



Bark assortments for tall oil production

Barksortiment för produktion av tallolja



Photo: Peter Jons

Patrik Isacsson

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Rapport från Institutionen för Skogens Biomaterial och Teknologi

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Keywords: Tall Oil; Bark; Extractives; Lipophilic compounds; CTO; TOFA; TOR; Fatty acids; Resin acids; Rosin; Norway spruce; Scots pine; Picea abies; Pinus sylvestris

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Preface

This is a Master Thesis written at the Swedish University of Agricultural Sciences in Umeå during the academic year of 2015/2016. It shows a potential in an underestimated forest residue – bark – as a feedstock for biorefinery applications. As a forestry student, I found this as an exciting topic which has the potential to broaden the use of the forest resource. Hopefully, it will motivate further research in this field.

I am grateful to the competent and committed people who have showed their interest in this project. I would like to address a special thanks to Holmen and in particular Jörg Brücher for the recognition of this project idea and the financial support, which have been fundamental for the realisation of this project. Danke vielmals.

During the collection of the sample bark in October 2015, Anna Olsson at the district office of Holmen Skog in Delsbo helped me to find suitable forest stands for sampling. The sampling was made possible by Peter Jons, forest entrepreneur, who helped me with the felling and bucking of the sample trees. Thanks both of you.

At last but not least I would like to regard the supervisors of this thesis, Daniel Eriksson and Mehrdad Arshadi, who has guided me through this work and contributed with appreciated feedback and advises. I am glad that I had you as my supervisors. Thank you very much.

Umeå, April 2016

Patrik Isacsson

Abstract

Fatty and resin acids in bark residues from forest industries can be used to produce high-value green chemicals. Of the assortments investigated, the bark of spruce pulpwood held the highest amount of these compounds with an average yield of 0.9 kg per cubic meter of wood. The variations were found by analysing fresh bark and tree data from homogenous stands of Norway spruce (*Picea abies*) and Scots pine (*Pinus sylvestris*). The concentrations of fatty and resin acids in Norway spruce bark showed positive relationships with annual ring increment. The compounds showed negative relationships with both the tree diameter and the bark age as well. The best economical prerequisites for processing the bark were found at pulp mills which only use spruce. Some results support theories about polymerisation of fatty and resin acids due to aging. Since the bark in this study were carefully treated and kept fresh, further research for industrial relevance can preferably focus on the non-fresh bark residues of spruce pulpwood at mill sites.

Keywords: Bark, Tall oil, Extractives, Lipophilic compounds, CTO, TOFA, TOR, Fatty acids, Resin acids, Rosin, Norway spruce, Scots pine, *Picea abies*, *Pinus sylvestris*

Sammanfattning

Fett- och hartssyror i barkavfall från skogsindustrier kan användas för att producera värdefulla gröna kemikalier. Bland undersökta sortiment står bark från granmassaved ut med stora mängder av dessa ämnen, med ett medelutbyte på 0,9 kg per fastkubikmeter ved. Det upptäcktes genom att analysera färsk bark och träddata insamlad från homogena bestånd av gran (*Picea abies*) och tall (*Pinus sylvestris*). Halten av fett- och hartssyror visade positiva samband med årsringstillväxten och negativa samband med diameter och barkens ålder. Massabruk som endast hanterar granmassaved visade sig ha de bästa ekonomiska förutsättningarna för att förädla barken. En del resultat stödjer teorier om att fett- och hartssyror polymeriseras med åldern. Eftersom det här arbetet endast använt bark som hanterats varsamt och behållits färskt, bör fortsatte studier för industriell relevans studera ej färskt barkavfall vid industri.

Nyckelord: Bark, Tallolja, Extraktivännen, Lipofila ämnen, CTO, TOFA, TOR, Fettsyror, Hartssyror, Harts, Gran, Tall, *Picea abies*, *Pinus sylvestris*

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Introduction

Bark is an underutilised resource. Despite a potential to use bark extractives to produce green chemicals, it is commonly used as bioenergy at the mill or a nearby power plant (Kemppainen, et al., 2014). Bark from Scots pine (*Pinus sylvestris*) and Norway spruce (*Picea abies*) both contain relatively high amounts of fatty and resin acids (Valentín, et al., 2010) (Krogell, et al., 2012), which constitutes the main parts of crude tall oil (CTO) (Biermann, 1993).

CTO is today a by-product of softwood kraft pulping, used as a raw material for fuels and chemicals (Research and Markets, 2015). Fractionated distillation of CTO separates the fatty and resin acids, which are sold as tall oil fatty acids (TOFA) and tall oil rosin (TOR). TOFA and TOR are valuable chemicals used in many applications as production of ink and perfume.

Holmen, a forest industry enterprise, runs three production sites in Sweden. Iggesund and Braviken are two integrated mills and Hallsta is a pure paper mill (Holmen, 2016). Iggesund uses mostly timber and pulpwood of pine. The saw mill in Braviken is specialised in sawing spruce timber, but since the third quarter of 2015 it has started to saw pine timber as well. The paper mills Braviken and Hallsta produce thermo-mechanical pulp (TMP) and are therefore using spruce pulpwood only. Since Iggesund paper mill is the lone kraft pulp mill of Holmen, it is the only site with a current production of CTO.

Timber and pulpwood of Scots pine and Norway spruce are the most important forest assortments in Sweden (Skogsstyrelsen, 2014). If bark should be used as a feedstock for industrial production of tall oil, it can be questioned whether or not bark from all the assortments are rich enough in fatty and resin acids. The chemical profile differs between the two species (Valentín, et al., 2010) (Krogell, et al., 2012) (Norin & Winell, 1972), but the compositions show great variations and the reasons of this are not clear. It might be possible that the variations can be explained by additional parameters.

The concentration of other compounds than lipophilic compounds has been proved to differ along other variables than just species. For example, Jyske et al. (2014) reports a significant variation of stilbene glucosides in the bark of Norway spruce along the trunk and a difference between different age groups. Thereby, signs of variations do not only exist between pine and spruce, but also between different assortments. It is still though unknown what the variations in the lipophilic extractive contents are. To conclude if bark from one assortment is more suitable than another to produce tall oil, knowledge about the variations are needed.

Purpose

To explore variations in softwood bark lipophilic extractive contents and analyse the potential of softwood bark as a feedstock for production of CTO, TOFA and TOR.

Objectives

- To describe the variability of lipophilic extractives in the bark of Scots pine and Norway spruce according to measured tree parameters
- To investigate the techno-economical prerequisites of using bark as a feedstock for industrial production of tall oil at the production

Materials and Methods

Sampling

The bark was collected in October 2015 from four stands (Table 1) in the Holmen Skog district of Delsbo in mid-Sweden. Studies have shown a difference in the chemical profile of pine bark due to growth rate (Villari, et al., 2014), why site productivity was kept similar between the stands.

Table 1. Stand data from the stand database of Holmen Skog.

Parameter	Pine Thinning	Pine Final Felling	Spruce Thinning	Spruce Final Felling
Species composition	Pine (100%)	Pine (100%)	Spruce (100%)	Spruce (100%)
Site Productivity	5.9 m ³ /ha ^{-yr}	6.2 m ³ /ha ^{-yr}	6.2 m ³ /ha ^{-yr}	6.1 m ³ /ha ^{-yr}
Canopy structure	Single-layered			
Stand density	1840 st/ha	681 st/ha	1984 st/ha	867 st/ha
Standing volume	172 m ³ /ha	408 m ³ /ha	167 m ³ /ha	354 m ³ /ha
Lorey's Mean Height	115 dm	225 dm	113 dm	214 dm
Basal area	29 m ² /ha	33 m ² /ha	29 m ² /ha	35 m ² /ha
Stand age	44 yr	96 yr	41 yr	88 yr
Measured stand age	45 - 48 yr	90 - 93 yr	46 - 47 yr	111 - 117 yr

Three stand-representing trees (Figure 1) without visible defects were chosen as sample trees from each stand. Sampled trees were similar to their neighbouring trees with regard to height, canopy height, diameter in breast height and age. The canopy base was defined as the lowest green branch of the tree.

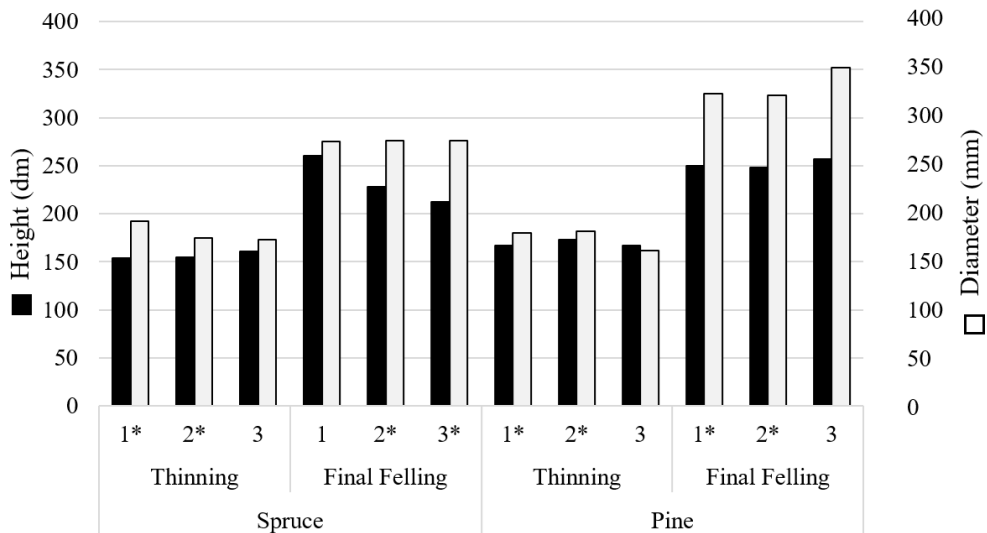


Figure 1. Height and diameter at 1.3m height of sample trees.
*Sampled for chemical analysis.

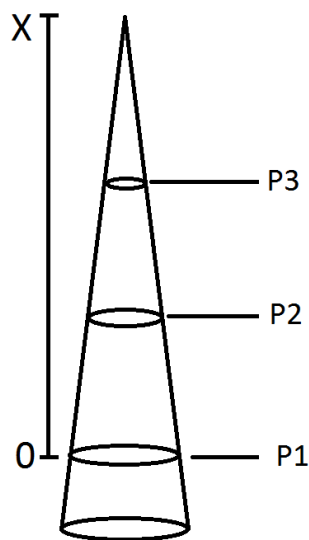


Figure 2. Sampling positions P1, P2 and P3. X is equal to the distance between 1.3 meters height and tree top.

Chosen trees were felled with chainsaw. The cuts were labelled with a marker and photographed. The trees were cut at three positions; P1, P2 and P3. P1 were cut in breast height, P2 at the height of $P1 + \frac{1}{3} X$ and P3 at the height of $P1 + \frac{2}{3} X$ (Figure 2).

For each of the sample positions the same procedure was repeated. Bark of the Scots pine were visually categorised as either smooth or rough bark. The diameter outside bark (diameter o.b.) was measured with a calliper (1 mm precision) and thereafter sawed off with the chainsaw to a 1-2 dm thick stem section. The cut was labelled with a marker and photographed together with a small calliper (1 mm precision).

The stem section was debarked with a knife. Three pieces of bark à 10 gram were removed for density analysis and put into labelled plastic bags. The remaining bark was put in other labelled plastic bags which were sealed with tape. Fatty and resin acids may be degraded by autoxidation during storage (Nielsen, et al., 2009), why the samples were stored in cool-box with ice packs.

After a day of sampling, bark samples for the chemical analysis were put in a freezer (-18°C). The smaller samples were dried in oven (105°C) over night for density measurements. The photographs were used in the image analysis software Digimizer version 4.6.1 (MedCalc Software, 2015) for counting the number of annual rings, the thickness of inner and outer bark and the average annual ring width of the last 10 years.

Classification of assortments

According to a local pricelist, the demarcation between timber and pulpwood was 140 mm diameter under bark (diameter u.b.) (Holmen Skog, 2015). The double bark thickness was subtracted from the diameter o.b. for each sample position to gain the diameter u.b. and thereby classified as pulpwood or timber. The assortments were divided in pine and spruce.

Bark analysis

Basic density

The green volume and oven-dry weight was measured in a laboratory of the Iggesund paper mill according to a modified version of a standard (SCAN, 1995). The bark samples were dried in oven at 105°C the same day as collected and weighted the following morning. The samples were stored dry in separate labelled, sealed plastic bags. The samples were later soaked in water for 48 hours to restore their green volumes. A 2 litres plastic can was put on a scale (precision 0.01 g) and filled with water. A fixed grip was soaked down into the water until the surface tension was in line with a mark on the grip. The weight was noted. A bark sample was rigged in the grip and the new weight was noted. The procedure was repeated for each sample. The basic density was calculated as shown in Equation 1.

$$X = \frac{M}{\Delta V * \rho} \quad \text{Eq.1}$$

where

- X = basic density
- ΔV = change in weight between immersion of the grip with and without bark sample
- ρ = density of water in room temperature
- M = oven-dry weight of bark

Content of lipophilic extractives

Bark from two sample trees from each stand (Figure 1) were chosen for analysis. The remaining bark was stored in freezer in event for the need of extra analyses. A laboratory in Örnsköldsvik¹ measured and identified the content of lipophilic extractives in the bark samples according to a modified standard method (SCAN 2003). The samples were dried in 40^oC followed by a Soxhlet extraction with cyclohexane and acetone (9:1) as solvent. The solvent was evaporated after extraction and the extract was dried in 105^oC. The extracts were analysed with gas chromatography with a short column according to a technique developed at Åbo Academy for the identification of different chemical groups rather than single molecules (Örså & Holmbom, 1994). The chemical analysis identified the presence of five groups of lipophilic extractives; fatty acids, resin acids, triglycerides, sterols and steryl esters.

Calculation of yield and statistical analyses

The basic density of every sample point was combined with its corresponding diameter and bark thickness to calculate the mass in relation to wood volume (Equation 2). The yield of extractives per volume wood was calculated through multiplication of the extractive contents. The results from the yield calculations, sampling measurements, chemical analysis and basic density measurements were analysed with regression and variance analysis in MiniTab 17 (Minitab Inc, 2016) and SIMCA 13.0 (Umetrics, 2016). A significance level of $p \leq 0.05$ was used in all tests.

$$\frac{\text{Bark mass}}{\text{Wood volume}} = \text{Basic density} \times \frac{\left(\left(\frac{\text{Diameter o.b.}}{2}\right)^2 * \pi\right) - \left(\left(\frac{\text{Diameter o.b.} - 2 * \text{Bark thickness}}{2}\right)^2 * \pi\right)}{\left(\frac{\text{Diameter o.b.} - 2 * \text{Bark thickness}}{2}\right)^2 * \pi} \quad \text{Eq.2}$$

Since the glycerol molecule in triglycerides is small in comparison with fatty acids of the triglyceride (Liébecq, 1992), free fatty acids and triglyceride bounded were categorised as the same group in the statistical analysis. The sum of fatty acids, triglycerides and resin acids was named “tall oil” in the statistical analysis. The difference between the total extract content and the content of identified extractives was called “unidentified extracts”. The ratio between the sum of the identified content and the total extracted content was called “ratio of explanation”.

¹ MoRe Research AB, Hörneborgsvägen 10, SE89250 Domsjö. +46660-751 00 <http://www.more.se/en/>

Techno-economic analysis

Suitable processing methods for extraction and refining of the bark lipophilic extractives and their different costs were reviewed through literature studies in the reference data bases Web of Science (Thomson Reuters, 2016) and Google Scholar (Google, 2016). Since processing of softwood bark lipophilic extractives are not at common topic for research, studies on similar matter as softwood sawdust were reviewed as well.

Values of the critical cost, i.e. the processing cost which gives zero net revenue, were calculated for the production units and sites in the aspect of SEK/tonne of bark. Current market prices of CTO, TOFA and TOR were collected from Independent Chemical Information Service (ICIS) (ICIS, 2016). The market prices were combined with data of the annual treatment of softwood bark at the industries of Holmen together with the average bark extractive contents of each assortment. The calculations were simplified by assuming the industries to be absolute in their choices of assortments; Iggesund production units were assumed to only use pine assortments while the rest of the industries were assumed to only use spruce.

Results

Physical data from the sampling

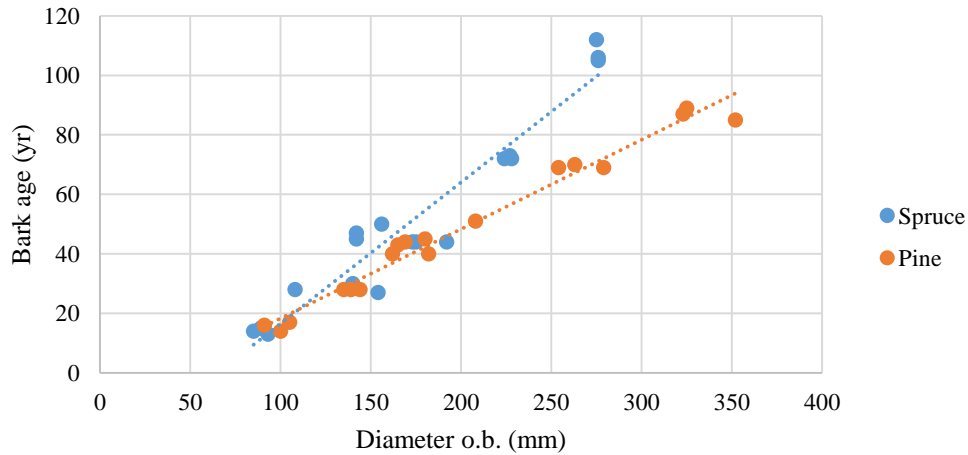


Figure 3. The correlation between bark age and the diameter over bark at different sampling positions.

The number of annual rings of each sample point, i.e. the age of the bark, and the diameter were closely related for both spruce ($R^2 = 0.93$) and pine ($R^2 = 0.98$) (Figure 3). The age of spruce bark showed a negative relationship with the ratio of inner bark thickness to total bark thickness as well ($R^2 = 0.79$). As seen in Figure 4, the annual ring increment in the spruce samples shows negative exponential relationship with the bark age ($R^2 = 0.79$), implying higher growth in younger samples. This relationship was not applicable for pine.

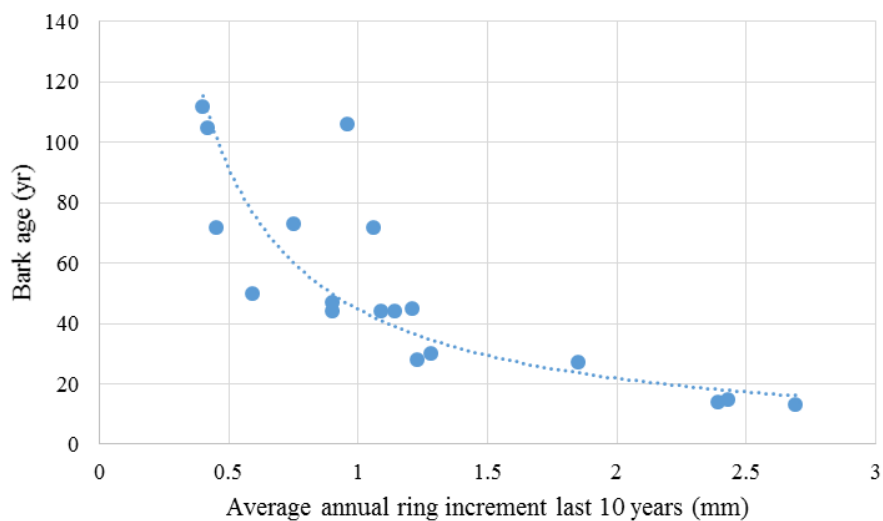


Figure 4. The relationship between bark age and the increments in spruce samples.

Thickness of spruce outer bark showed positive relationships with both the bark age ($R^2 = 0.82$) and the diameter o.b. ($R^2 = 0.69$). The total bark thickness of spruce had a positive correlation with both the diameter ($R^2 = 0.85$) and the bark age ($R^2 = 0.79$). It did also show a negative relationship with the average annual ring increment of the last 10 years ($R^2 = 0.79$).

The average spruce inner bark was thicker than the average of pine bark (3.0 mm vs. 1.3 mm) and the standard deviations of spruce and pine were 0.5 and 0.4 mm. Despite the variations within the species, no relationships with the other parameters than the species could be found. Rough bark on the pine sample trees was found only on sampling position lowest sampling point at 1.3 m height. Rough outer bark was on average 6.4mm thicker than smooth outer bark.

The diameters of the sample points were overall smaller and the bark younger in the thinning stands. Samples within the green crown had a smaller diameter than the samples outside green crown. The categories green crown and non-green crown overlapped to a large extent with classes pulpwood and timber; 29 out of 36 sample points showed the relationship pulpwood = green crown or timber = no green crown.

Basic density

There were no significant differences in the basic density between the pine assortments, nor between the rough and the smooth bark. Spruce bark differed; spruce timber bark had higher basic density than spruce pulpwood bark. Spruce bark had also overall higher basic density than pine bark (Figure 5). No other significant differences or relationships were found.

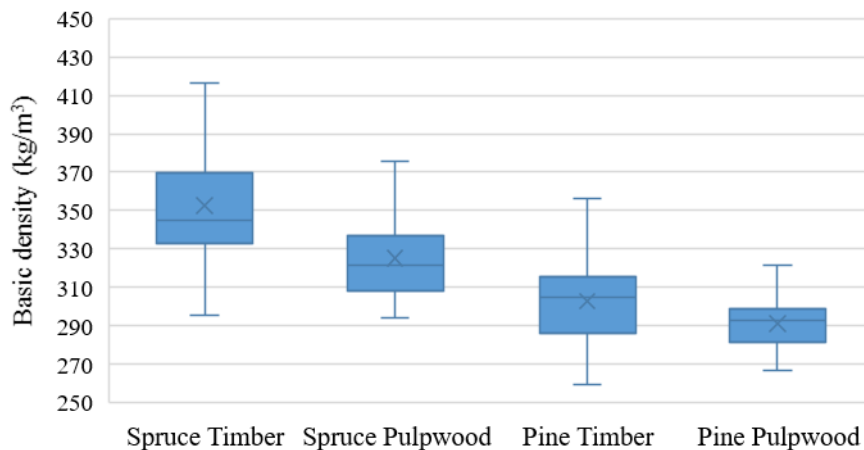


Figure 5. Bark basic density of different assortments. The cross signifies the arithmetic mean of each assortment. The box and the whiskers show the distribution of data into quartiles.

Chemical profile

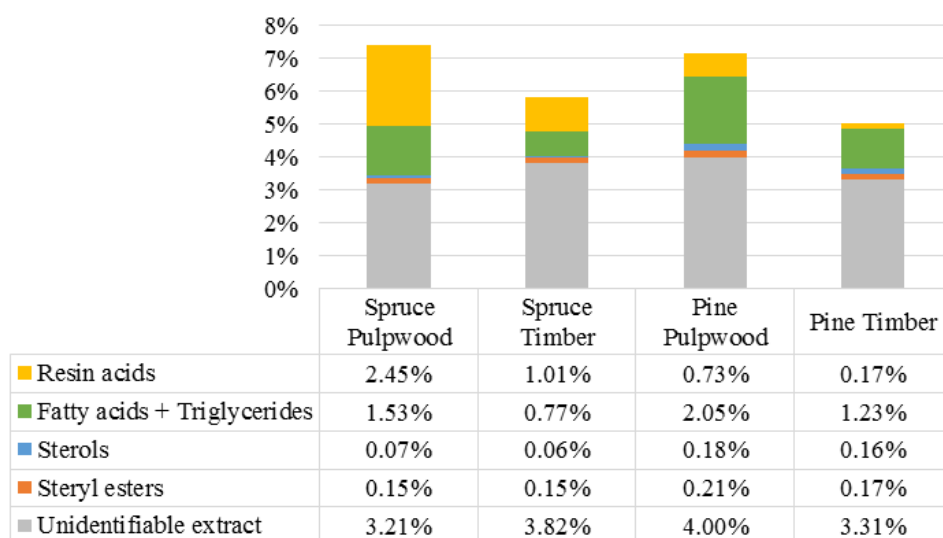


Figure 6. The average content of identified and unidentified lipophilic extractives in bark.

Bark of spruce pulpwood seemed to have the highest content of lipophilic extractives (Figure 6) but was only significantly differing from the bark of pine timber (Table 2). Concentrations of sterols as well as steryl esters were low in comparison to other extractives. Bark of spruce pulpwood had higher levels of tall oil and resin acids than other assortments. Pine bark contained more sterols than spruce bark. The levels of steryl esters did not differ between the assortments.

Table 2. Results of ANOVA analysis with Tukey grouping. Variables which do not share letters were significantly different from each other ($p \leq 0.05$). Ratio of explanation is ratio of identifiable to total extracts.

	Spruce Pulpwood	Spruce Timber	Pine Pulpwood	Pine Timber
Total extract	A	A, B	A, B	B
Sterols	B	B	A	A
Steryl esters	No significant difference			
Free fatty acids	A	B	B	B
Triglycerides	A, B	B	A	A, B
Fatty acids	No significant difference			
Resin acids	A	B	B, C	C
Unidentifiable extracts	No significant difference			
Tall oil	A	A, B	B	B
Ratio of Explanation	A	B	A, B	B

The bark within a green crown had higher content of total extracts as well as resin acids and tall oil. The ratios of explanation were higher within the green crown as well. Spruce bark of the thinning stand contained significantly more resin acids than the other stands.

In the aspect of tall oil content, the bark of young spruces differed from the mature stands but not from the bark of young pines. Except for steryl esters and sterols, the means of the different extractive contents were smaller in the category of young spruces than the assortment spruce pulpwood, vice versa for mature spruce and spruce timber. The same differences could not be observed for the corresponding pine stands and assortments.

A number of correlations were found between the lipophilic extractive contents and the measured tree parameters (Table 3 and Table 4). Some parameters were very well fitted to some of the extractive distributions ($R^2 \geq 0.75$). Extractives of spruce bark showed higher R squared values in regression analysis with tree parameters than the extractives of pine bark did.

Table 3. Resulting R square of linear regression analysis of Norway spruce bark extractive and measured tree parameter, no outliers removed. *Significant ($p \leq 0.05$). (+) indicates positive relationship and (-) negative.

	Diameter over bark	Bark age	Inner bark	Outer bark	Total bark	Inner bark ratio	Height	Increment
Sterols	0.02 (+)	0.16 (+)	0.29 (-)	0.18 (+)	0.02 (+)	0.19 (-)	0.00 (+)	0.01 (+)
Steryl esters	0.18 (-)	0.33 (-)	0.19 (+)	0.29 (-)	0.10 (-)	0.26 (+)	0.04 (+)	0.01 (+)
Resin acids	0.60* (-)	0.51* (-)	0.00 (+)	0.55* (-)	0.61* (-)	0.55* (+)	0.02 (+)	0.70 (+)
Free fatty acids	0.61* (-)	0.57* (-)	0.00 (+)	0.63* (-)	0.64* (-)	0.63* (+)	0.02 (+)	0.78 (+)
Triglycerides	0.70* (-)	0.87* (-)	0.06 (+)	0.85* (-)	0.68* (-)	0.81* (+)	0.03 (+)	0.41 (+)
Fatty acids	0.77* (-)	0.81* (-)	0.02 (+)	0.85* (-)	0.78* (-)	0.84* (+)	0.03 (+)	0.73* (+)
Tall oil	0.69* (-)	0.64* (-)	0.00 (+)	0.68* (-)	0.69* (-)	0.67* (+)	0.02 (+)	0.74* (+)
Total	0.26 (-)	0.38 (-)	0.15 (+)	0.59* (-)	0.34* (-)	0.62* (+)	0.04 (-)	0.33 (+)

Relationships between the diameter and the content of tall oil as well as resin acids were observed, following a reversed exponential relationship (Figure 7). After removing a sample regarded as an outlier, clear relationships were visible between the diameter and the content of tall oil ($R^2 = 0.92$) as well as resin acids ($R^2 = 0.88$).

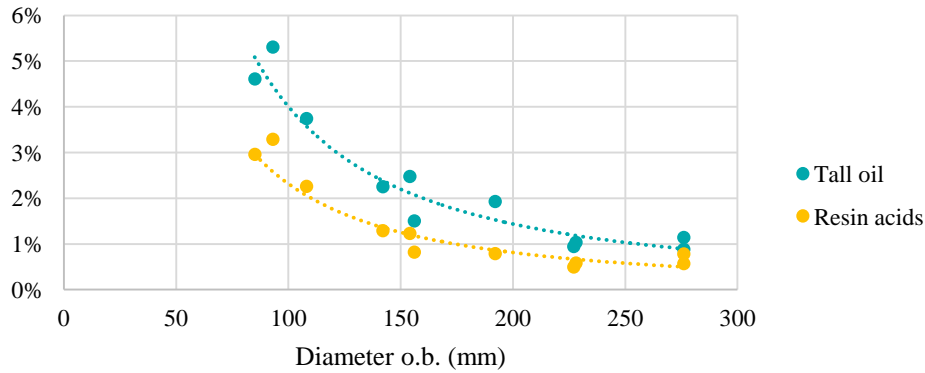


Figure 7. The relationship between the diameter and the concentration of bark extractives, one outlier removed.

Fatty acids overall and triglycerides in particular had a distinct linear relationship with the bark age of spruce (Table 3). When excluding one sample considered as an outlier, the R squared value reach as high as 0.97 (Figure 8). The youngest spruce bark sample had a content of about 0.8% of triglycerides, while the oldest had 0.2%.

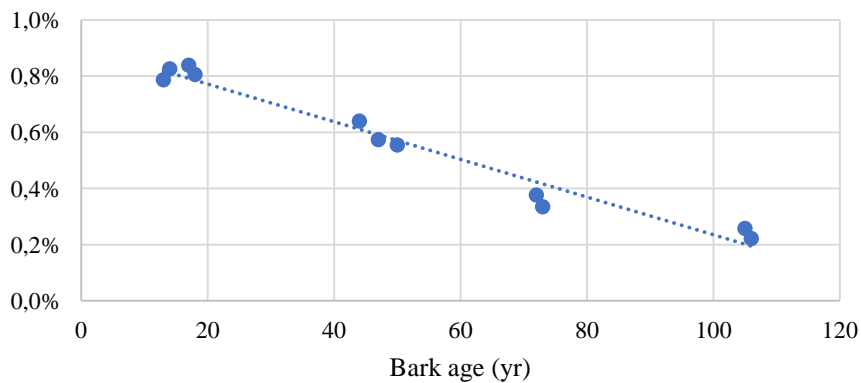


Figure 8. The relationship between the bark age and the contents of triglycerides. One outlier was removed.

The average annual ring increment over the last 10 years had significant positive relationships with some extractives of spruce bark (Table 3). After removing one sample considered as an outlier, the regression analyses showed an even clearer fit (Figure 9). Wider annual rings implied higher concentrations of tall oil ($R^2 = 0.85$), resin acids ($R^2 = 0.82$) and fatty acids ($R^2 = 0.82$). The relationship was not present for the sterols and steryl esters, nor for the pine bark.

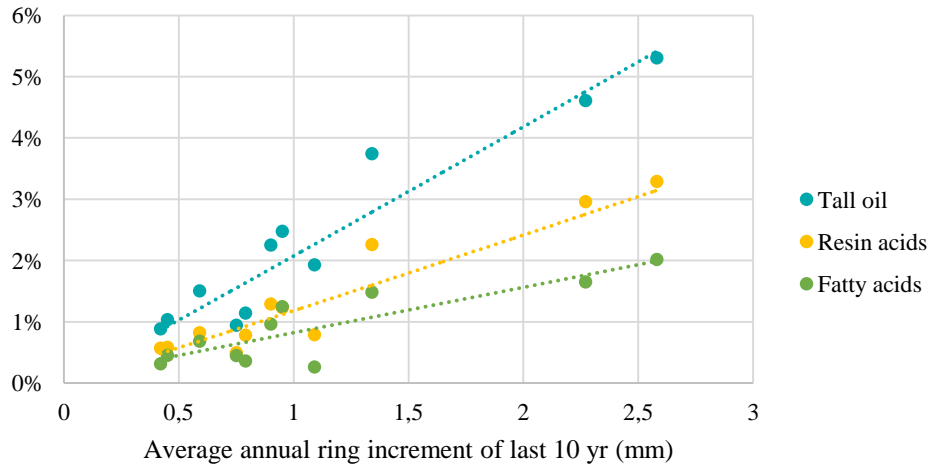


Figure 9. The relationship of different extractive contents and the wood increment.

The extractive contents showed relationships with the bark parameters too, except for inner bark thickness. This is the case for both spruce and pine (Table 3 and Table 4). The contents showed a significant negative relationship with both total bark thickness and outer bark thickness. The content of spruce bark fatty acids as well as triglycerides had exceptional high R square values (Table 3).

Table 4. Resulting R squares of linear regression analyses of Scots pine bark extractives and measured tree parameters, no outliers removed. *Significant ($p \leq 0.05$). (+) indicates positive relationship and (-) negative.

	Diameter over bark	Bark age	Inner bark	Outer bark	Total bark	Inner bark ratio	Height	Increment
Sterols	0.18 (-)	0.16 (-)	0.08 (-)	0.54* (-)	0.54* (-)	0.70* (+)	0.35 (+)	0.03 (+)
Steryl esters	0.17 (-)	0.16 (-)	0.04 (-)	0.46* (-)	0.46* (-)	0.46* (+)	0.32 (+)	0.11 (+)
Resin acids	0.46* (-)	0.49* (-)	0.01 (-)	0.09 (-)	0.09 (-)	0.11 (+)	0.00 (+)	0.11 (+)
Free fatty acids	0.04 (-)	0.03 (-)	0.59* (+)	0.00 (-)	0.00 (-)	0.00 (+)	0.09 (-)	0.21 (-)
Triglycerides	0.40 (-)	0.36 (-)	0.10 (-)	0.59* (-)	0.60* (-)	0.70* (+)	0.46* (+)	0.12 (+)
Fatty acids	0.40* (-)	0.36 (-)	0.09 (-)	0.59* (-)	0.60* (-)	0.70* (+)	0.46* (+)	0.12 (+)
Tall oil	0.54* (-)	0.51* (-)	0.08 (-)	0.58* (-)	0.58* (-)	0.69* (+)	0.38 (+)	0.15 (+)
Total	0.58* (-)	0.53* (-)	0.02 (-)	0.47* (-)	0.46* (-)	0.58* (+)	0.33 (+)	0.14 (+)

For the pine bark extractives, the ratio of inner bark to outer bark (inner bark ratio) were a measured tree parameter with high R squared values in the regression analyses (Table 4). The coefficients were all positive, indicating higher concentrations of lipophilic extractives in the inner bark than in the outer bark. This is also indicated by the negative slopes of the outer bark relationship with extractives, even though the regression lines are not as well fitted (Table 4).

The concentrations of unidentifiable extracts were more or less constant through all samples, with an average of 3.54% and a standard deviation of 0.48%. One sample with a concentration of 8.8% unidentifiable extracts was excluded. No parameter could explain the distribution. Samples with old bark age showed a tendency to have low explanation ratio; $R^2 = 0.72$ for spruce and $R^2 = 0.57$ for pine (Figure 10).

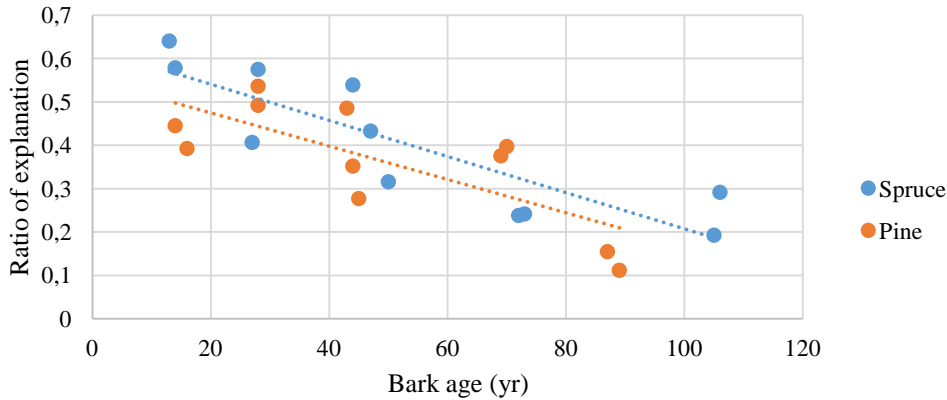


Figure 10. The relationship between bark age and the ratio of explanation, i.e. the ratio of identifiable extracts to total extracts.

Yield

The ratio of dry bark mass and the solid wood volume differed between the assortments. ANOVA analysis revealed significant differences between bark of spruce pulpwood and the pine assortments (Figure 11). Bark of spruce timber did not differ significantly from any of the assortments.

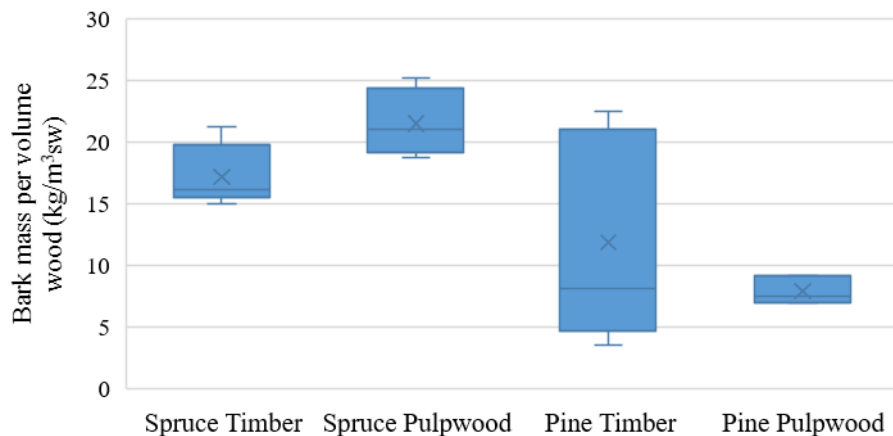


Figure 11. Bark mass to wood ratio as a box diagram. The crosses signify the arithmetic means. The box and the whiskers show the distribution of data into quartiles.

The spruce pulpwood assortment had the highest ratio of tall oil per volume of solid wood under bark and differed clearly from all the other assortments (Figure 12), with an average yield of 0.9kg of bark tall oil per cubic meter of wood compared to a corresponding average of 0.2 for the other assortments. The variation within the spruce pulpwood assortment was larger than in the other assortments.

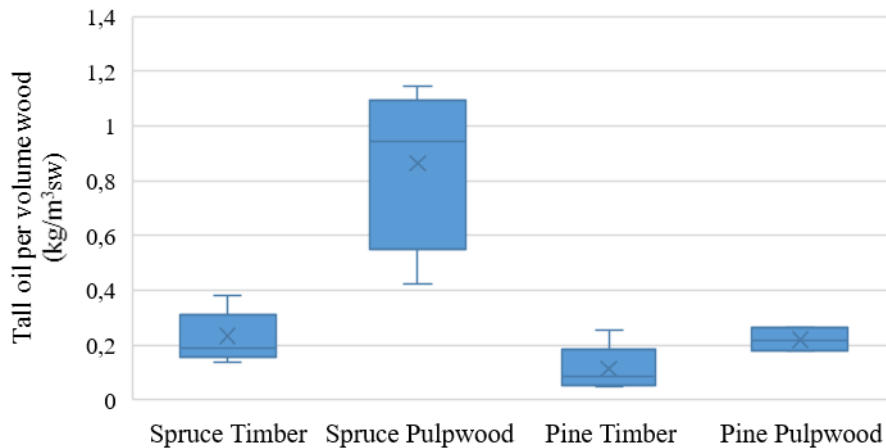


Figure 12. Tall oil to wood ratio as a box diagram. The cross signify the arithmetic mean. The box and the whiskers show the distribution of data into quartiles.

Techno-economic analysis

Suitable processing methods

Tall oil is conventionally produced through kraft pulping, which also could be used as an extraction method for bark. The product will be CTO, which needs extra processing to separate TOFA and TOR (Biermann, 1993). Process and capital costs for a full scale production unit were high and exceeded the potential income of CTO as well as TOFA and TOR.

The process can also be integrated in existing kraft pulping process though, and thereby need a separate digester for the bark plus costs of logistics only. The capital cost for a digester of the size needed exceeded the potential income from produced tall oil though (Korpunen, et al., 2012). Stoffel et al (2014) described a method to extract fatty and resin acids from sawdust with low-alkaline and low-acid solvents. The extraction equipment was suggested to be cheaper than normal kraft pulping units, but the costs were not specified.

Supercritical carbon dioxide extraction (SFE) has been reviewed as an efficient method for extracting fatty and resin acids from sawdust (Arshadi, et al., 2012). Attard et al (2016) presents a cost of 642 €/tonne of sawdust using SFE with a

yield of 80% of the extractives. The size of the production unit was categorised as pilot or semi-pilot scale with a capacity of 0.45 tonnes of sawdust per hour. The costs were mainly associated with capital and energy costs.

Solvent extraction of the same principles used for the chemical analysis is another relevant method, which was currently used for producing biodiesel of biomaterials rich in lipophilic matter (Kumar & Sharma, 2008). However, a study on essential oil processing revealed SFE to be 13-23% cheaper than solvent extraction (Moncada et al., 2016). This implies high costs for processing bark with the solvent extraction method.

Critical costs for processing

CTO was reported to have a market value of 670 USD/tonne, 1 600 USD/tonne for TOFA and 1 800 USD/tonne for TOR (ICIS, 2016). It was equal to a CTO price of 5 500SEK/tonne, 13 000 SEK/tonne for TOFA and 15 000 SEK/tonne for TOR with a currency index of 1 USD = 8.2 SEK.

Table 5. Production Sites of Holmen and the economical prerequisites for production of crude tall oil (CTO), tall oil fatty acids (TOFA) and tall oil rosin (TOR) out of bark. The production of TOFA and TOR implicate further processing of the CTO. *Critical cost of extracting TOFA and TOR in the same process.

Site	Unit	Dry bark (tonnes/yr) ²	Production Volume (tonnes/yr) ²			Critical cost (SEK/tonne bark)			
			CTO	TOFA	TOR	CTO	TOFA	TOR	TOFA & TOR*
Iggesund	Paper mill	30 188	839	620	219	153	267	109	376
	Saw mill	14 040	197	179	18	77	166	19	185
	Overall	44 228	1036	800	236	129	235	80	315
Braviken	Paper mill	34 190	1361	526	835	219	200	366	566
	Saw mill	20 708	362	163	199	96	102	144	246
	Overall	54 898	1723	689	1034	173	163	282	445
Hallsta	Overall	54 537	2171	839	1332	219	200	366	566

Hallsta paper mill, which only use spruce in its TMP process, holds the highest potential both in terms of production volume and critical cost of processing the bark to CTO as well as TOR, while Iggesund holds the lowest (Table 5). This is also true if TOFA and TOR are produced together. However, if TOFA is about to be produced separately, Iggesund tolerates the highest critical cost among the production sites.

² Softwood bark, compilation from 2015. Personal communication with Jörg Brücher, Holmen, 2016-04-08

Discussion

The purpose of this work was to explore variations in softwood bark lipophilic extractive contents and analyse the potential of it as a feedstock for the production of CTO, TOFA and TOR. Fresh bark samples were investigated, analysed and compared to the characteristics of the sample trees.

The stand data base reported similar site productivity for the stands, which did not seem to be the case according to Figure 3. The mature pine had greater increment compared to the mature spruce. Since older trees have slower growth, the increment discrepancies could be explained to the difference in stand age. The difference in age and increment made comparisons between the two mature stands imperfect though.

The choice of the sampling positions gave an objective sampling procedure. However, it favoured timber assortments over pulpwood. The smaller number of pulpwood observations made the results less reliable. Only two of the sample trees from each stand for the chemical analyses reduced the number of observations even further. The deviations were small though, and the pulpwood of spruce showed high R squared values in regression analyses with several tree parameters.

The basic densities were measured with a standardised method for wood chips (SCAN 1995). The masses of the bark samples were much smaller than the suggested mass of wood chips suggested for this method, why the precision of this method could be questioned. A scale with higher precision were used though, and combined with the rig arrangement adjusted for the relatively small samples the precision should be satisfying.

The height of the sample points did not show any relationships with the bark thickness, but the diameters do. Hannrup (2004) reports a distinct non-linear correlation between the tree height and the bark thickness, a relationship which were not observable in this work. However, Hannrup (2004) uses the diameter at 1.3 m height as a constant for the calculation of the rest of the bark thickness along the trunks. A wider diameter gives thicker bark, which is in line with findings in this work.

The bark samples were dried in 40°C and the extracts were evaporated at 105°C. Climate chamber studies by Nielsen et al. (2009) shows higher rates of autoxidation of fatty and resin acids with elevated temperature. The reported values might therefore be an underestimation. Other extraction methods could have been used instead. The samples could have been freeze dried, for example, or been extracted with a gentler extraction method as supercritical CO₂ extraction.

The ratios of explanation were overall low, a result important to have in mind when concluding the results. Krogell et al. (2012) reports 2% of the bark dry matter to consist of unidentifiable extracts, which when analysed seemed to have similar molecule size as triglycerides and steryl esters. This implies a bigger size of the unidentifiable molecules. Lipophilic extractives in aspen wood and bark polymerise with aging, resulting in high molecular fatty and resin acids (Sithole, et al., 2013). If the unidentifiable extracts to a large extent consists of fatty and resin acids, the expected yield of tall oil might be even higher.

Pulpwood bark showed higher concentrations of different lipophilic extractives (Table 2), but the assortment coincidence with the green canopy categorisation and makes it difficult to address the relationship dependency. Since the extractive contents fitted well to regression lines with the annual ring increment, a connection between the extractive content and the vitality of the crown could be suggested. On the other hand, the relationships between tall oil content and diameter o.b. showed in Figure 7 argue for role of the diameter or age.

If the concentrations of extractives had relationships with diameter rather than the bark age, the concentrations would theoretically be higher in slow-grown trees rather than fast-grown trees. The relationships seen in Figure 9 indicate that this is not the case. Rather, the content is higher in bark from sample points with higher increment of the annual rings. This is not the same as fast-grown trees have higher content of lipophilic extractives, but it indicates that growth matters.

This is in line with the results of Villiari et al (2014), who reports an increase of pine bark terpenoids with greater annual ring increment. This is surprising, because resin acids as well as terpenoids are associated with the chemical defence of plants and a lower growth rate are supposed to induce higher concentrations of the chemical defence (Zavala et al., 2008).

A source of error can be found in the increment measurements. The annual ring width was measured in photos of the discs. The ring width of slow-growing sample points was narrow which made it difficult to visually determine the presence of an annual ring. In some cases, only parts of the discs were photographed while bark all around the stem section were analysed. A number of measurements were made for each photo, but since they only covered a part of the disc it might be misleading. Trees have uneven increments in different horizontal directions.

Several R squared values are unusually strong in comparison with other studies aimed for associate forest parameters with chemical profiles of trees. In the stem wood, extractives are highly associated to the heartwood (Arshadi et al., 2013) and

predictive models focus on modelling heartwood formation. Wilhelmsson et al. (2002) created combined linear and non-linear models from a wide set of variables which explain the heartwood formation to 94%. In this work, single measured tree parameters could make predictions of the bark extractive contents at the same level of explanation.

One explanation could be the prevention of errors by collecting the bark samples carefully, keeping the samples cold and make accurate measurements. In addition, forest parameters such as latitude, site productivity and canopy structure, known to affect wood properties, were similar between the sample stands. This might explain the results too. Geographical variations, soil fertility as well as genetic factors can be assumed to have no major influence on the results. A greater variation and number of samples should be needed if this work will be verified.

One sample had an unusually high concentration of unidentifiable extractives though; 8.8% compared to the average of 3.5%. This could be explained by the presence of a callus resin, which has a more complex chemical composition with lignified lipophilic acids (Holmbom, 2016).

Triglycerides of spruce bark have an extraordinary strong correlation with bark age (Table 3, Figure 8). This may depend on the biology of the tree and the time of year when the bark was sampled. Increment is higher in younger parts of the tree. During autumn, trees has showed to allocate energy reserves for the spring in the tree were the growth needs to be high (Hou, 1985) and triglycerides are used by the trees as energy reserves. The bark of this study was collected in October. If the bark had been collected in another time of the year, the content of triglycerides or other fatty acids might have been lower due to a focus on producing glucosides or other easy-to-consume organic compounds.

The freshness of the bark is one important aspect to bear in mind when applying an industrial perspective on the result, since extractives transform or decompose during storage (Nielsen, et al., 2009) (Sithole, et al., 2013). The bark of this study were fresh when analysed, in reality the bark would not be as fresh when it is debarked at the industry. Logs arriving to the industry might have been stored along a road or a terminal for several weeks in addition to the storage in the log yard.

This refers not as much to the spruce pulpwood as it does to the rest of the assortments, due to the use of spruce pulpwood in TMP processes which demands fresh spruce logs to avoid discoloration of the pulp (Biermann, 1993). The freshness of the logs arriving at the TMP mills at Braviken and Hallsta gives an extra advantage of the spruce pulpwood assortment. If the

aim is to process the bark residues at the industries, it might be of interest to analyse the incoming bark at an industry to overcome the uncertainties of autoxidation and polymerisation.

The process methods reviewed in this work are, according to existing literature, not economically feasible for extraction of tall oil from softwood bark. However, the scale of production units reviewed was small. The SFE unit used by Attard et al (2016) is in pilot scale and large savings can probably be done if the production units are scaled up (Núñez & del Valle, 2014). Moreover, the economic analysis is built on producing tall oil and its fractions only. Biorefinery concepts often include various products to produce synergetic effects to reduce costs (Martin & Grossman, 2013). There is a potential to use spruce bark as a feedstock of tannin production (Kemppainen, et al., 2014) and bioactive stilbenes can be used for various pharmaceutical applications (Pietarinen, et al., 2006).

A study by Hytönen & Hakala (2013) reveals a net revenue of 85 €/kg extract by extracting bark lipophilic compounds of *Eucalyptus globulus* with a SFE pilot plant, considering all possible products in the economic evaluation. The chemical profile of bark from *Eucalyptus globulus* differ from the species studied in this work though, but using spruce pulpwood bark would in theory give a higher yield since the content of lipophilic extractives in *Eucalyptus globulus* bark is just about 15% of the contents in spruce pulpwood bark.

Spruce pulpwood is the assortment which holds the best prerequisites for processing bark extractives to tall oil and its fractions. Some of the lipophilic extractives could not be identified though. The Results of this study support the theories of polymerisation of fatty and resin acids due to aging, implying a possibility that the yield of tall oil might be higher. The extractives in the spruce bark samples showed well-fitted relationships with tree diameter, bark age and annual ring increment. This could act as a platform for future research, aiming for modelling the resource.

The economic feasibility for producing tall oil from softwood bark needs more research. A scaled-up techno-economic analysis of SFE together with an analysis of synergetic effects with other products is a promising option. Analyses of bark lipophilic extractives in future studies should pay attention to the methodology used in the extraction process. The lipophilic extractives are sensitive and a more careful method should be used. Since the bark in this study were carefully treated and kept fresh, further research for industrial relevance can preferably focus on the non-fresh bark residues of spruce pulpwood at mill sites.

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