Extractives in the Scandinavian pulp and paper industry

Current and possible future applications

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1. BACKGROUND

The forest industry is one of Sweden's most important business sectors. Thanks to its biobased raw materials and products, the forest industry plays a key role in the development towards a sustainable, circular economy. To meet market needs, and to drive the growth of the circular economy, the forest industry is continually developing its processes and products. It is seeking to use its raw material, the forest, as efficiently as possible and is constantly seeking to improve quality and incorporate new functions into materials and products.

Pulp and paper makes up the largest part of the forest industry, followed by sawn wood products and products made from paper and paperboard. 3.9 million tons of pulp and 10.1 million tons of paper were produced in Sweden in 2016.

The pulp and paper industry uses stem wood as its raw material. Stem wood consists of cellulose, hemicellulose, lignin, and extractives. Cellulose and hemicellulose are separated in the pulping process and the economically most important components in wood. Lignin and extractives are usually burned to provide the mill with heat and power, but the use/needs has changed over time due to development of more energy efficient mills. Today lignin is extracted from the black liquor for external use, while extractives are fractionated and used for production of a wide range of products such as, biodiesel, adhesives, and chemical intermediates.

The extractives make up between 3 and 5 weight-% of the wood and consists of a wide range of compounds. The majority of those compounds are fatty acids such as oleic- and linoleic acid and rosin acids, such as abietic- and pimaric acid. The remaining compounds are commonly referred to as "neutrals" and are dominated by β-sitosterol. The extractives in Scots pine for example, consist of 70 % fatty acids, 20 % rosin acids and 5 % neutrals.

Today, the extractives are separated at the pulp and paper mills during the regeneration of cooking chemicals into a product called crude tall oil (CTO). 2.5 million metric tons of CTO is produced globally with 80% of the production situated in North America and Scandinavia. 1.3 million tons is produced in North America and 600 000 tons is produced in Scandinavia. 2.0 million metric tons is currently refined globally, while the rest is used internally by the mills for the production of heat and power.

CTO is currently refined into a range of products which can be divided up into (i) chemical intermediates, (ii) biodiesel, and (iii) tall oil pitch. The chemical intermediates are mostly used for the production of adhesives, while the biodiesel is used as a transport fuel, and the tall oil pitch is used for production of heat and power.

To meet market needs, and to drive the growth of the circular economy, extractives could potentially be used for the production of other products, either through new refinement routes of CTO or novel extraction and separation methods from the raw material. In order to identify opportunities for the production of other extractives based products, the extractives value chain must first be mapped. Second, refinement routes as well as extraction and separation methods suitable for isolation and processing of valuable compounds must be identified.

The objective of this work is to identify opportunities for the production of new products based on extractives as raw material. This literature review focuses on the use of extractives in the

Scandinavian pulp and paper industry and is divided into two parts. The aim of the first part of the work is to review handling of extractives in the Scandinavian Pulp and paper industry

- applications
- products
- operators/stakeholders

The first part of the review will answer two main questions:

1. Who are handling extractives?
2. How are they handling them?

The aim of the second part of this work is to identify

- valuable extractives currently used for combustion
- extraction-, separation-, and processing methods for those compounds

The second part of the review will answer two main questions:

1. Which extractives could potentially be used to produce new products?
2. How can those compounds be isolated from the raw material/CTO and processed?

The information collected in the first and second part will be discussed with regard to possible business opportunities.

2. WOOD EXTRACTIVES BASICS

Trees are the basic raw material of the Scandinavian pulp and paper value chain. Trees are made up of wood which consists of two major parts: lignin (18-35 %) and carbohydrates (65-75 %) [1]. There are two forms of carbohydrates, i.e. cellulose, and hemicellulose. There are also minor amounts of ash as well as a set of compounds that are collectively referred to as extractives. Many of the extractives function as intermediates in tree metabolism, as energy reserves, or as part of the tree´s defense mechanism against microbial attack. They contribute to wood properties such as color, odor, and decay resistance. The extractives make up about 2-10 % of the trees that grow in temperate climate but can make up as much as 20 % in trees that grow in tropical climate. Scandinavia (except the most northern parts) has temperate climate.

Common to all extractives is that they are non-cell wall components which can be extracted (hence the name) using solvents, e.g. ethanol, acetone, or water. There are thousands of individual compounds which can be divided into groups and subgroups. The major groups are (i) aliphatics (ii) terpenoids, (iii) phenolics, and (iv) others (Figure 1). The most important aliphatics are fatty acids and triglycerides. The Aliphalics group also include fatty alcohols and waxes. Within the terpenoid group you find a vast number of different terpenes built up by isoprene units. The most important terpenoids are pinenes, carenes and limonene, which are examples of monoterpenes. There are four subgroups of phenolics, i.e. simple phenolics, stilbenes, flavonoids, and lignans. The remaining extractives are divided into monosaccharides, alkenes, and proteins.

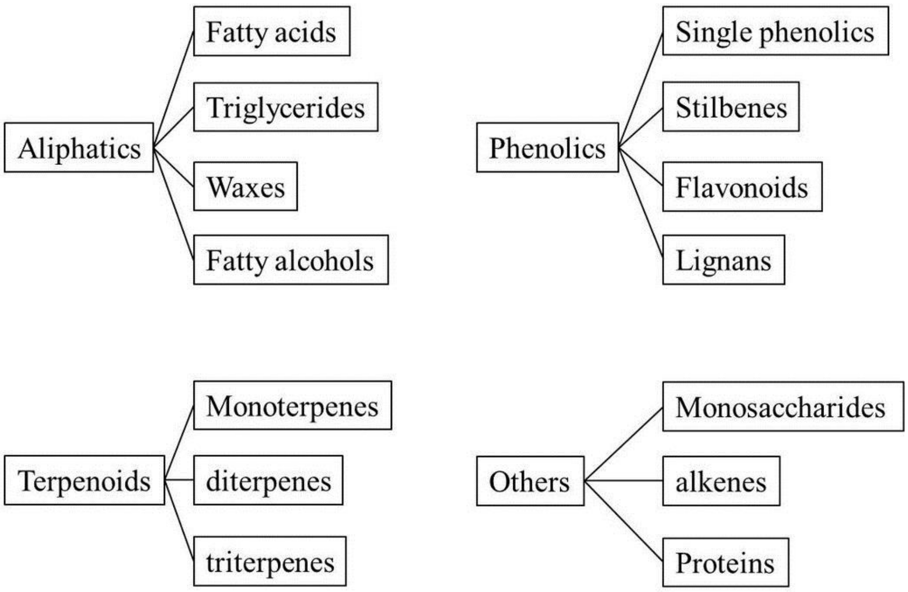


Figure 1. Extractives groups and subgroups

Out of the aliphatic compounds, the fatty acids and the triglycerides are the most useful. The dominating fatty acids are oleic and linoleic acid (Figure 2). Triglycerides are fatty acid esters of glycerol (example shown in Figure 2). Fatty acids are separated from the CTO at several places in Finland and Sweden and can be further converted to consumer products.

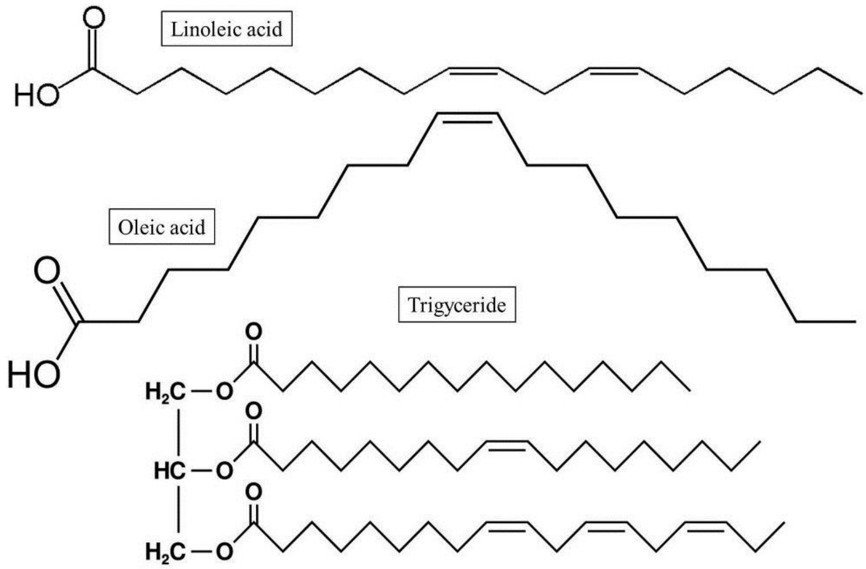


Figure 2. The chemical structures of linoleic and oleic acid and an example of a triglyceride.

The terpenoids in the diterpene subgroup are dominated by abietic and pimaric acid. These are also referred to as rosin acids. Rosin acid based products are for example sold by Forchem for use as raw materials in the production of printing ink binders and adhesive resins.

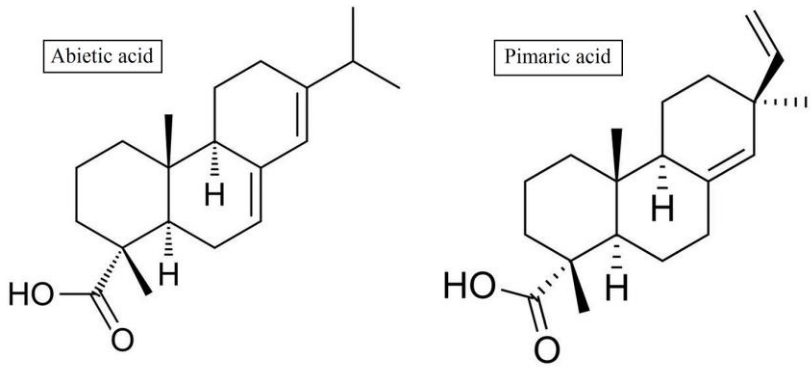


Figure 3. The chemical structures of abietic and pimaric acid, a.k.a. rosin acids.

Several compounds from the phenolic subgroups stilbenes, and flavonoids, have been suggested for use as pharmaceuticals and dietary supplements. The most intensely studied compounds are Pinosylvin (a stilbene) [2-5] and Pinocembrin (a flavonoid) [3-8] (Figure 4). Lignans also have biological effects and the extraction of lignans from pine and spruce has been investigated by many, for example B Holmbom et al. They have found that lignans is most abundant in softwood knots and they have developed a technique to separate knots from wood chips. Removing the knots would help in the pulp and paper process as well, since knots often leaves the process uncooked [9].

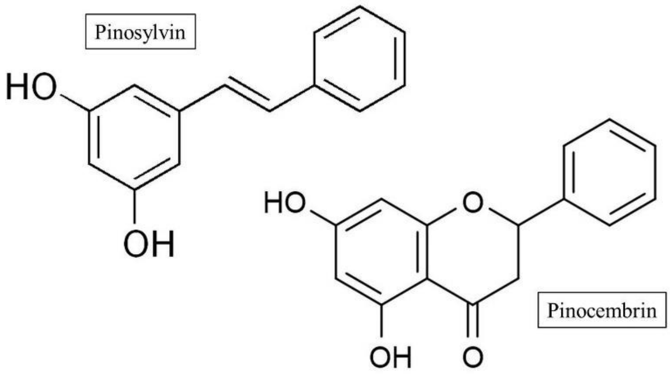


Figure 4. The chemical structure of Pinosylvin (a stilbene) and Pinocembrin (a flavonoid).

2.1 Extractives from other parts of the tree

The tree consists mostly of wood but a fairly large part of the biomass is also bark and needles or leaves. The composition of those differs from pure wood. Bark normally contains more extractives than wood and some of the components are limited to the bark. For example condensed tannins and suberin are present in bark but not in wood [10]. Tannins are water soluble polyphenols that have shown antimicrobial effects [11].

In birch bark betulin can be found, a terpenoid which has been studied for a long time and is used in many applications, in both pharmaceuticals and cosmetics. Betulin is the compound which gives birch bark its white colour and is also mainly found in white bark birches [12].

One way of utilizing the water soluble extractives from bark could be from the bark press water, from the debarking of the tree logs. The press water will differ in content depending on season and from mill to mill. One problem with the press water is that it often is highly diluted.

Needles and leaves contain the highest amount of extractives out of any part of the tree. The composition differs greatly depending on the species [13].

2.2 Distribution of extractives

Attempts to compare the distribution of extractives between heartwood (inner part of stem) and sapwood (outer part of stem, excluding bark) has shown inconclusive results [14] as well as large variations within populations [14]. Other attempts have shown no significant difference between heartwood and sapwood [15].

3. HANDLING OF EXTRACTIVES IN THE SCANDINAVIAN PULP AND PAPER INDUSTRY

Below the value chain for crude tall oil from wood to special products is described. A flow chart of it can be seen in Figure 5.

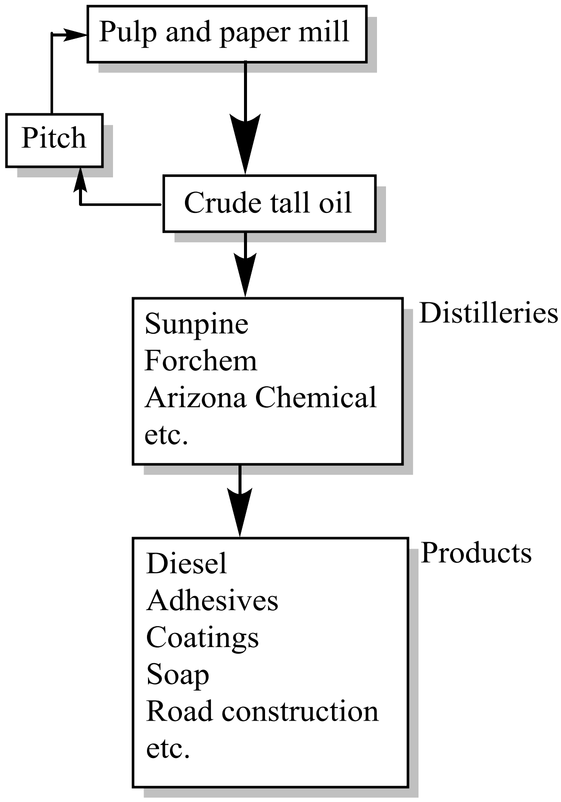


Figure 5: Schematic picture of the value chain for crude tall oil.

3.1 Flow of extractives through the pulp and paper value chain

The Scandinavian pulp and paper industry uses stem wood as its raw material. The stem wood is in turn derived from the forest, where trees are collected, processed, and transported. Pine and spruce are the most common tree species in Scandinavia, especially in the northern parts where you find about half of the number of pulp and paper mills. Therefore, pine and spruce are the most common tree species used to produce stem wood for the Scandinavian pulp and paper industry. Birch is the third most used tree species.

The first step towards production of stem wood for the pulp and paper mills is the felling of trees. Second, branches are removed, and the remaining logs are cut and separated. Branches can be chipped on site and shipped to heat and power plants where they are combusted in boilers. The top parts of the logs are shipped directly to the pulp and paper mills. The bottom parts are shipped to saw mills for the production of timber products. Stem wood waste material from the saw mills is either shipped to the pulp and paper mills for use in the pulping process or to a pelletizing plant for production of pellets. Stumps are currently not used.

At the pulp mills, the degradation of the wood is started. At first, the raw material is debarked and chipped to specific sizes. The wood fibers are then chemically or mechanically treated to produce a pulp. Examples of such treatments are, (i) cooking of the wood chips in a digesters with chemicals, as in the Kraft process (sulfate process), and (ii) milling of the wood in special refiners, as in the mechanical pulping process. The produced pulp is washed, to produce a pulp, which can be bleached to reach higher whiteness before entering the paper making process [16].

There are many different types of pulp mills, which use different processes to refine the wood into pulp. In Sweden, there are 20 pulp industries listed as members of Skogsindustrierna as of 2018. Their locations and names can be seen in Figure 6.

Ahlstrom-Munksjö AB
Ahlstrom-Munksjö Aspa Bruk AB
BillerudKorsnäs Aktiebolag (publ)
BillerudKorsnäs Rockhammar AB
Domsjö Fabriker AB
Holmen AB
Metsä Board Sverige AB
Nordic Paper Bäckhammar AB
Nordic Paper Seffle AB
Rottneros Bruk AB
SCA Graphic Sundsvall AB
SCA Munksund AB
SCA Obbola AB
Smurfit Kappa Kraftliner Piteå AB
Stora Enso Paper AB
Stora Enso Pulp AB
Stora Enso Skoghall AB
Södra Skogsägarna ek för
Waggeryd Cell AB
Vallviks Bruk AB

Figure 6: Swedish pulp mills listed as members of Skogsindustrierna. Grey symbols represent pulp mills and grey/ orange symbols represent pulp and paper mills. The ones only producing paper are not shown here [17, 18].

The recovery of extractives from the pulping process will be different depending on the process used, but consists of the same principles; to separate the extractives from the pulp to get as fine and strong paper as possible. In the Kraft process, the recovery of the extractives results in a crude tall oil (CTO) fraction.

In the Kraft process, the cooking chemicals, dissolved lignin, and extractives that are separated from the pulp are called black liquor. Since the process is alkaline, the resin and fatty acids will form sodium salts and correlate to unsaponifiable extractive compounds. These can be separated from the black liquor, for example by floating to the surface of the black liquor at different stages of the chemical recovery process. The fractions are called black liquor soap.

In the first step of regeneration of the black liquor, different types of washing systems are available. However, this is considered not to be the most efficient time of removing the soap even though skimming of the liquor surface is possible. A lot of the soap still remains in the black liquor phase after the washing. The weak black liquor is then collected in tanks from where the soap is lead from the top sides as foam to the foam tank. In the foam tank, the soap is further separated from remaining black liquor with foam breakers that densifies the foam. The black liquor concentrates on the bottom and is recycled back to the weak liquor tanks. The efficiency of the soap recovery can be improved by injecting water saturated with air to the bottom of the tanks, creating small bubbles which carry colloidal soap particles to the surface, use electricity to charge the particles, or adding surfactants to flocculate the particles.

The black liquor soap can be converted to crude tall oil (CTO) in many ways. One way is to mix it with sulfuric acid at elevated temperatures, around 100 ^{o}C. After the reaction is complete, the crude tall oil will form one phase along with other phases including one with precipitated calcium sulphate, a sodium sulphate solution and a precipitated lignin-tall oil layer. These can be separated by gravity or centrifugation [19].

In Sweden, the crude tall oil production in 2007 was around 280 000 tons [20]. The same year in Europe, the total amount of extractives, including crude tall oil and turpentine, produced in pulp mills was 1 500 000 tons [21].

In pulp mills using birch wood as raw material, the extractives contain more hydrophobic (neutral) compounds than for the softwoods. This makes the separation of extractives from the pulp difficult. In order to increase the efficiency in the extraction of neutral extractives, rosin acids and fatty acids from tall oil can be added to form micelles that solubilize the neutrals in the aqueous environment [22].

3.2 Operators/stakeholders

3.2.1 Pulp and paper mills

Crude tall oil comes from the Kraft process/sulfate process. The CTO can be used at the pulp mill as fuel, usually in the lime kiln, or be sold to a refinery. Mills in Sweden that are members of Skogsindustrierna and uses the Kraft process are listed below:

Billerud Gruvöns Bruk	SCA Packaging Munksund AB
BillerudKorsnäs Karlsborg AB	SCA Packaging Obbola AB
BillerudKorsnäs Skog och Industri AB, Frövi	SCA Östrands Massafabrik, Timrå
BillerudKorsnäs Skog och Industri AB, Gävle	Smurfit Kappa Kraftliner, Piteå
BillerudKorsnäs Sweden AB, Solna	Stora Enso Packaging, Skoghalls Bruk
Holmen Iggesunds Bruk, Iggesund	Stora Enso Pulp AB, Skutskärs Bruk
Metsä Board Sverige, Husum	Södra Cell Mönsterås
Mondi Dynäs AB, Väja	Södra Cell Mörrum
Munksjö Aspa Bruk AB	Södra Cell Värö
Munksjö Paper AB, Billingsfors Bruk	Vallviks Bruk AB
Nordic Paper Bäckhammar AB, Kristinehamn	

Source: [17]

3.2.2 Sunpine

Sunpine operates a CTO refinery in Piteå, Sweden which produces four product streams (i) turpentine, (ii) rosin acids, (iii) crude biodiesel (TOFA) and (iv) tall oil pitch. The turpentine is used by the perfume industry, while the rosin acid stream is used by Lawter in Kallo, in Belgium as a raw material to produce adhesives, such as glue and tape. The crude biodiesel is Sunpines most important product stream. It is shipped to Preems refinery in Gothenburg, Sweden where it is refined to biodiesel. The tall oil pitch is returned to the pulp and paper mills for heat and power production.

3.2.3 Arizona Chemical

Arizona chemical is a multinational corporation with its headquarters in the Netherlands. They operate a CTO refinery in Sandarne, Sweden with 110 employees where chemical fractionation is carried out to produce mainly rosin acid products. Now Arizona chemical is owned by Kraton, a company located all over the world. Their market includes adhesives, coatings, consumer and personal care products, sealants and lubricants, and medical, packaging, automotive, paving, roofing and footwear products [23].

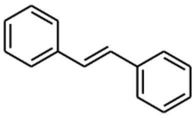
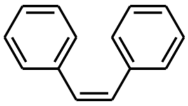
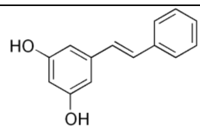
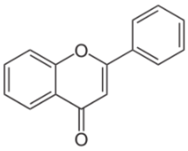
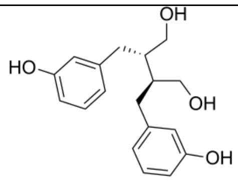
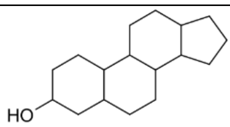
3.2.4 Forchem

Forchem is based in Finland and uses CTO as raw material. Fractioned distillation is carried out to produce three main product lines: TOFA (tall oil fatty acid), TOR (tall oil rosin) and DTO (distilled tall oil). They also offer a custom product which is a mixture of the above products in compositions in accordance with the client’s requests. The fractioned distillation process also produces a bio-oil stream called fortop600 which is a tall oil pitch. The products from Forchem are used in manufacturing of for example coatings, lubricants, soaps, paper size, ink resins and adhesives [24].

4. EXTRACTIVES COMPOUNDS WITH POTENTIAL TO BECOME NEW PRODUCTS

4.1 Compounds in extractives with new potential applications

Table 1. Compounds found in wood extractives with possible uses in the chemicals industry

Stilbenes (E left Z right)	**Pinosylvin (a bioactive stilbene)**
 	
Uses: Precursor to derivatives used as dyes, optical brighteners, phosphors, and scintillators. Gain medium in dye lasers.	Uses: Food supplement and pharmaceuticals development.
Found in: Scots pine	Found in: Scots pine
Ref: [25]	Ref: [25]
Flavonoids (image showing flavon backbone)	**Lignans (image showing enterodiol)**
	
Uses: Possible uses within pharmaceuticals development	Uses: Anti-inflammatory, health food
Found in: Scots pine, spruce	High amounts in softwood knots
Ref: [25, 26]	Ref: [27, 28]
Sterols (image showing sterol backbone)	
	
Uses: Dietary, pharmaceutical	
Found in spruce (mostly esterified)	
Ref: [29]	

Polyphenols can be divided into several classes, such as: lignans, flavonoids, stilbenes and phenolic acids. Some of these have antifungal, and antioxidant effects. Some of these compounds are so-called secondary metabolites.

Knot extracts have shown antioxidant properties. This has been quantified by inhibition of lipid peroxidation *in vitro*. Other lignans (secoisolariciresinol, pinoresinol, eudesmin, lariciresinol, and lariciresinol-4-methyl ether) has been separated from stem wood and investigated for antifungal activity [30] . Secoisolariciresinol has shown significant antifungal activity.

Extracting phenolic compounds from pine knots has been carried out by crushing the knots into a powder, and drying it at room temperature [3]. The dry powder was then mixed with an ethanol/water (85:15 v/v) solution and agitated while heated to 60 °C. The anti-mildew activity of the pine wood extract was investigated [3].

Flavonoids and stilbenes have been shown to have an impact on zoospore mobility and mildew development [3]. The best results were achieved with pinosylvin, pinosylvin methyl ether (both stilbenes) and pinocembrin (a flavonoid). Pine knot extract contained all these compounds. Therefore, the anti-mildew activity of pine knot extract could be attributed to the presence of the above noted stilbenes and the flavonoid [3].

Several extractives have been suggested to be bioactive. In the field of nutrition, bioactive compounds are distinguished from essential nutrients. While nutrients are essential to the sustainability of a body, the bioactive compounds are not essential since the body can function properly without them, or because nutrients fulfil the same function. Bioactive compounds can have an influence on health; however, since they are not essential, advice on daily intake is not regulated.

Vek et al. [31] suggests using analysis of extractives as an indicator for wood properties such as susceptibility to discolouration and stage of wood decay. Catechin for example, is regarded as a major precursor for the development of coloured compounds of beech wood. Therefore, the concentration of catechin in wood could be used as an indicator of future discoloration. To enable this type of analysis to be used in industry, a standardized methodology needs to be developed, including methods for collecting representative wood samples, sample preparation, extraction and quantification.

Fernándes-Costas et al. [32] presented a method for impregnating wood with an extractives based solution containing extractives separated from wood using ethanol and toluene mixed with laccase and phosphate buffer.

4.2 Extraction methods for the groups of extractives

Extractives can be separated from wood using solvents. The characteristics of the compounds in the extractives groups differ with regards to their affinity towards different solvents. In other words, compounds from different groups dissolve more readily in different solvents. This has been utilized in bench scale experimental work to separate extractives from wood and to simultaneously separate groups of extractives from each other.

All methods used to separate extractives from wood apply the same principle: during contact between wood and solvent the extractives compounds move from the wood to the solvent. The first step towards separating extractives from wood is drying and milling of the wood. Milling is carried out in order to increase contact between wood and solvent by increasing the surface area of the wood. Drying is carried out in order to remove moisture and volatiles.

The apparatus used to enable contact between wood and solvent differ but the most common apparatus is the Soxhlet setup. Another common apparatus is the acceleration solvent extraction (ASE) setup. Both of these methods involve adding wood and solvent to a container and heating it. In the Soxhlet setup, the solvent is allowed to evaporate and is lead to a cooling unit where it is allowed to condense out of the gas phase and return to the container. This cycle is then repeated. ASE applies an increased pressure to the container, resulting in the solvent remaining in liquid form. A less sophisticated approach is to add solvent and wood to a container, heating and stirring the mixture, and then separating the solvent and wood by filtration.

The most common solvents used in extraction of wood are hexane, ethanol and acetone. Hexane is used on its own while ethanol and acetone usually is mixed with water in 95:5 to 70:30 ratios (v/v). Several studies have separated extractives from wood in a Soxhlet apparatus using a series of solvents with the aim of separating the different extractives groups according to their polarity.

Despite the use of different solvents there are many individual extractives compounds in each group which display a wide variation in polarity. Therefore, the polarities of compounds from different groups overlap. As a result, a given solvent cannot exclusively separate out a specific group of extractives. In order to separate out a specific compound from a group, chromatographic methods have been applied.

Separating extractives from wood using solvents has only been used in bench scale basic research. These separation methods have not been investigated for scale up since that would most likely not be economically sound. A viable scale up method for extraction should be energy efficient and include a solvent recovery process step. Also, the solvent used cannot be too expensive and has to be as environmental friendly as possible.

5. SUMMARY

There are several compounds not used today with potential for new uses but they exist in such small quantities that it would be difficult to separate them out into a single value stream as part of a viable business case. In order to separate possibly valuable extractives compounds from the current pulp and paper value chain, this would have to be done from the CTO. Quantities are reduced in the current value chain due to losses during storage and transportation. There are alternative methods for separation of extractives from wood that have been used on laboratory scale. These are effective at separating out individual compounds and could replace current methods. However, these would be challenging to apply at large scale.

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