids [204]. In the rosin fraction (colophony), Holmbom [205] found 62–80% of the resin acids from the crude tall oil feed.

From a product point of view, CTO products can be divided into chemical intermediates, biodiesel, and tall oil pitch. Pitch is currently just used for heat and power generation, whereas the chemical intermediates, rich in resin acids, are used as adhesives and in paintings and printing inks [203]. The fatty acids of tall oil can be converted into

biodiesel by esterification with the challenge of removing the remaining sulfur [206]. However, tall oil biodiesel is one way to add more value to CTO. In Finland, the first industrial-scale CTO biodiesel plant worldwide produced more than 100,000 tons of biodiesel per year, already in 2015 [207, 208].

7 Concluding remarks and outlook

Wood extractives are still a big issue for the pulp and paper industry. They lower pulp quality and cause many problems for the pulping process itself due to the formation of sticky deposits. Some established process steps already decrease the extractives content to a certain extent, i.e., debarking, chemical pulping, and bleaching. Additionally, many alternative technologies for reducing accessory wood compounds have been developed to replace or supplement the conventional process steps, as shown in Fig. 1.

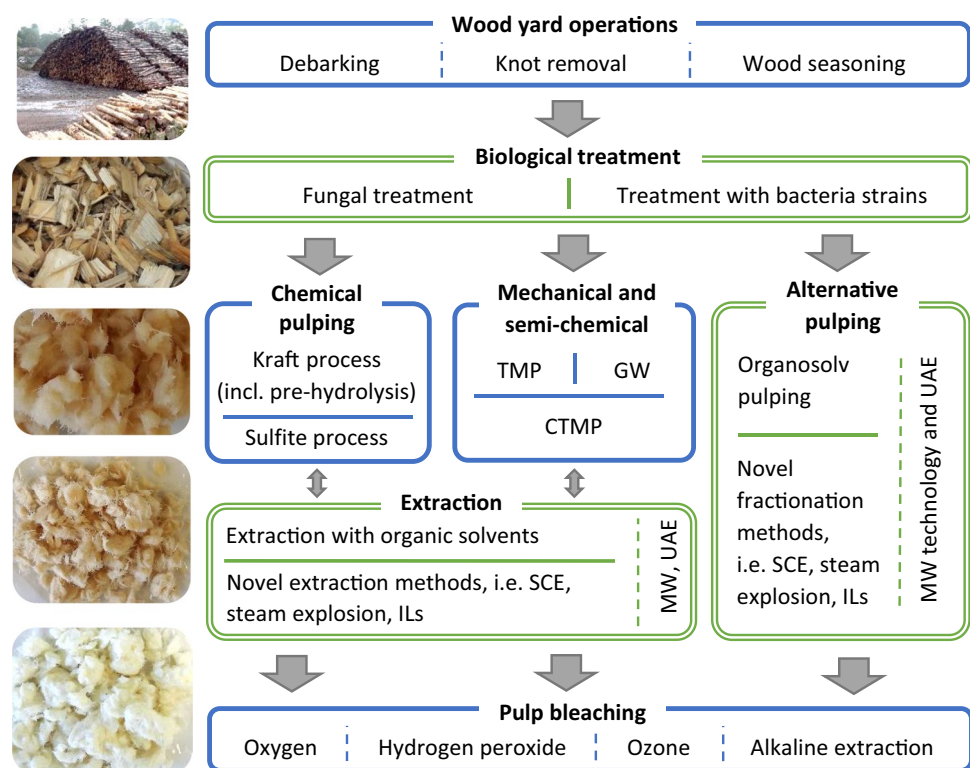
Wood debarking as a well-established technology is a very effective method to reduce the wood extractives content. In bark, wood extractives account for 20–40% [23] of the dry matter compared to less than in wood. Research about the extractives content of different wood parts showed that besides bark, also knots contain large amounts of extractives from 4.5 wt% up to 32 wt% [112]. Knots are also denser and stronger than heart- and sapwood, which allows rejecting knot-containing chips. Wood

seasoning after chipping can also reduce the accessory compounds even prior to pulping. Still, it requires well-suited storage conditions and long storage times for significantly lowering the extractives content. Otherwise, wood decay and/or fungal attack might lead to quality losses. On the other hand, several studies proved different fungi and bacterial strains to effectively decrease the extractives content by more than 60% [124] without decreasing wood quality. However, the main drawback for an industrial-scale use is the requirement of controlled conditions in a bioreactor for several weeks required for such a biological treatment.

Conventional pulping also removes wood extractives to a certain extent. At mechanical pulping, just a small part of hydrophilic and lipophilic wood extractives are released into the process water, but Rodrigues et al. [133], for example, could remove in their work nearly 85 wt% (based on initial dry wood) of acetone-soluble wood extractives by the acid sulfite process. Kraft pulping was found to remove even more extractives than the sulfite process does. Furthermore, pulp bleaching plays an important role in decreasing the amount of accessory wood compounds. With the right choice of pulping stages, the residual extractives content can be lowered significantly, leaving mainly just sterols and sterol esters in the bleached pulp.

Additionally, a number of organic-solvent-based pulping and extraction methods have been developed to remove the accessory compounds from wood and

Fig. 1 Overview of established and alternative methods for removing wood extractives at pulp production. *Description:* Blue solid-line frames are established conventional processes, green double-line frames are novel alternative methods. Solid lines inside the frames separate different process stage; dashed lines indicate possible combinations of different methods



pulps. The extraction with organic solvents, as one of the most used extraction techniques for woody biomass, even allows quantitatively removing wood extractives and is therefore also the method of choice for determining the extractives content. However, the typical organic solvents like ethanol, acetone, or cyclohexane are quite volatile and highly flammable. This has led—together with economic challenges for solvent recycling—to the development of novel extraction methods, ranging from alternative solvents like supercritical fluids or ILs through MW technology as an alternative heating method to UAE for enhancing the extraction by mechanically damaging cell wall structures. All these extraction-based methods are not only technically suitable for removing wood extractives but can also be used as an alternative pulping method for wood fractionation and delignification, as proved by many studies. Moreover, the extraction-based removal of wood extractives allows using the extracted accessory compounds of wood, i.e., as natural biocides or platform chemicals. However, further research is required to overcome the problems of novel extraction methods which are currently hindering the application for removing wood extractives on an industrial scale. On the one hand, there is a need for better synthesis and recycling processes to reduce operating costs (ILs). On the other hand, there are several technical issues, like high pressures (SCE) and irradiation power input and distribution for large geometries (MW technology and UAE).

This need for research has also been intensified by enhancing environmental legislation. On the one hand, state-of-the-art processes for avoiding negative impacts of wood extractives on pulp and paper quality by adding chemicals will most likely be restricted by law. Most additives, i.e., complexing agents against lipid oxidation of wood, are already considered as risks for the aquatic ecosystems. On the other hand, higher wastewater treatment requirements and fresh water usage regulations have led to increased process water system closure and, consequently, to an accumulation of wood extractives in process waters. The resulting lower product quality and higher maintenance costs (due to blockages and web breaks, for example) can only be avoided by expensive process water treatment. An alternative solution is removing wood extractives as pulp (pre-)treatment, which is still in the research and development stage. Nevertheless, some novel methods, like extracting wood with supercritical fluids or ILs and using MW and UAE technologies, are still performed on a lab scale but already delivering promising results for solving this issue in the near future.

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Declarations

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