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From Norway Spruce Bark to Carbon Foams: Characterization, and Applications

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Fresh bark from spruce *Picea abies* was milled and extracted with hot water. The extracts were purified in a number of steps in order to get tannin-extracts pure enough to prepare tannin-based carbon foams. The chemical composition of the extracts were analyzed. The foams were maturated and thermally treated to obtain desired properties, such as specific surface area, porosity, and compressive strength. It was possible to produce carbon foams even if they contained carbohydrate impurities. Differences in the properties of the carbon foams such as compressive strength, specific surface areas, and pore size distributions might be related to the compositions of the extracts. The foams were finally activated chemically and physically and were tested in adsorption of methylene blue. Results from the adsorption tests showed that adsorption was highly related to the total pore volume and the amount of mesopores created inside the foam structure during the thermal treatment.

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INTRODUCTION

Substantial amounts of forest biomass are consumed in Nordic countries. In 2018, this volume amounted to 78.2 Mm^3 in Finland (Torvelainen 2019). The accumulation of by-products, such as bark, is significant in the debarking process of wood. For example, the amount of spruce bark generated at mills in Finland is 0.8 to 1.2 Mt/a (d.m.), calculated with an estimated average dry density of 380 kg/m^3 (Kemppainen 2015). Bark is currently primarily used in producing heat and power or in landscaping (Feng *et al*. 2013); however, spruce bark is a rich source of important polyphenolic extractives and natural antioxidants, such as tannins and stilbenes (Krogell *et al*. 2012), and these compounds have the potential to be utilized in high-value applications. Tannins can be defined as polyphenolic compounds presented in plant structure, where they are bonded to the cores of polyol, flavan-3-ol (catechin) or triterpenoid units (Khanbabaee and van Ree 2001).

Tannins are usually water-soluble polyphenols that differ from most other natural phenolic compounds in their ability to precipitate proteins from solution (Scalbert 1991). Some high-molecular-weight tannins or tannins complexed with proteins or polysaccharides may be water-insoluble. Due to the existence of a variety of tannin molecules, they are divided into 3 categories, as presented in Fig. 1, proanthocyanidins, commonly known as condensed tannins, hydrolyzable tannins, or phlorotannins.

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Condensed tannins (CT), are oligomers made of polyhydroxyflavan-3-ol units, which can differ in their hydroxylation pattern (Bianchi *et al.* 2014). In European softwood and hardwood species, they are largely procyanidins with varying proportions of the 3-flavanol units catechin and epicatechin (Holmbom 2011). The main sources of commercially produced condensed tannins are the bark of black wattle (*Acacia mearnsii*) and quebracho heartwood (*Schinopsis balansae* and *S. lorentzii*) (Bianchi *et al.* 2014; Holmbom 2011). However, extraction of pine and spruce bark has been shown to give economical yields of CTs. (Lacoste *et al.* 2015) Furthermore, CTs in quebracho and wattle are predominantly profisetinidins and prorobinetidins (Pash *et al.* 2001) with a resorcinol type A-ring while spruce CTs have essentially a phloroglucinol type A-ring, *i.e.* they are mostly procyanidins and to some extent prodelphinidins. Phloroglucinol type A-ring is much more reactive towards formaldehyde than a resorcinol type counterpart (Pizzi 2008), indicating that spruce bark could be an excellent source of high quality CTs for wood adhesive industry.
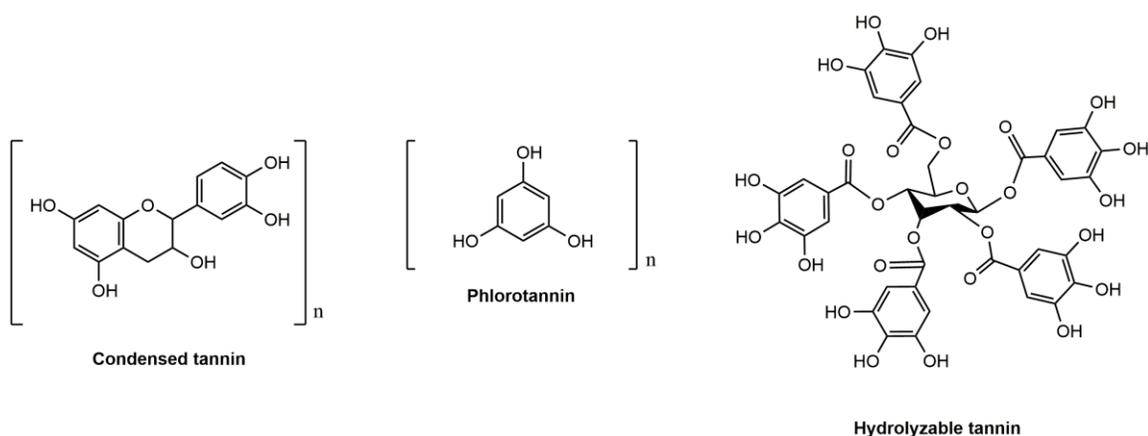

Fig. 1. Main structural units of different tannin types. Letter n, after the square brackets, indicates that a number of monomers are attached to the condensed tannin and phlorotannin polymer.

When planning the whole process chain for the production of extractives-based chemicals, there are multiple aspects that need to be considered, starting from the raw material acquirement. This is the reason that many initial extractives suitable for potential raw material applications are either rather volatile or chemically unstable (Alén 2000). The extractives content starts to decrease immediately after tree felling (Assarsson *et al.* 1963; Ekman 2000). All the phases of the wood handling process and the duration of each of the phases in the procurement chain, as well as environmental conditions, are important with respect to changes in extractives content and composition. This needs to be taken into account when aiming at the development of new valuable extractives-based bio-chemicals.

The growing demand of nature-derived ingredients to replace synthetic chemicals, and the search for the green and sustainable extraction methods, has initiated new research and developments in the field of plant extraction (Royer *et al.* 2012; Pfennig *et al.* 2011; Chemat *et al.* 2013). Recent trends in extraction techniques have largely focused on finding solutions that minimize the use of organic solvents. Thermolability of the molecules should be taken into account when choosing the extraction method. This also means that temperature and other extraction parameters should be optimized (De Monte *et al.* 2014). In general, extractions can be facilitated by increasing the temperature to favor solubilization and diffusion (Seidel 2012; Zhang *et al.* 2018). However, the presence of thermolabile compounds sets limits for extraction temperature, as too high temperatures

may cause decomposition of these compounds. Another disadvantage of high extraction temperature is that it may lead to extracts of undesirable impurities and solvent losses. There is also optimum time range for the duration of extraction. While the contact time between solvent and solid material must be sufficient to allow mass transfer to properly take place, increasing time will increase the extraction efficiency only to a certain point (Pfennig *et al*. 2011; Zhang *et al*. 2018). Increasing time does not have an effect after the equilibrium of the solute is reached inside and outside the solid material. Here the aim was to produce the tannins by an eco-friendly extraction process; thus hot-water extraction was the chosen extraction technique.

Extraction of plant biomass typically leads to a mixture of components in the resulting extract (Pfennig *et al*. 2011). For this reason, several treatment steps are required after extraction. Typically these include: filtration to separate solids, concentration of extracts by evaporation of solvents, enrichment of target components (*e.g*., by liquid-liquid extraction, chromatography, membrane separation, and crystallization), removal of impurities like heavy metals by complexation, or polyaromatic hydrocarbons by adsorption technologies, and drying of products and product forming technologies for solid extracts (*e.g*., spray drying, granulation, *etc*.). The choice of concentration and purification steps has an influence on energy usage and the life cycle of tannin production (Ding *et al*. 2017). Adsorbents such as XAD4 (hydrophobic polyaromatic), XAD7HP (aliphatic acrylic crosslinked polymer), XAD761 (phenol-formaldehyde), XAD1180 (hydrophobic polyaromatic), XAD16N (Cross-linked polyaromatic), and FPX66 (cross-linked polyaromatic) have been used to purify blueberry tannins (Buran *et al*. 2014) and juice pomace (Sandhu and Gu 2013).

Leather tanning and winemaking together with applications within the building material sector dominate and drive a growing international tannin market (Grand View Research 2017). CTs are also used as a component in adhesives. More recently, the use of tannins in rigid insulating foams has been demonstrated (Link *et al*. 2011).

Carbon foams (CF) can be produced in a number of ways using polyphenolics such as lignin or tannins as building blocks. In many of these foam structures, formaldehyde is used as a crosslinking agent between individual -OH groups (Tondi *et al*. 2009; Tondi and Pizzi 2009). Due to the high toxicity of formaldehyde, there has been intensive research for replacing reactions. One of these formaldehyde-free routes to produce carbon-foams is to polymerize tannins in a catalytic reaction using furfuryl alcohol as a crosslinking agent. (Link *et al*. 2011)

Previously only pre-cleaned tannin powders with a high degree of purity have been used in the foaming as described earlier by Celzard *et.al*. (2010). Similarly, in an earlier study (Varila *et al*. 2019) the authors successfully produced CF using purified tannin acid as a reagent. The novelty of the present study is that the whole process chain from native spruce bark over pre-treatment, extraction, extract cleanups to the production of tannin-based CF is described. Finally, the extracts are used to produce CF, which are thermally maturated and activated into activated CF and tested in adsorption of methylene blue.

EXPERIMENTAL

Fresh Norway spruce bark (*Picea abies*) was provided by UPM-Kymmene Oyj Pietarsaari sawmill on February 15, 2019 for the extractions. The logs had come from clear cut stands of various origins. They were debarked with a rotor debarker at UPM Pietarsaari

mills. The sample material was retrieved from the debarker bin immediately after it had been peeled off the logs. All material was in a frozen state, as sampling took place in the middle of the winter season. Some 15 m^3 of bark was loaded in a truck and transported to Luke's Kannus terminal for screening.

For the CF, purified extractives from spruce bark were kindly delivered by Luke (Natural Resources Institute Finland). Furfuryl alcohol (98%) and the surfactant polyoxyethylenesorbitan trioleate (brand name Tween 85) were ordered from Acros Organic. The catalyst, p-toluenesulfonic acid monohydrate (PTSA, 99%), and the blowing agent (n-pentane, 99.4%) were ordered from Merck KGaA (Darmstadt, Germany). For the chemical activation, technical grade (97%) $ZnCl_2$ was ordered from VWR Chemicals (Helsinki, Finland).

Pretreatment of Bark and Extraction of Tannins

A 4 m^2 screen with 20 x 20 mm mesh size was used to remove fines from the sawmill bark. This was done in order to minimize the risk of flow restrictions in the extraction chamber. A total of 431 kg of acceptable fresh bark material was produced. Of this mass, 20 random samples were taken for determination of bark, moisture, and ash contents. Based on these samples the bark material was found to contain 97.3% (standard deviation, SD = 1.1) bark, the rest being sapwood. This inclusion of wood is unavoidable, as the bonding between wood and inner bark is very strong in winter months. The emphasis of industrial debarking is to produce bark-free logs and not wood free bark. The moisture content of the bark fraction was 63.2% ($s = 0.61$) and ash content 3.3% ($s = 0.03$).

The accepted fraction was used as a feedstock in pressurized hot water extraction (PHWE). Spruce bark was utilized as soon after debarking as possible to guarantee a reasonable extraction yield in the pilot-scale process. A 10 day time-lapse took place prior to extraction, during that time the material was stored in cold, ambient winter conditions.

Spruce bark samples were extracted using a 300 L hot water extraction system (Kilpeläinen *et al.* 2014). The samples were extracted with hot water in batch mode. Two extractions were conducted with 39 kg oven-dried (O.D.) bark (102 kg fresh) in both extractions. Extraction temperatures were 70 °C for 80 min and 90 °C for 40 min. The extraction parameters for pilot scale extractions were determined by analyzing the results from laboratory-scale hot water extraction with ASE (Accelerated Solvent Extractor) using the response surface methodology (results will be published later by Brännström *et al.*). Tannin extract 1 is from the first extraction at 70 °C and tannin extract 2 is from the second hot water extraction at 90 °C. Extracts were collected in containers and samples were taken. Samples were frozen and were stored at -20 °C in dark. Extraction yields were calculated on a dry bark basis.

Purification of Extracts

Hot water extracts were purified using 7 kg of XAD7HP adsorbent (Dow, Chauny, France). The adsorbent was packed in a glass column and washed before use. Hot water extract was transferred to a column and extract was added until nearly the whole adsorbent was reddish. Tannins were then eluted out of column using ethanol as eluent and the ethanol eluents were finally dried using a rotary evaporator. The dried samples of XAD7HP purified extracts are denoted Dried tannin 1 and Dried tannin 2, and the samples are from 70 °C, 80-min and 90 °C, 40-min, hot water extractions, respectively.

Analytical Methods

Moisture and ash content of the bark was determined according to the standard methods SFS-EN 14774-2 (2010) and SFS-EN 14775 (2010), respectively. Wood content in the bark fraction was determined according to the standard method SCAN 53:94 (1994). Altogether 20 samples were taken for the determination of wood content.

The amount and composition of sugars and hemicelluloses in extract were determined with acid methanolysis (Kilpeläinen *et al*. 2014). Acid methanolysis depolymerizes hemicelluloses and pectins and converts sugars to methyl glycosides. Solid samples were treated for 5 h and extracts for 3 h. Resorcinol was used as an internal standard. Samples were silylated and analyzed with Shimadzu GC-2010 gas chromatograph (Kyoto, Japan) equipped with HP-1 column (25 m length, 0.2 mm ID and 0.11 µm film thickness) and flame ionization detector (FID). Hydrogen was used as a carrier gas.

The amount of polyphenols was determined using Shimadzu UV-Vis spectrometer UV2401PC at 280 nm. The total polyphenolic yield is called tannin yield further on in-text (Ding *et al*. 2017). Purified industrial tannin, Tannino QL-SOL (Silvateam, San Michele Mondovi, Italy) was used as an external standard and treated the same way as samples. Samples were diluted in 0.1 M NaOH, and UV absorption at 280 nm was determined.

CT was determined with three analytical replicates of each sample by HPLC after thiolytic degradation according to Mattila *et al.* (2018). Briefly, samples were weighed (20 to 30 mg) into 1.5 mL Eppendorf vials and 1 mL of depolymerization reagent (3 g cysteamine / 4 mL 13 M HCl / 56 mL methanol) was added. The vials were sealed and incubated for 60 min at 65 °C, after which the degradation products, *i.e*., free flavan-3-ols (terminal units) and their cysteaminyl derivatives (extension units), were determined by HPLC equipped with diode array detection (DAD) and fluorescence detection (FLD).

The analytical pyrolysis of purified and dried extract samples was performed with a foil pulse Pyrola 2000 MultiMatic (Pyrola AB, Lund, Sweden) pyrolyzer coupled to an Agilent 7890B gas chromatograph (Py-GC; Santa Clara, CA, USA). No replicate pyrolysis analyses were conducted. The column was an Agilent HP5-MS capillary GC column (30m × 0.25 mm, film thickness 0.25 µm). Detection was carried out with an Agilent 5977B quadrupole mass selective detector (MSD) with electron impact (EI) ionization. Interpretation of the mass spectra of the pyrolysis products was based on a commercial database, Wiley 10th/NIST2012. Semi-quantification was done by calculating the relative abundance of each pyrolysis product, *i.e.*, peak area-% of total peak area. Thermally assisted hydrolysis and methylation (*Py*-THM-GC–MSD) was also performed for the samples. For THM-GC–MSD, approximately 500 µg of the dried extract was dissolved in 10 µL of tetramethylammonium hydroxide (25% in methanol), whereafter the solution was added to the Pt filament and pyrolyzed at 380 °C for 2s.

Production of Tannin-Based Carbon Foams

The tannin-based CF were produced from the purified extracts (tannins) delivered by Luke using the method described earlier by Link *et al*. (2011). In short, the extracts were added to the mixture of water, surfactant, and crosslinker and mixed thoroughly to make a fine paste. After a homogeneous mixture was obtained, the blowing agent and catalyst are added followed by further mixing. Finally, the resulting solution is mixed and left for foaming overnight in a furnace.

The matured tannin-based CF was cut into pieces. The pieces were inserted into a steel reactor in a tubular oven and treated thermally in a flow of nitrogen gas. Further, some

pieces were converted into activated CF by either physical activation (steam activation in an atmosphere of nitrogen) or chemical activation (impregnation with $ZnCl_2$) followed by thermal treatment according to the method described previously (Varila *et al.* 2017).

Specific Surface Area, Pore Volume, Pore Size Distribution

Specific surface areas (SSA) and pore distributions were determined from the adsorption-desorption isotherms using nitrogen as the adsorbate. Determinations were performed with a Micromeritics ASAP 2020 instrument (Norcross, GA, USA). Portions of each sample (100 to 200 mg) were degassed at low pressure (2 mm Hg) and at a temperature of 413 K for 2 h in order to clean the surfaces and remove any gas adsorbed. Adsorption isotherms were obtained by immersing sample tubes in liquid nitrogen (-195.8 °C) to achieve isothermal conditions. Gaseous nitrogen was added to the samples in small doses, and the resulting isotherms were obtained. Specific surface areas were calculated from adsorption isotherms according to the Brunauer–Emmett–Teller (BET) method (Brunauer *et al.* 1938). Total pore volumes were calculated from the adsorption isotherm at a relative pressure (P/P_0) of 0.985 (Seaton *et al.* 1989) assuming slit-formed pores (Lastoskie *et al.* 1993).

The pore size distribution (PSD) of pore volumes (vol.%) was calculated from the individual volumes of micro-pores, meso-pores, and macro-pores with density functional theory (DFT- model) (Seaton *et al.* 1989) assuming slit-formed pores (Lastoskie *et al.* 1993). With the instrumental setup used, micro-pores down to 1.5 nm in diameter could be measured, even if there might have been some contribution from smaller pores. The micro-pore areas and volumes were calculated by the t-plot using Harkins and Jura (1943) equations. According to previous works, the SSAs were measured with a precision of 5% (Hackley and Stefaniak 2013).

Compressive Strength of Carbon Foams

Compressive strengths (σ) of foams were determined using a Zwick/Roell Z010 testing machine (Kennesaw, GA, USA) with a load cell of 10 kN. The loading speed was 0.1 mm/s, and the measurement ended when the force decreased by 50% from maximum or deformation reached 30%. Compressive strength was calculated with Eq 1.

$$\sigma = F / A \tag{1}$$

where F (N) is the maximum force at the linear region of the compression curve and A (mm^2) is the surface area. The accuracy of the instrument was ± 1%.

The stress-strain curve of cellular material typically has three distinguishable regions: linear part at low strain, a plateau region (collapse of the cell layers), and densification (all cell layers are compressed). The compressive strength can be defined as the value at the plateau whereas the slope of the linear part represents the elastic modulus (*i.e.*, resistance against elastic or non-permanent deformation). The curve roughness ("noise") is a result of the redistribution of the compression after the fracture of layers of cells and subsequent loading of the next cell layers.

Adsorption of Methylene Blue

The activated carbon (AC) foams were tested for their adsorptive properties using the adsorption of methylene blue (MB) into the pores by the method described in Raposo *et al.* (2009). In short, a solution containing 1000 mg of MB per liter H_2O was prepared. A total of 50 mL of this solution was transferred into Erlenmeyer flasks 250 ml in volume,

50 mg of the AC foam was added, and the solutions were continuously agitated for 48 h on an orbital shaker to achieve equilibrium between the adsorption and desorption of the test dye. The portions of each solution were filtered and diluted if needed, and the absorbance of the solution was measured at 664 nm on a Shimadzu UV-Vis 2401 PC double-beam spectrophotometer. The concentration of the solution was calculated from a calibration line obtained with known concentrations of MB. The adsorbed mass was calculated using Eq 2, and the percentage of MB removed was calculated using Eq. 3,

$$q(\text{abs}) = (C_0 - C_t) \times (V / m) \qquad (2)$$

$$\% \text{ removed} = (C_0 - C_t) / C_0 \qquad (3)$$

where C_0 is the initial concentration of MB (1000 mg/L), C_t is the measured concentration after 48 h, V is the volume of MB solution used, and m is the mass of the AC foam used.

RESULTS AND DISCUSSION

Results from Extraction and Extract Cleanup

The amount of collected extracts was 233 kg and 232 kg. Hot water extracted 111 mg/g and 110 mg/g of spruce bark. Polysaccharide composition of spruce bark and XAD7HP treated dried tannins are presented in Fig. 2.
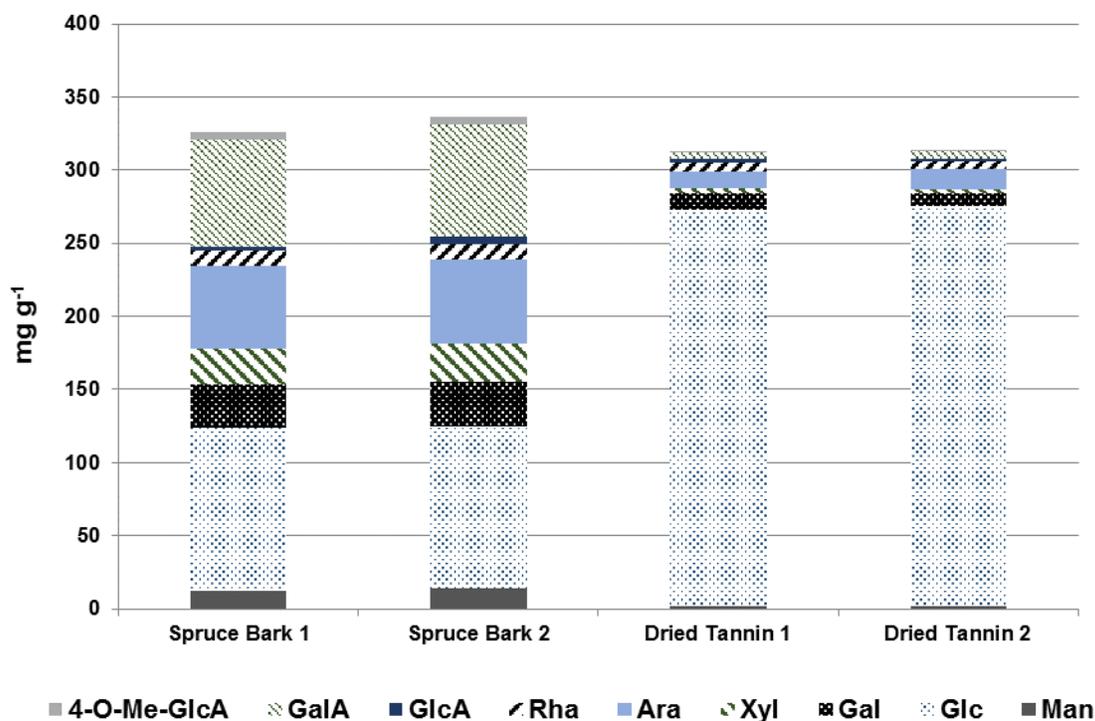

Fig. 2. Non-cellulosic carbohydrate composition of original spruce bark and XAD7HP treated dried tannins.

The original spruce bark contained mainly glucose, arabinose, and galacturonic acid. Galacturonic acid and rhamnose are from pectins, and there were 84 mg/g and 87 mg/g of pectins in the original barks. Bark contained mannose 12 mg/g and 14 mg/g and galactose 30 mg/g and 31 mg/g from spruce hemicellulose galactoglucomannan (GGM). Glucose originates from hemicelluloses, inner bark sugars, and glucosides.

Hot water extraction (HWE) removed mainly glucose from the bark. The proportion of other sugars did not change during HWE. XAD7HP treated and dried crude tannins had 313 mg/g of sugars that were mainly glucose 271 mg/g and 274 mg/g consisting of 87 w% of sugars. Only minor amounts of pectins 9 mg/g and 10 mg/g were present in dried tannins. Additionally, only small amount of softwood hemicellulose sugars galactose and mannose, 10 mg/g and 11 mg/g, respectively, could be found in dried tannin samples.

Dried XAD7HP treated extracts had 554 mg/g and 670 mg/g of tannins according to UV280 nm measurement. Tannin yield might include some polyphenols derived from lignin since these compounds have absorption in the same wavelength range. Still, extraction temperatures were relatively low and softwood lignins usually degrade at higher temperatures.

CTs in Norwegian spruce bark composed mostly of (epi)catechins but also (epi)gallocatechins were detected as minor subunits agreeing with previous studies (Matthews *et al*. 1997; Bianchi *et al*. 2014; Hammerbacher *et al*. 2014) CT content in the bark samples was 3% of the dry matter (Fig. 3), and the average degree of polymerization was 6.0 to 6.1.
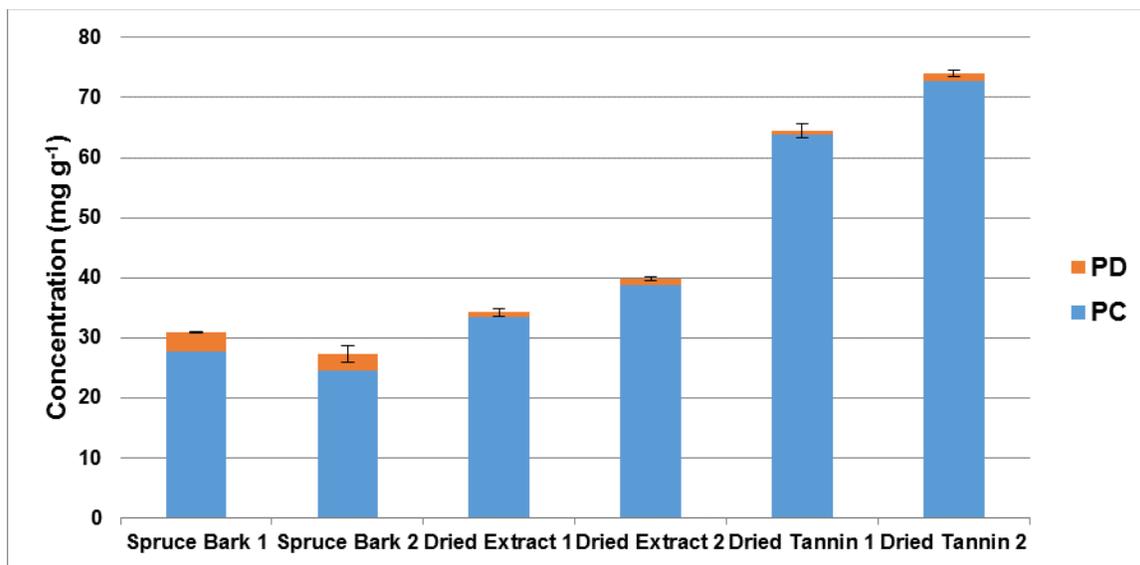

Fig. 3. Condensed tannins in samples of original spruce bark, dried hot water extracts, and dried XAD7HP treated extracts (dried tannins). PD = prodelphinidins (structural units of (epi)gallocatechins), PC = procyanidins (structural units of (epi)catechin)

CT concentration in the extracts varied between 3.3 to 3.9% of the dry matter and was only slightly higher than in the initial bark, which indicates that hot water extraction was not very selective for CTs. Previously, Krogell *et al*. (2012) extracted tannins from Norwegian spruce bark with hot water, and the CT contents in the extracts were quite similar to the contents determined in the present study. Somewhat higher tannin content (6.6% of dry matter) was reported by Bianchi *et al*. (2015) when they compared hot water extracts of barks of different softwood species. This is probably mostly due to different

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analytical methods applied. In the present study, CTs were determined by thiolysis and only proanthocyanidins, *i.e.*, flavan-3-ol polymers, were included in the results while Bianchi *et al.* (2015) used total phenol assay (Folin-Ciocalteu) for quantification of CTs. They used thiolysis for qualitative analysis and they noted that only 26% of phenolics in Norwegian spruce bark extract were quantifiable by thiolysis indicating that the majority of the phenolics were actually not composed of proanthocyanidins. XAD7HP treatments roughly doubled the content of CTs in the extract and after treatments, the content varied between 6.5 to 7.3% of dry matter.

The pyrolysis products of Dried tannin 1 and Dried tannin 2 had a high amount of methoxyphenols, 36% and 29%, respectively (Fig. 4). The group, denoted as methoxyphenols consisted mainly of guaiacol derivatives, which are typical softwood lignin pyrolysis products (Kawamoto *et al.* 2014; Kawamoto 2017; Ghalibaf *et al.* 2019). Catechol derivatives are not only formed during lignin pyrolysis, but they are also typical tannin pyrolysis products (Ismayati *et al.* 2017; Pinto *et al.* 2019). Pinto *et al.* (2019) and Ismayati *et al.* (2017) confirmed this by model compound, namely catechin, pyrolysis studies. The main products from pyrolysis were catechol and 4-methylcatechol from the B-ring of catechin and epicatechin. The content of catechol derivatives, *i.e.* catechol and 4-methylcatechol, was 19% in Dried tannin 1 pyrolysate and 12% in Dried tannin 2 pyrolysate.
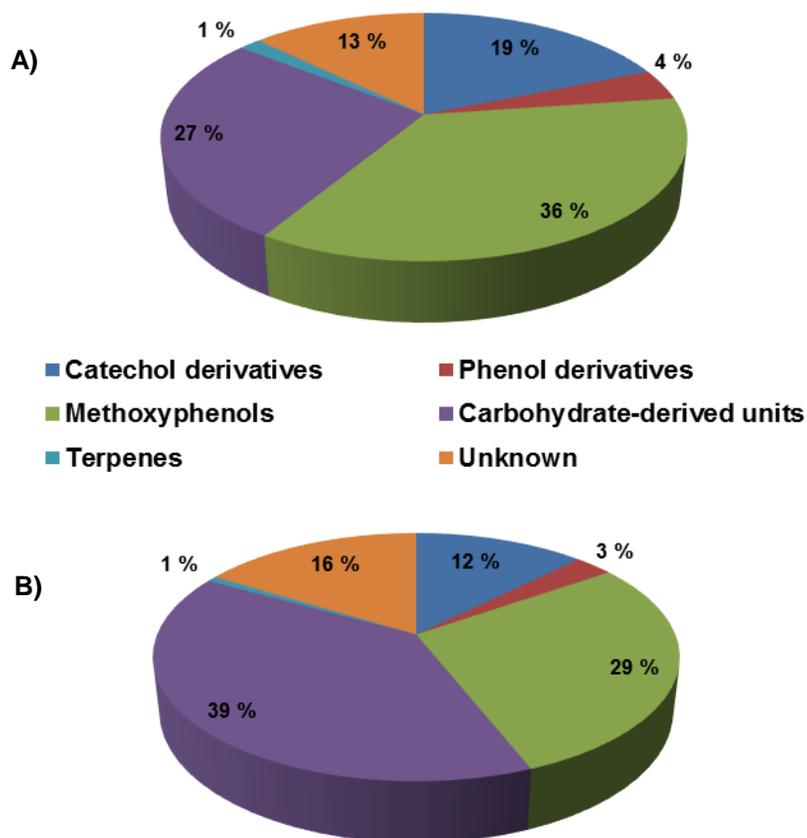

Fig. 4. Relative distribution of volatile compounds produced during Py-GC/MSD of purified (resin-treated) and dried spruce bark hot water extracts. A) Dried tannin 1, and B) Dried tannin 2 extract.

Phenol derivatives, such as *p*-cresol are also typically formed in lignin pyrolysis. However, according to Pinto *et al.* (2019) also catechin pyrolysis produces a relatively high

amount of different phenol derivatives. Thus, it is not possible to conclude which portion of catechol derivatives or phenol derivatives originate from lignin and which are formed due to the thermal degradation of tannins. Other phenolic extractives present in the extract complicate the issue further. The proportion of carbohydrate-derived products was also high, 27% and 39% for Dried tannin 1 and Dried tannin 2, respectively. This is in agreement with the chemical analysis results (Fig. 2). A small amount of lipophilic extractives, *i.e.*, terpenes, was also detected in Py-GC/MSD studies. Based on these studies it could be concluded that the extract contained high lignin content as indicated by methoxyphenols in pyrolysate. However, the pyrolysis results are semi-quantitative which means that based on these results the amount of lignin could not be concluded. *Py*-THM-GC-MSD results also confirmed the presence of lignin in the extract. In addition to carbohydrate- and lignin-derived units, 3,5,4'-trimethoxystilbene and 3,5,3',4'-tetra-methoxystilbene were also detected.

Specific Surface Areas and Pore Size Distributions of the Activated Carbon Foams

According to the data obtained from the surface analysis, presented in Table 1, physically activated CFs derived from Dried tannin 1 and 2 had similar specific surface areas and pore volumes. PSD, calculated using DFT-model, shows that most of the pores created during the activation were in the microporous region, 88% and 94%, and the rest of the remaining pores were in the mesoporous region. These results are in line with the results from the t-plot method using Harkins and Jura (1943) equations, as can be seen from Table 1.

Table 1. Surface Analyzes of Activated Carbon Foams Activated With Steam and Zinc Chloride

		Samples			
		Activating agent $ZnCl_2$		Activating agent steam	
Calculation method	**Unit**	**Dried tannin 1**	**Dried tannin 2**	**Dried tannin 1**	**Dried tannin 2**
BET					
SSA	m^2g^{-1}	1275	1495	335	351
Pore volume	cm^3g^{-1}	0.731	0.816	0.151	0.148
Langmuir surface area	m^2g^{-1}	1516	1783	362	383
t-plot					
Micropore volume	cm^3g^{-1}	0.169	0.18	0.11	0.121
Micropore area	m^2g^{-1}	410	431	284	313
External surface area	m^2g^{-1}	865	1064	51	38
DFT					
Pore volume	cm^3g^{-1}	0.575	0.668	0.123	0.121
Micropores	cm^3g^{-1}	0.361	0.425	0.108	0.114
Mesopores	cm^3g^{-1}	0.213	0.243	0.015	0.007
Macropores	cm^3g^{-1}	0.001	0	0	0
Micropores	%	63	64	88	94
Mesopores	%	37	36	12	6
Macropores	%	0	0	0	0

The chemically activated CFs, Dried tannin 1 and Dried tannin 2, with $ZnCl_2$, had much higher specific surface areas and pore volumes than CFs activated with steam, as can

be seen from Table 1. PSD of chemically activated CFs were different than in the case of steam activation. Up to 36 to 37% of pores were in the mesoporous region, but a majority of the pores, 63 to 64%, were still in the microporous region according to the DFT-model.

Compressive Strength

As demonstrated in Fig. 5, the compressive strength of CFs made with Dried tannin 1 extract was much higher after the thermal treatment compared to the compressive strength of CFs made from Dried tannin 2 extract. The reason behind this finding can be due to the different compositions of Dried tannin 1 and Dried tannin 2 extracts. Pyrolysis of dried tannins showed that dried tannin 2 had a higher relative ratio of carbohydrate-derived compounds and less of methoxyphenols that could have an effect on the compressive strength. Overall tannin yield and concentration of CTs was higher in Dried extract 2, but there is no direct correlation between compressive strength and tannin yield of the extracts. A possible explanation of the difference in compressive strength after thermal treatment between the foams prepared from Dried tannin 1 and 2 can be due to the different amount of lignin or sugars inside the extracts, but there might be other possible explanations. Hot water extraction was performed higher temperature at 90 °C for dried tannin 2 than 70 °C extraction of dried tannin 1. Hot water extraction temperature may have an effect on the quality of tannins but this needs to be confirmed with further experiments.
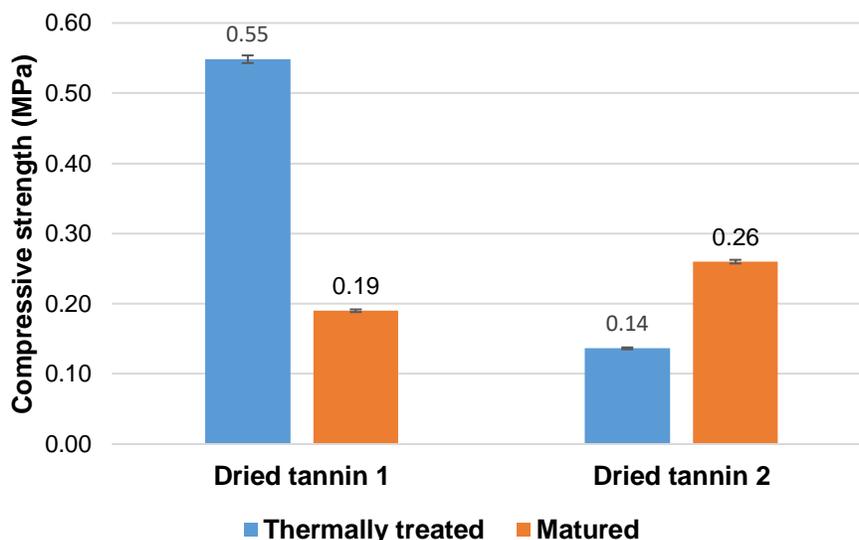

Fig. 5. Mechanical strength of the foams before and after thermal treatment

Adsorption of Methylene Blue

Activated CFs prepared from Dried tannin 1 and Dried tannin 2 extracts were tested in adsorption of methylene blue, and the results are presented in Fig. 6. Adsorption is highly dependent on the pore volume and especially on the mesoporosity of activated CFs. Results presented here are in good agreement with our earlier publication (Varila *et al.* 2019). Chemically activated CFs adsorbed methylene blue much more efficiently than steam activated CF due to the higher degree of mesoporous structure and higher pore volumes.
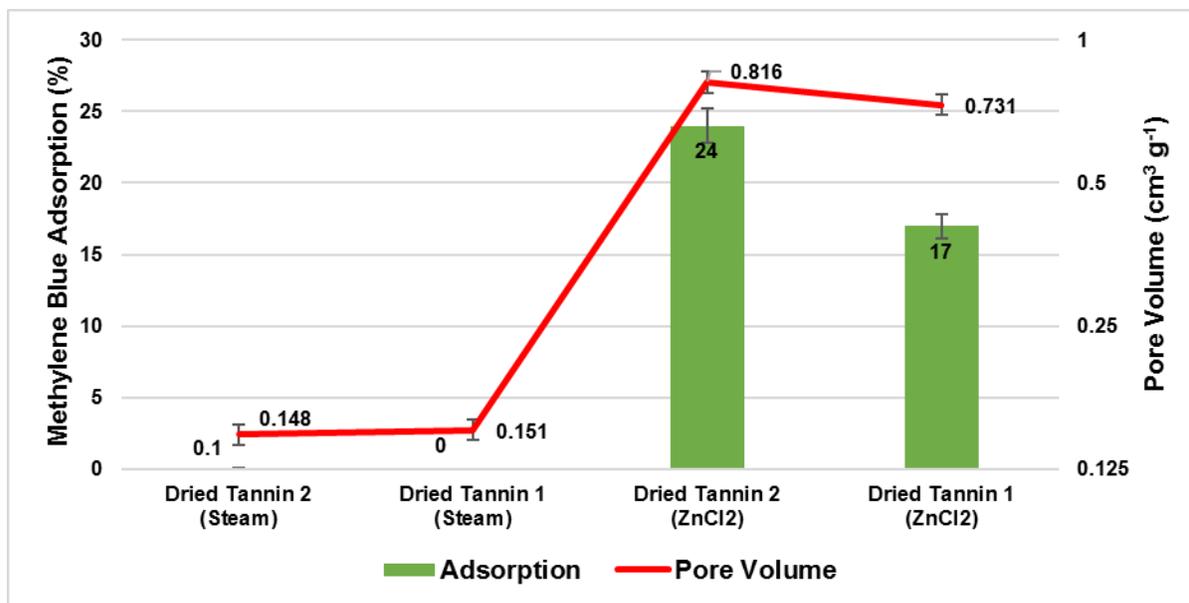
Fig. 6. Adsorption of methylene blue before and after activation procedures

CONCLUSIONS

1. The extraction of tannins from bark is a complicated process, and a number of cleanup steps are needed to produce clean tannins. Even if several cleanup procedures are used, the extracts obtained in this study appear to contain, besides the tannins, other compounds, such as sugars and lignin.

2. For the production of tannin-based carbon foams, tannins of high purity have normally been used. The results from this study indicate that crude tannin extracts containing sugars and lignin can be used for the production of carbon foams.

3. The foams produced can be further physically or chemically activated into activated carbon foams having tailored properties such as high specific surface area and well-defined porosity.

4. The compressive strength of carbon foams can be tailored to some extent with thermal treatment at high temperatures.

5. The adsorptive properties (measured with methylene blue) depend on the pore volume created inside the activated carbon foam structure during the thermal treatment.

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