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Applicability of hybrid aspen (*Populus tremula* L. × *P. tremuloides* Michx.) bark extract as a precursor of rigid carbon foam and activated carbon

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ABSTRACT

Hybrid aspens have long attracted scientific interest, but the research on their use as feedstocks for chemical applications are still very limited. The bark biomass of the poplar species contains many valuable extractives that can be utilized as value-added products. This paper examines the applicability of hybrid aspen (*Populus tremula* L. × *P. tremuloides* Michx.) bark extract as a precursor of rigid carbon foam and activated carbon. To explore this, the study considers 1) the basic chemical composition of the bark in terms of added value potential, 2) the basic chemical composition of the bark extract and the effect of its pretreatment on the extract composition, 3) the production of rigid carbon foam, and 4) the chemical activation of carbon foam with different impregnating agents. The study determines that the bark extract of the hybrid aspen can be used as a precursor for rigid carbon foam and further processed into an activated carbon product. Therefore, the bark extract of *Populus tremula* L. × *P. tremuloides* Michx. can be assessed as a potential value-added product that increases the use value of the hybrid aspen biomass.

1. Introduction

Populus tremula L. × *P. tremuloides* Michx. has been selected for the study due to the high extractive content of the bark [1], great potential for versatile exploitation according to the cascading use principle [2], and fast biomass production potential of the species [3–6]. Bark extracts are the value-added products of woody biomass, as their compounds can be separated before the lignocellulose is diverted to other production processes, such as thermochemical conversion to produce herbicide and fungicide active chemicals [2] or biochar [7]. Due to the high content of phenolic compounds and carbohydrates in the bark, bark extract is a potential precursor for material science. This research explores the utilization potential of the hydrophilic extractives of *Populus tremula* L. × *P. tremuloides* Michx. bark as a precursor for activated rigid carbon foam.

Aspen species and their hybrids have long been the subject of research interest due to their rapid growth, breedability and crossbreeding potential, as well as their cultivability in forestry; but they also have a susceptibility to plant diseases and pest damage [8–10]. Isebrands & Karnosky [11] described many ecological benefits of poplar cultivation, but aspen species also have the potential to serve as a versatile source of biomass for a wide range of uses. Poplars grow over a very large area in the northern hemisphere, and their cultivation provides us the opportunity to produce biomass close to areas in need of feedstock. Different aspens and their bred hybrids have been utilized as timber, panel material, feedstock for pulp and paper, furniture, and energy [12], but they have hardly been used as a feedstock for the chemical industry. When fast-growing tree species are consumed as a biofuel in energy production, there is rarely a need to separate the bark into its own side stream. However, wood bark accumulates as a side stream if the wood is used, for example, as a raw material for chemical pulp, where only debarked wood is utilized. The bark accumulated as a side stream is still valuable as a biofuel, but in the direct burning of

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virgin biomass, the opportunity to utilize bark extracts for the needs of the chemical industry is lost. When the bark extracts are separated into their own side stream, the bark extraction residue can be used, for example, in the production of platform chemicals through catalytic conversion [13] or produce both bioactive chemicals and solid biofuel by using thermochemical conversion methods such as torrefaction [2]. In such a setting, the bark can be utilized in an enhanced and multi-product manner by producing chemicals [2], functional materials such as rigid foam and activated carbon [14,15], and solid fuel in accordance with the cascading use principle.

In this research, rigid carbon foam and activated carbon made from hydrophilic extractives of the bark are investigated as parallel applications, as activated carbon can be produced from rigid carbon foam by further processing [14]. Rigid carbon foams are sponge-like materials that have unique properties, depending on the raw materials and the parameters used in the carbonization process [15]. Rigid carbon foams have been studied for their properties as absorbents, e.g., making the material suitable for the separation of metal cations from solutions [16] or for the treatment of wastewater in general [17,18]. In addition to its sorbent properties, the suitability of the material has been studied in other applications of materials technology, such as acoustic materials [19], foam material for seasonal thermal storage [20], and lightweight panel structures [21]. The material is well suited in applications where heat resistance is required, as carbon foams typically have high fire resistance. This does not necessarily mean that they are fireproof under an oxidizing atmosphere. However, Tondi and coworkers [22] showed that thermally treated (900 °C) tannin-based carbon foams can withstand acetylene flames in an oxidizing atmosphere of up to 2750–3050 °C without ignition. Earlier, we studied tannin-based carbon foams [23,24], which are generally produced by using cross-linking agents that form chemical bridges between the individual condensed or hydrolysable tannin molecules. Depending on the composition of the extract used as a precursor, the final quality of the rigid foam product can be improved by different purification steps. The widely used XAD (column loaded Amberlite™ XAD7HP polymer adsorbent) -purification treatment is applied in situations where the goal is to concentrate tannins and other phenolic compounds in the extract [23,25–27]. The rigid carbon foam product is finished by a heating step, where the carbonization process is carried out at high temperatures of 600–900 °C under a nitrogen atmosphere.

Activated carbon is a carbonaceous material in which the surface area of the porous structure of a substance is maximized by various physical, chemical, or physiochemical methods [28]. Coal has been used as a precursor in activated carbon production, but today, equivalents for coal have been sought from nonfossil sources, such as lignocellulosic biomass [28–30] and agricultural residues [31–33]. As described previously, rigid carbon foam could act as an adsorbent, but the surface area (m^2/g) of the material is still relatively small. However, chemical activation can be used to increase the surface area, after which carbonaceous material is a suitable product for activated carbon applications [14,34].

In chemical activation, chemical agents, e.g., $ZnCl_2$, KOH, NaOH, and H_3PO_4, can be used with different mass ratios for activating carbons [35–39]. Chemical activation is carried out in three stages. First, the biomass is wet impregnated with a selected activation agent. The chemical creates an opening in the surface of biomass, allowing the agent to be imbedded within the biomass structure when dried in an oven. In the second stage, the impregnated biomass is activated in the furnace under an inert atmosphere. Lastly, to obtain clean activated carbon, the chemical activation agent is refluxed away with mineral acid, filtered, washed until a neutral pH value is reached, and finally dried in an oven. The chemical activation process is better for tailoring the activated carbon porosity than physical activation. The final carbon yields are much higher, and it requires lower activation temperatures than physical activation [40–42]. From an environmental point of view, chemical compounds are not environmentally friendly substances and are corrosive to the equipment used in this research [43,44].

The bark biomass of the *Populus tremula* L. × *P. tremuloides* Michx. clone examined in this study was selected based on previous research by Korkalo et al. [1]. In the preceding research, several clone types were collected, of which the most interesting bark biomass was traced for its added value potential. Based on these results, hybrid aspen clone and its bark were selected for this bark extract utilization research. This study examines whether the water-soluble extractives of the bark of *Populus tremula* L. × *P. tremuloides* Michx. can be used as precursors for rigid carbon foams and activated carbons, and what the effect of purification pretreatment of extractives and activation methods of carbon on the final properties and yields of carbon-based products is. XAD purification performed as a pretreatment of the extracts is generally known to be advantageous if the goal is to produce a porous biobased rigid foam, but the utility of the XAD treatment still needs to be examined if the rigid foam made from the bark extract is further led to the activation processes. Necessity of the XAD treatments should also be studied from the perspective of the atomic economy of production. This is particularly crucial when the goal is to utilize the carbon in lignocellulosic biomasses as efficiently as possible. To explore this, the study focuses on the 1) basic chemical composition of hybrid aspen barks, 2) basic chemical composition of bark extracts and the effects of XAD7HP column purification pretreatment on the extract compositions, 3) production of rigid carbon foams, and 4) chemical activation of carbon foams with different impregnating agents. Fig. 1 illustrates the proposed flow chart from biomass acquisition of hybrid aspen clone plantations to utilization of the extract as a precursor for rigid foam and activated carbon foam.

The fast-growing hybrid aspen tree and its bark are interesting source of biomass, for example as fuel for energy production, but the tree species also has excellent properties for more versatile use. With this research, an insight is brought into new potential value-producing side streams that can be formed from bark-derived biomasses before the material is utilized as part of energy production.

2. Materials and methods

2.1. Research materials and extraction methods

2.1.1. Populus tremula L. × P. tremuloides michx. Trees and bark samples

The hybrid aspen trees (n = 6), national register ID C05-99-14 [45], were collected from the experimental area of the Natural Resources Institute Finland (Luke) in Lohja, Finland (60° 12′N, 23° 55′E). The type of clone of hybrid aspen was chosen based on our previous study [1]. The bark of the clone selected for this study was found to have the highest concentrations of hydrophilic extractives, total phenols, and condensed tannins among the three studied clones. The extractable bark mass was collected from the lower part of the tree trunk (1.3 m, e.g., breast height) according to a method described previously [1], and the lower parts of the tree have the most abundant extractive concentration. The bark mass, including both the inner and outer layers of the bark, was collected shortly after felling and stored freshly in a freezer at −20 °C. Chemical determinations of the bark were performed on all six clone samples from which the averages and standard deviations (Mean ± SD) of chemical composition were calculated. For hot water extraction (HWE), the bark samples from six trees were pooled into a single sample representative of the clone type (n = 1).

2.1.2. Hot-water extraction

Nondried bark (n = 1) was hot-water extracted for 120 min at 90 °C with a ratio of 1200 g/8000 g (*bark dry matter:water 1:6.7*). The extraction was carried out in a steel pot with a capacity of 10 L at normal atmospheric pressure. After hot-water extraction, the extract was separated from the bark mass and pre-concentrated with a rotary evaporator under vacuum at a temperature of 60 °C to a 10% solid concentration. The dry matter content of the wood bark extract was determined by evaporating a known volume of the extract, after which the dry matter

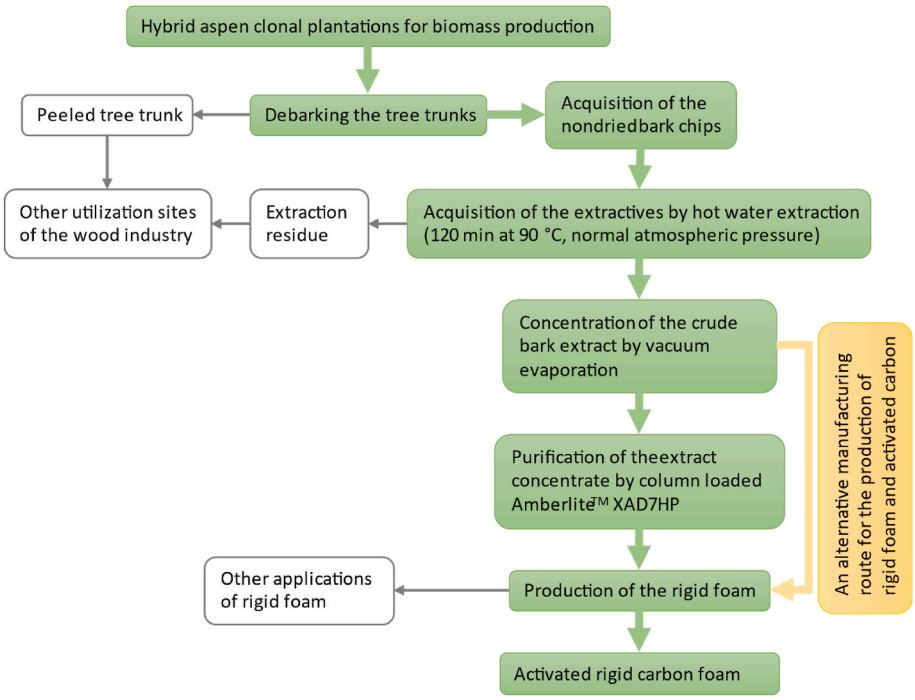

Fig. 1. Proposed flow diagram of the utilization of bark extracts of hybrid aspen trees to manufacture rigid foam and activated rigid carbon foam. Alternative routes to generate extract-based rigid foam, which is an intermediate product to produce activated carbon from the bark extracts, are outlined in the flowchart.

content of the solution was determined based on the mass of solid residue left after evaporation. The extract concentration of the solution was adjusted to 10% by adding distilled water. The pre-concentrated extract was divided into two parts, of which the first half was saved to be foamed as a crude extract, and the second half was cleaned by the solid phase extraction method using the column loaded XAD7HP adsorbent prior foaming. The collected crude extract half was evaporated to dryness by using a rotary evaporator and saved for foaming.

2.1.3. Extract XAD purification treatment

A column loaded with 500 mL of XAD7HP polymer adsorbent (Amberlite™ XAD7HP 20–60mesh, Sigma-Aldrich Production GmbH, France) was used to concentrate the phenolic compounds in the extract prior to foaming. The XAD column was pre-rinsed with 500 mL of water, after which 250 mL of pre-concentrated extract (n = 1) was loaded into the column. Then, the extract was rinsed with 1000 mL of water and eluted from the column with 650 mL of ethanol. The XAD treatment cycles were repeated until all the extract to be cleaned had been processed and collected. The collected ethanol-based extract was evaporated to dryness by using a rotary evaporator and kept for the foaming process.

2.2. Chemical analysis

2.2.1. Bark wood chemical composition

The basic chemical composition of the bark of hybrid aspen tree (n = 6) was determined by chemical assay methods modified from various studies. Hydrophilic and lipophilic extractive contents of the bark were determined by the accelerated extraction (ASE) method [46]; total lignin content was measured as the sum of acid-soluble and acid-insoluble lignin [47]; cellulose content was determined by acid hydrolysis method [48]; and hemicellulose content was analyzed by the acid methanolysis method [49]. The chemical analysis methods applied in the study are described in detail in Korkalo et al. [1].

2.2.2. Total phenol content of the extracts

The total phenol content of the bark extract (bulk sample, n = 1) and XAD-treated extract (bulk sample, n = 1) was determined by the modified Folin-Ciocalteu method [50,51]. The total phenol content was determined as the equivalent of gallic acid (3,4,5-trihydroxybenzoic acid monohydrate, Fluka) by measuring the absorbance of the sample solutions at 725 nm with a spectrophotometer (Shimadzu UV-2600, Simadzu Europa GmbH, Duisburg, F.R. Germany). A gallic acid stock solution was prepared by dissolving solid gallic acid in a small amount of ethanol, followed by dilution with water. For the reference curve, a set of standard samples were prepared from the stock solution by dilution with water. Sample solutions were prepared from bark and extract samples. A total of 250 μL of sample solution, 2000 μL of water, and 250 μL of Folin-Ciocalteu reagent were measured in the sample tubes. The samples were mixed thoroughly and allowed to settle for 5 min. Then, 250 μL of 10% aqueous sodium carbonate solution was added to the samples and mixed thoroughly. The samples were allowed to react for 60 min, after which the absorbances were measured at 725 nm and compared to the reference standard calibration curve. The total phenol content of the samples was calculated per dry matter (mg/g) and reported as a percentage of dry matter of the extracts.

2.2.3. Condensed tannin content

The condensed tannin (CT) content was analyzed according to the method reported by Korkalo et al. [1]. Briefly, after thiolysis, free flavan-3-ols (terminal units) and their cysteamine derivatives (extension units) were determined by ultrahigh performance liquid chromatography (UHPLC) using diode array detection (DAD) and fluorescence detection (FLD). Catechin, epicatechin, gallocatechin, epigallocatechin (Sigma–Aldrich, Espoo, Finland) and thiolyzed procyanidin B2 (Extrasynthese, Lyon, France) were used as reference standards for calibration. A bulk sample (n = 1) was used as samples of unextracted and extracted bark, both of which were used to determine the concentration of condensed tannins to investigate the effectiveness of hot water extraction for separating hydrophilic compounds from the bark mass. Condensed tannins were also determined from the untreated bark extract (bulk sample, n = 1), as well as from the XAD-treated extract (bulk sample, n = 1). This result is used to investigate the effect of XAD-pretreatment on tannin concentrations in extracts.

2.2.4. Carbohydrate profile of the extracts

The carbohydrate profile of bark extract (bulk sample, n = 1) and XAD-treated extract (bulk sample, n = 1) was characterized by a modified acid methanolysis method [49]. For the determination of monomeric sugars, crude extract of bark and the XAD-treated extract were freeze-dried, and the carbohydrate concentrations were subsequently determined per extractive dry matter.

2.3. Synthesis and activation of rigid carbon foam

2.3.1. Synthesis of rigid carbon foam

First, aspen bark extracts (bulk sample, n = 1) purified with XAD or as such (30 g) were placed in a 400-mL beaker, followed by the addition of water, surfactant (polyoxyethylene sorbitan trioleate nonionic surfactant, Tween 85), and furfuryl alcohol. In the case of unpurified aspen bark extracts, the mixture was gently heated on a hot plate at 100 °C to melt the extractives so that mixing of the solution with a spatula was possible. With purified extracts, heating was not needed due to the good solubility of extracts in water. The solution with unpurified aspen bark extracts was allowed to cool down before adding pentane and catalyst (para-toluene sulfonic acid monohydrate, pTSA, 65% water solution) to the solution. The solution was then mixed for 10 s with a spatula. Foaming occurred within a few minutes after placing the beaker in an oven at 100 °C. The foam was hardened for 24 h at this temperature before further use.

2.3.2. Chemical activation of rigid carbon foam

Prior to the chemical activation, rigid foams produced from untreated extract (n = 1) and XAD-treated extract (n = 1) were crushed into fine powder in a mortar followed by the addition of an activation agent with proper ratios to perform the impregnation. Based on our prior knowledge [52], the ratio between the activating agent and foam samples was selected to be 4:1 in all three cases. The impregnation process was performed as follows: 10 g of finely crushed foam was placed in a 600 mL beaker followed by addition of 40 g of $ZnCl_2$, H_3PO_4 or KOH, which were either dissolved or diluted in 100–200 mL of deionized water before adding them into the same 600 mL beaker. The obtained solution was then stirred using a stirring bar at 80 °C for 3 h with the addition of deionized water from time to time if the water level of the solution decreased considerably. Finally, the impregnated wet biofoam was dried in an oven at 105 °C for 48 h. Then, the dried impregnated materials were placed in a stainless-steel reactor heated by a tubular oven. Activations were carried out at 600 °C for 4 h, and nitrogen gas was flushed through the reactor the entire time to avoid sample oxidation. After activation, the reactor was cooled to room temperature, and the samples were collected. In the case of $ZnCl_2$ and KOH, the remaining activation agent was first refluxed with a solution of 1 M HCl at 105 °C for 1 h. The samples were then washed with deionized water to pH neutrality and placed in a ventilated oven to dry overnight. In the case of H_3PO_4 activation, the samples were washed with hot deionized water several times until a neutral filtrate was obtained, followed by drying in an oven overnight.

2.3.3. Characterization of surface properties of activated carbon foam

After chemical activation, the specific surface area (SSA), total pore volume (TPV) and pore size distribution (PSD) of activated carbon foam samples based on hybrid aspen bark extracts were determined at −196 °C with a Micromeritics 3 Flex physisorption instrument (Micromeritics Instruments, Norcross, GA, USA). Prior to the actual measurement itself, 100–200 mg of activated carbon sample was weighed in a sample tube (n = 1), followed by degassing with a Micromeritics smart VacPrep gas adsorption sample preparation device at pressure of 0.67 kPa and at temperature of 140 °C for 3 h to remove any adsorbed gas or moisture inside the samples. After degassing, the sample tubes were placed in the Micromeritics 3 Flex physisorption instrument for analysis. From the physisorption analysis, the adsorption isotherms were obtained by immersing the sample tubes in liquid nitrogen (−196 °C) to achieve constant temperature conditions and by dosing volumes of gaseous nitrogen into the samples.

The obtained data were processed with 3Flex version 5.02 software. SSAs were calculated from adsorption isotherms according to the Brunauer–Emmett–Teller (BET) method [53]. The model selected to estimate the PSD and TPV of activated carbon material was nonlinear density functional theory (NLDFT), with improved contrast and resolution (version 2-deconvoluation selected), based on a model of independent slit-shaped pores specifically designed for carbon structured materials [54–57]. The pore size distribution was calculated from the individual volumes of micropores, mesopores, and macropores with the NLDFT model. By using the instrumental setup, micropores down to a diameter of 0.35 nm can be measured. A previous study reported that SSAs are typically measured with a precision of 5% [58].

2.3.4. Total carbon content

The total carbon (TC) percentage present in each sample (n = 3) was measured using a Skalar Primacs MCS instrument. Dried samples were weighed in quartz crucibles and then combusted at 1100 °C in a pure oxygen atmosphere the resulting CO_2 was then analyzed by an IR analyzer built in the Skalar Formacs analyzer. Carbon content values were obtained by reading the signal of the IR analyzer from a calibration curve derived from known masses of a standard substance, citric acid. The carbon content of the individual samples was calculated as a percentage of the initially weighed mass.

2.3.5. Total yield

The mass yield (wt.%) for each sample (bulk samples, n = 1) was calculated as the measured mass of bark-based activated carbon foam divided by the mass of the initial sample before carbonization and activation.

3. Results and discussion

3.1. Value-added compounds of bark

The chemical composition of bark varies significantly among different tree species of softwoods and hardwoods, and the chemical compositions of the bark largely determine the bark utilization potential [59,60]. The bark mass of the *P. tremula* L. × *P. tremuloides* Michx. contains high amounts of extractable value-added biochemicals [1]. The biochemicals that are separable by different extraction methods can be divided into groups of soluble and insoluble compounds. Soluble compounds can be extracted from bark biomass by a simple solvent extraction method, while insoluble extractives require organic-based pH-adjusted solvent mixtures to be removed. For example, the extraction and isolation of suberic fatty acids (Table 1) of interest as a potential

Table 1
Populus tremula L. × *P. tremuloides* Michx. *bark (n = 6) basic wood chemical composition (Mean ± SD). The basic chemical composition of the bark studied in this research was determined in a previous investigation conducted by Korkalo* et al. *(2022)* [2].

Basic composition	Contents (*mg/g*)
Lipophilic extractives	27.3 ± 7.1
Hydrophilic extractives	168.0 ± 66.5
Condensed tannin	2.30 ± 0.11
Suberic fatty acids	23.7 ± 1.6
Cellulose	200.2 ± 5.8
Hemicellulose	300.4 ± 18.9
[a]Lignin (total)	266.4 ± 15.5
Acid insoluble lignin	223.6 ± 14.3
Acid soluble lignin	42.8 ± 2.8

[a] Total lignin content is the sum of acid insoluble and acid soluble lignins.

value-added product require strong basic conditions [61–63]. From lipophilic and hydrophilic extractive groups (Table 1), the hydrophilic compounds, including condensed tannins [64], can be extracted by hot water. Table 1 shows how the proportion of hydrophilic extractives in the bark biomass is strongly represented, making the fraction a potential value-added product. Condensed tannins are generally thought to be the key precursor in the production of rigid carbon foams [16,65], but in the case of *P. tremula* L. × *P. tremuloides* Michx., the availability of tannins is limited. In addition to the extractable content, the bark biomass contains cellulose, hemicellulose, and lignin, which after hot water extraction can be diverted to other value-added applications according to the cascading use principle [2].

3.2. Extractive yields and chemical compositions

3.2.1. Bark's condensed tannins and extraction efficiency

To evaluate the efficiency of the extraction, the total content of condensed tannins (proanthocyanidins, *i.e.*, the sum of condensed tannins and monomeric flavan-3-ols) was determined from the bark samples by the thioacidolysis method before and after hot water extraction ('*Bark*' and '*HWE Bark*'; Fig. 2a–c). In both, (epi)catechin and (epi)gallocatechin structural units were detected. Thus, it can be stated that the condensed tannins in the bark consist of a mixture of procyanides and prodelphinides. The applied hot water extraction method appears to be more effective in extracting condensed tannins with a shorter oligomeric chain structure, as the average amount of the subunits of condensed tannins remaining in the hot water extracted bark appears to be slightly higher (Fig. 2b). The ratios of (epi)gallocatechins to (epi)catechins in bark biomass also differ after hot water extraction (Fig. 2c), so the ratios between subunits in condensed tannins may also have a slight effect on yields. The main finding is that the bark of *P. tremula* L. × *P. tremuloides* Michx. has a remarkably low content of condensed tannins, which as such does not anticipate the best extractive composition for producing the desired tannin-based rigid carbon foam product. Furthermore, the hot water extraction method applied in this study does not appear to efficiently extract tannins from the bark material (Fig. 2a).

3.2.2. Extraction yields

The concentration of hydrophilic extractives shown in Table 1 indicates the availability of the value-added chemicals in the raw material but does not directly predict the actual yields possible to obtain from the feedstock. In addition to the extraction conditions, extractive yields are also affected by the particle size of the feedstock used and many other variables, which need to be optimized for the best acquisition results [66]. The hot water extraction method used in this study achieved nearly the same extraction yield as the one found in the original bark (Table 1). The extraction yield of 16.5 wt% of bark d.w (Table 2). was obtained, which is an excellent yield compared to the actual content of the hydrophilic compounds (168.0 ± 66.5 mg/g; Table 1). The XAD-purification processing step is expected to have a negative effect on the overall yield of the extractives, which was also observed in this study. However, the yield of the purified extract was found to be 8.95 wt % based on the dry weight of the bark (Table 2); thus, the yield can be considered reasonable if the desired product obtained is a more suitable precursor for the intended application.

Table 2
Conditions and yields for small scale hot water extraction (HWE) of hybrid aspen bark (Bulk sample, n = 1).

HWE	Bark sample mass, *m*	1200 g (d.w.)
	Extractant (H_2O), *m*	8000 g
	Extraction temperature	90 °C
	Extraction time	120 min
Crude extract yield	Obtained extract, *m*	5290.3 g
	Extract solid content, %	3.743%
	Total extractives, *m*	198.02 g (d.w.)
	Extractive yield	**16.5 wt% (of bark d.w.)**
XAD-treated extract yield	Extractive loss, %	45.8 wt% (of extractive d.w.)
	Extractive yield, %	54.2 wt% (of extractive d.w.)
	Extractive yield	**8.95 wt% (of bark d.w.)**

3.2.3. XAD purification of extract

Fig. 3a presents the concentrations of chemical groups of interest in both crude extract and XAD-treated extract. XAD treatment was not found to significantly increase the concentration of condensed tannins in the extracts as the concentration is increased only from 0.7 wt% to 1.0 wt% of d.w. Fig. 3a shows a slight increase in CT concentration due to the XAD treatment, however, the profile of the condensed tannins (Fig. 3c and d) does not change significantly, indicating that XAD purification concentrates CTs without separating different tannin structures from the extract. In this case, further physical and chemical changes in the rigid foams that are produced cannot be explained by the effect of XAD treatment on the change of tannin compositions alone.

The most significant increase in concentration achieved via XAD treatment was found with total phenol content, where the concentration was changed from 10.6 wt% to 17.0 wt% (Fig. 3a). The content of total phenols in the crude extract was unchanged in trembling aspen (*Populus tremuloides* Michx.) water extract [67]. One goal of XAD treatment is to reduce the sugar content of the extract to increase the proportion of phenolic compounds, but in the case of *P. tremula* L. × *P. tremuloides* Michx. bark, the result was the opposite. The sugar profile in Fig. 3b shows that glucose (Glc) is clearly quite abundant in both the crude extract and the XAD-treated extract. The chemical group of '*other substances*' in Fig. 3a refers to a fraction that was not characterized in detail in the scope of this study. The concentration of this undefined group of compounds represents the chemical composition, which has been calculated by subtracting the concentrations of condensed tannins, total phenols, and total sugars from the dry matter of the extractives. In summary, the effect of XAD treatment on the distribution change of condensed tannins, total phenols, and sugars in the extract was smaller

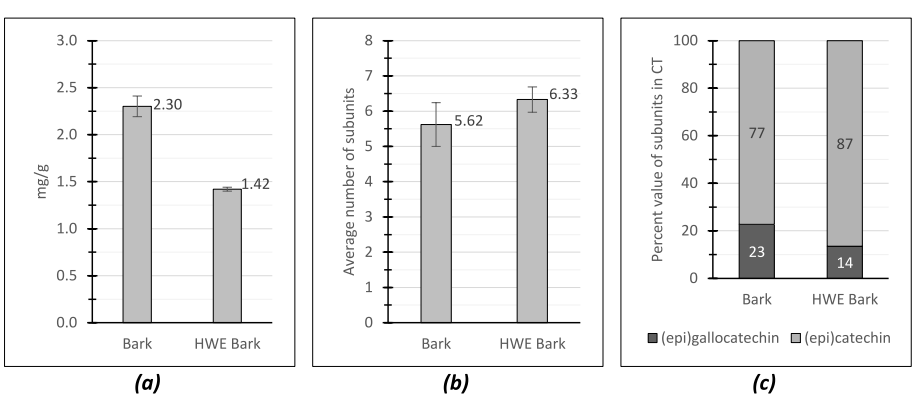

Fig. 2. **(a)** Total condensed tannin (CT) content: total flavan-3-ols (proantocyanidins; i.e., CT + monomeric flavan-3-ols); **(b)** degree of polymerization; and **(c)** PD/PC ratio (PD = prodelphidinins, i.e., (epi)gallocatechin subunits; PC = procyanidins, i.e., (epi)catechin subunits) in the hybrid aspen bark before and after hot water extraction. In the figures, 'Bark' refers to the nonextracted bark mass, and 'HWE Bark' refers to the hot-water extracted bark mass. Both bark samples and hot water extracted bark samples n = 3 (technical replicates used in the analysis methods, mean ± SD).

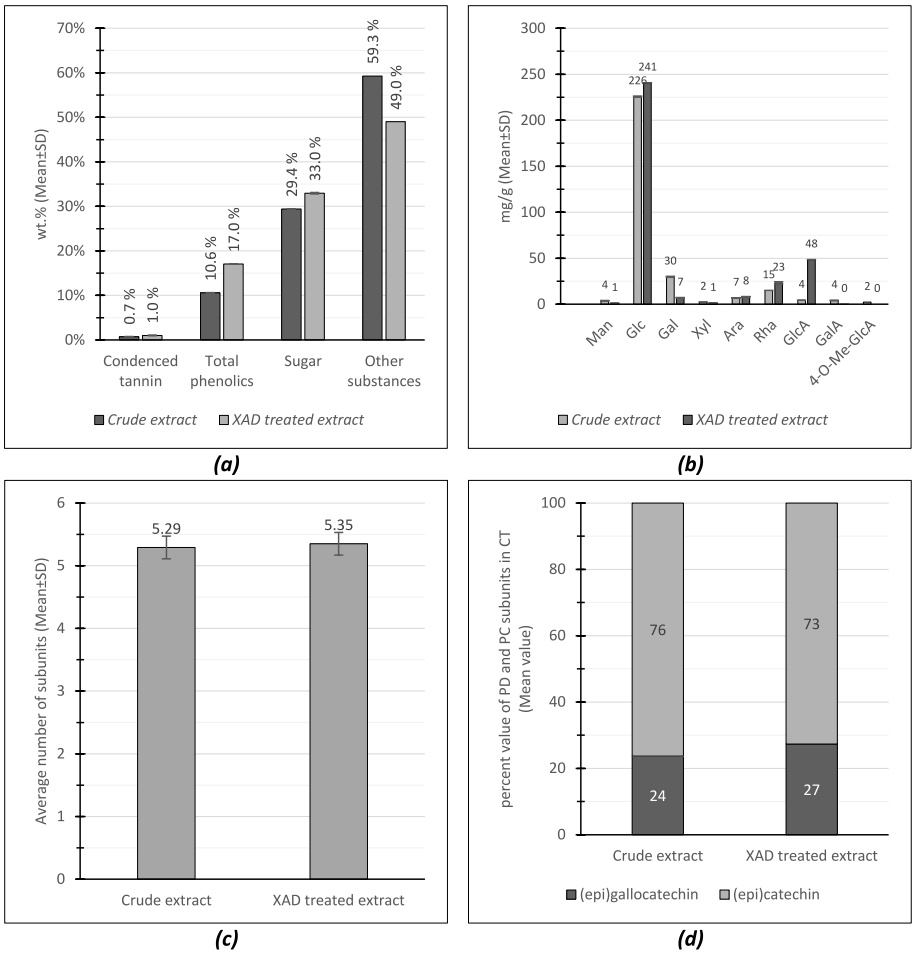

Fig. 3. a) Contents of condensed tannin (CT), i.e., total flavan-3-ols (proantocyanidins: CT + monomeric flavan-3-ols), total phenolics, total sugar, and other uncharacterized substances; expressed as a weight percentage (wt.%) of the dry matter of the crude and XAD-treated extractives; **(b)** Sugar profile (arabinose (Ara), glucose (Glc), glucuronic acid (GlcA), galactose (Gal), galacturonic acid (GalA), mannose (Man), rhamnose (Rha), 4-O-methylglucuronic acid (4-O-Me-GlcA), and xylose (Xyl)) of crude extract and XAD-treated extract; **(c)** degree of condensed tannin polymerization; **(d)** PD/PC ratio: PD (%) = percentage value of prodelphinidins, i.e., (epi)gallocatechin subunits, and PC (%) = percentage value of procyanidins, i.e., (epi)catechin subunits in CT.

than expected. For example, in a study by Varila et al. [23], XAD treatment increased the content of condensed tannins in Norway spruce bark extract.

3.3. Rigid carbon foam and activation

3.3.1. Effect of bark extract XAD treatment on carbon foam

The extract separated from the bark of *P. tremula* L. × *P. tremuloides* Michx. was found to be a suitable precursor for rigid carbon foam. XAD treatment was found to have a particularly good effect on the porosity of the rigid foam, which is detectable by its lower density and better rising capability. The rise in crude extract was found to be 150% with a density of 0.353 g/cm^3. For the XAD-treated extract, the rise of the rigid carbon foam was 550%, and the density was 0.14 g/cm^3. When the goal is to produce a low-density filler material from the extract, the structure achieved by XAD treatment has a significant advantage over the structure of the foam product. The improved foam formation could be explained by elevated levels of condensed tannins and other phenolic substances (Fig. 3). In addition, the purification clearly succeeded in removing components that inhibit foam formation, as the rise of the foam is clearly visible (Fig. 4).

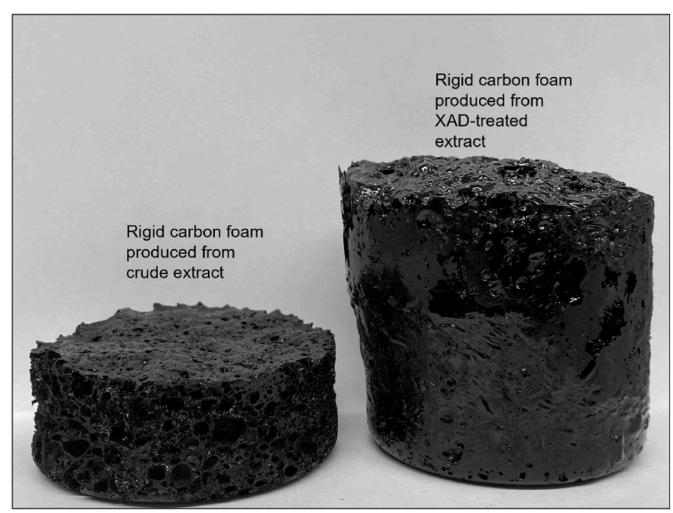

Fig. 4. Difference between crude extract and XAD-treated extract in the rigid carbon foam produced. XAD treatment of the extract improves the rise and therefore lowers the density of the foam.

3.3.2. Surface properties of chemically activated carbon foams

The surface properties of activated carbon foams obtained from physisorption measurements are presented in Fig. 5. As expected, the chemical activations worked well on bark extract-based carbon foams. The quality of the produced activated carbons was equal to or even higher than that of commercially available activated carbons [23,68]. As a comparison, activated carbons typically have a specific surface area of approximately 800–1200 m^2/g and close to 1 cm^3/g of total pore volume available; thus, the quality of activated carbons produced within this study was comparable. However, a deeper inspection of the results showed some variations in the values of the physical properties. For instance, with $ZnCl_2$ activation, using a ratio of 4:1, up to 1375 m^2/g (Fig. 5a) can be obtained with 1.36 cm^3/g of total pore volume (Fig. 6a),

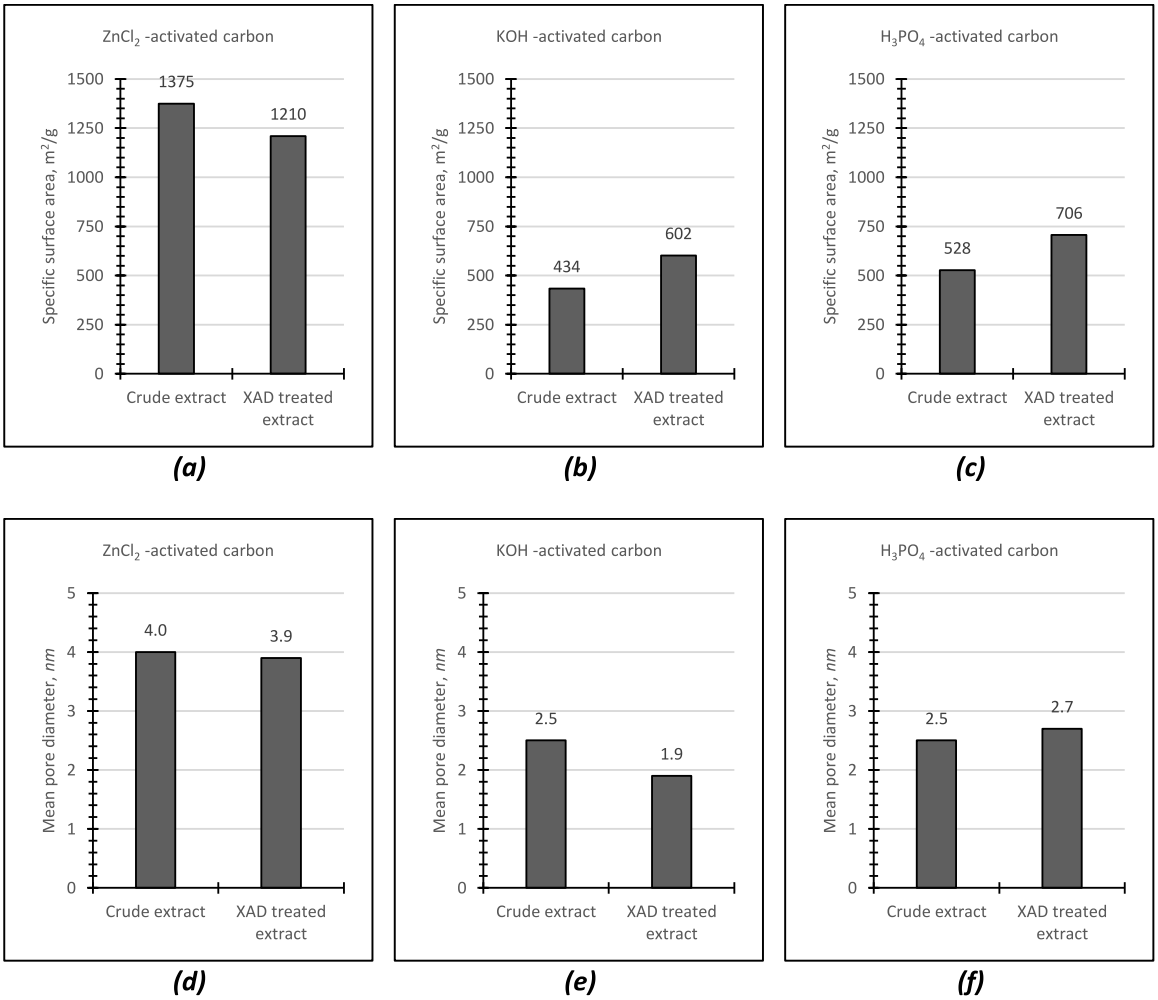

Fig. 5. The effect of different impregnating agents and XAD-treatment of the extract on the specific surface area **(a–c)** and mean pore diameter **(d–f)** values of the activated carbon products. Values are determined by the Brunauer–Emmett–Teller (BET) method (n = 1).

and 74% of this available pore volume is created by the mesopores inside the activated carbon structure (Fig. 6d). Similar results were achieved in our earlier studies with spruce bark extract-based activated carbon foams using a 2:1 ratio of $ZnCl_2$ [23]. Materials in general, with a vast amount of mesopores and great total pore volume, are typically utilized in the adsorption of large molecules from wastewaters, for example. Thus, activated carbon made from a bark extract of *P. tremula* L. × *P. tremuloides* Michx. by a $ZnCl_2$ impregnating agent could be suitable for wastewater treatment according to its surface properties. Chemical activation with KOH or H_3PO_4 produced specific surface areas of approximately 400 m^2/g to 700 m^2/g, respectively (Fig. 5b and c), depending on which extract was used. Chemical activation with KOH is usually performed at higher activation temperatures of 800 °C while using similar ratios as in this study to achieve a specific surface area over 2000 m^2/g and a pore size distribution that is overwhelmed by the micropores (>90%); however, an activation temperature of 600 °C was selected to compare the two activation methods. By comparing the values for activated carbons produced using H_3PO_4 as an activation agent from our previous studies with the results of the current study, we found that the ratio plays a key role in activation. For example, when using a ratio of 1:1 and similar temperatures, the results from H_3PO_4 activation are expected to be on the same level as those using KOH activation at 800 °C and to also have a great amount of micropores. By increasing the ratio, it seems to be possible to tailor the pore size distribution from microporous to mesoporous, as shown in Fig. 6. This is especially true for $ZnCl_2$ and H_3PO_4 activation. Interestingly, by comparing the pore size distribution of activated carbons that were activated with KOH or H_3PO_4 with those produced by $ZnCl_2$ activation (Fig. 6d–f), we can see that the total pore volume available is created by micropores rather than mesopores, especially in the case of KOH activation.

3.4. Total carbon contents and yields from activation

Based on the results in Fig. 7, a higher yield of activated carbon (AC) product was achieved in chemical activation by $ZnCl_2$ (Fig. 7a) rather than by KOH (Fig. 7b). The highest overall yields were obtained by H_3PO_4 activation (Fig. 7c). By examining the contents of total carbon before and after the activation process (rigid carbon foam, '*RCF*' vs. activated carbon, '*AC*'; Fig. 7d–f), it is observed that H_3PO_4 activation clearly decreases the total carbon content of the substance (Fig. 7f). The finding was anomalous; thus, the result was retested for confirmation. The only possible reason for this result is the excess (ratio 4:1) phosphoric acid used in the impregnation step. In our experience, when using an impregnation ratio of 1:1 with H_3PO_4, a higher total carbon content (75–80%) and lower activated carbon yields (45%) are obtained. An excess amount of phosphoric acid may lead to improper impregnation if the chemical activation agent settles on the surface of the foam and therefore cannot properly access the inside of the foam structure. In this situation, the chemical activator evaporates from the surface of the foam rather than from inside, making it impossible for the agent to efficiently produce a desired porous structure, which indicates the limitations of

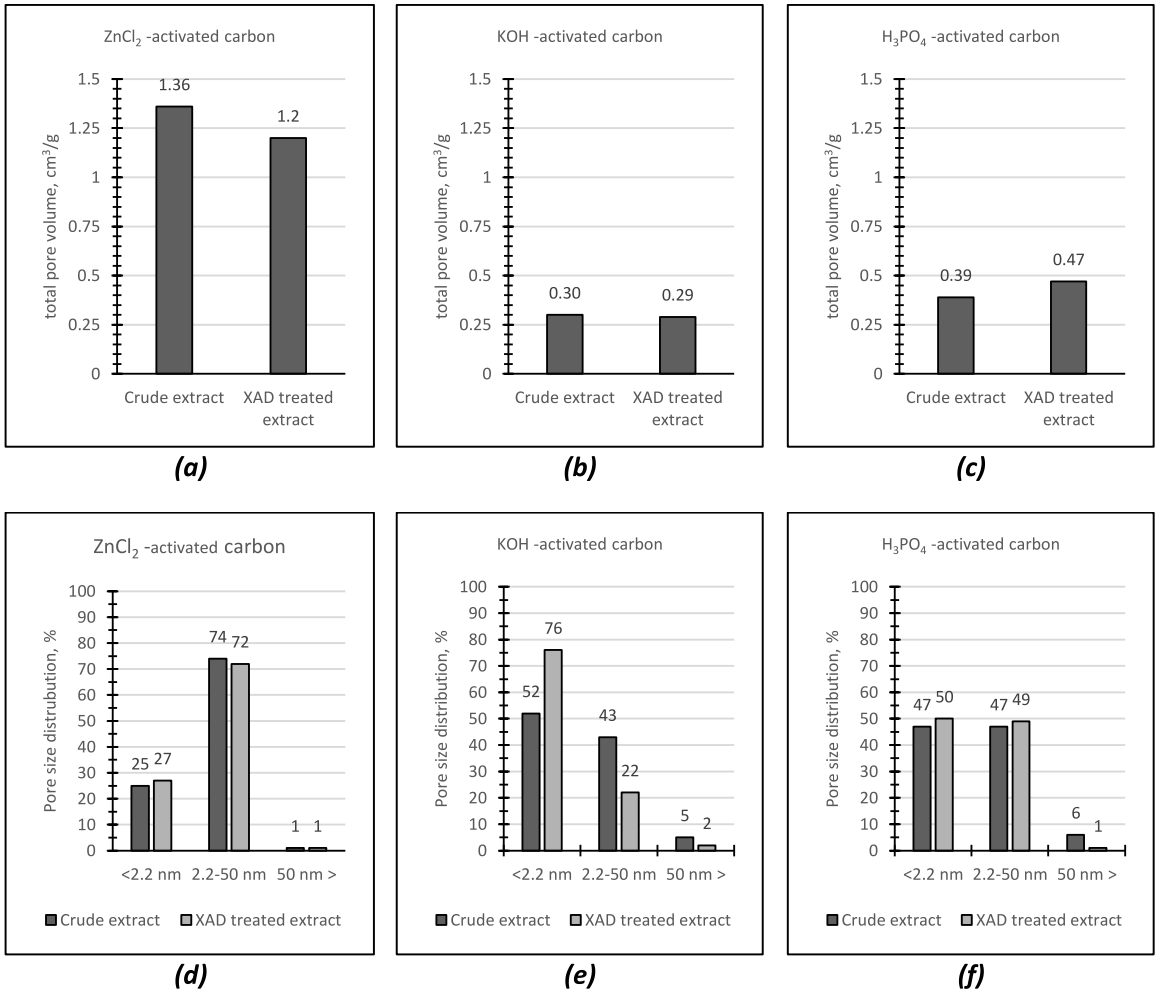

Fig. 6. Total particle volume and pore size distribution determined according to nonlinear density functional theory (NLDFT). Images illustrates the effects of XAD treatment of wood bark extract and different impregnation chemicals on activated carbon pore sizes (a–c) as well as size distributions (d–f) (n = 1).

phosphoric acid as a chemical activator.

3.5. Obtained yields and qualities of activated carbons in relation to the feedstock

Fig. 8 illustrates the activated carbon yields relative to the bark feedstock based on laboratory-scale experiments. The results are calculated considering the crude extract yield (bulk sample, n = 1) and the effects of XAD treatment on the actual extract yield (bulk sample, n = 1). Fig. 8a shows that the best activated carbon yield (9.7 wt%) was produced from the rigid carbon foam prepared from the crude extract by the H_3PO_4 impregnation agent. When activated by $ZnCl_2$, a yield of 8.3 wt% was achieved. The lowest yield (2.5 wt%) is generated when the bark extract is first treated by XAD purification prior to foaming and activated by KOH.

Since the active surface area and pore size are related to the absorption capacity, it is worth investigating how much of these traits can be produced relative to the feedstock. In addition to the best product yield, activation by $ZnCl_2$ clearly produces the largest specific surface area (Fig. 8b) as well as the largest pore volume (Fig. 8c) in relation to the bark feedstock consumed. In this case, this method produces more sorption capacity with less amount of raw material, implicating that the extract separated from the bark biomass has a higher use value.

The maximum product yield may come at the expense of quality, which is perfectly visible for H_3PO_4 activated carbon: the product yield is highest (Fig. 8a), while the actual specific surface area and total pore volume achieved are inferior (7b, c). Compared to $ZnCl_2$ activation, the yield of activated carbon produced by H_3PO_4 is slightly higher, but the actual sorption capacity produced is considerably lower relative to the bark biomass and its extract consumed. In this case, a greater amount of H_3PO_4-activated product is needed to make the total sorption capacity comparable to $ZnCl_2$ activated carbon.

Total carbon yield is an important parameter for the quality of activated carbon, but this also has an interesting connection from the point of view of carbon sequestration. Fig. 8d illustrates how much carbon is recycled relative to the bark biomass used by the total carbon content of activated carbon. Activated carbons produced from the crude extract with $ZnCl_2$ and KOH activators allowed approximately 15 wt% of the carbon to be recovered from the bark biomass. The poorest carbon sequestration is obtained by producing activated carbon from an XAD-treated extract with a an H_3PO_4 impregnating agent. However, it is important to understand that while a better result is achieved using $ZnCl_2$, the chemicals used in activation are harmful to the environment.

In summary, by producing activated carbon from a rigid carbon foam made from crude extract using a $ZnCl_2$ activator, the best utilization ratio for biomass and the highest quality activated carbon product are achieved. However, it is important to note that if the goal is to produce a value-added product that sequesters biomass carbon for reuse, rigid carbon foam is the best option among the products in this study. As illustrated in Fig. 7d–f, the loss of carbon in the production of rigid carbon foam is not very significant even with XAD treatment; thus, it can be assumed that a great portion of the carbon in the bark extract will be

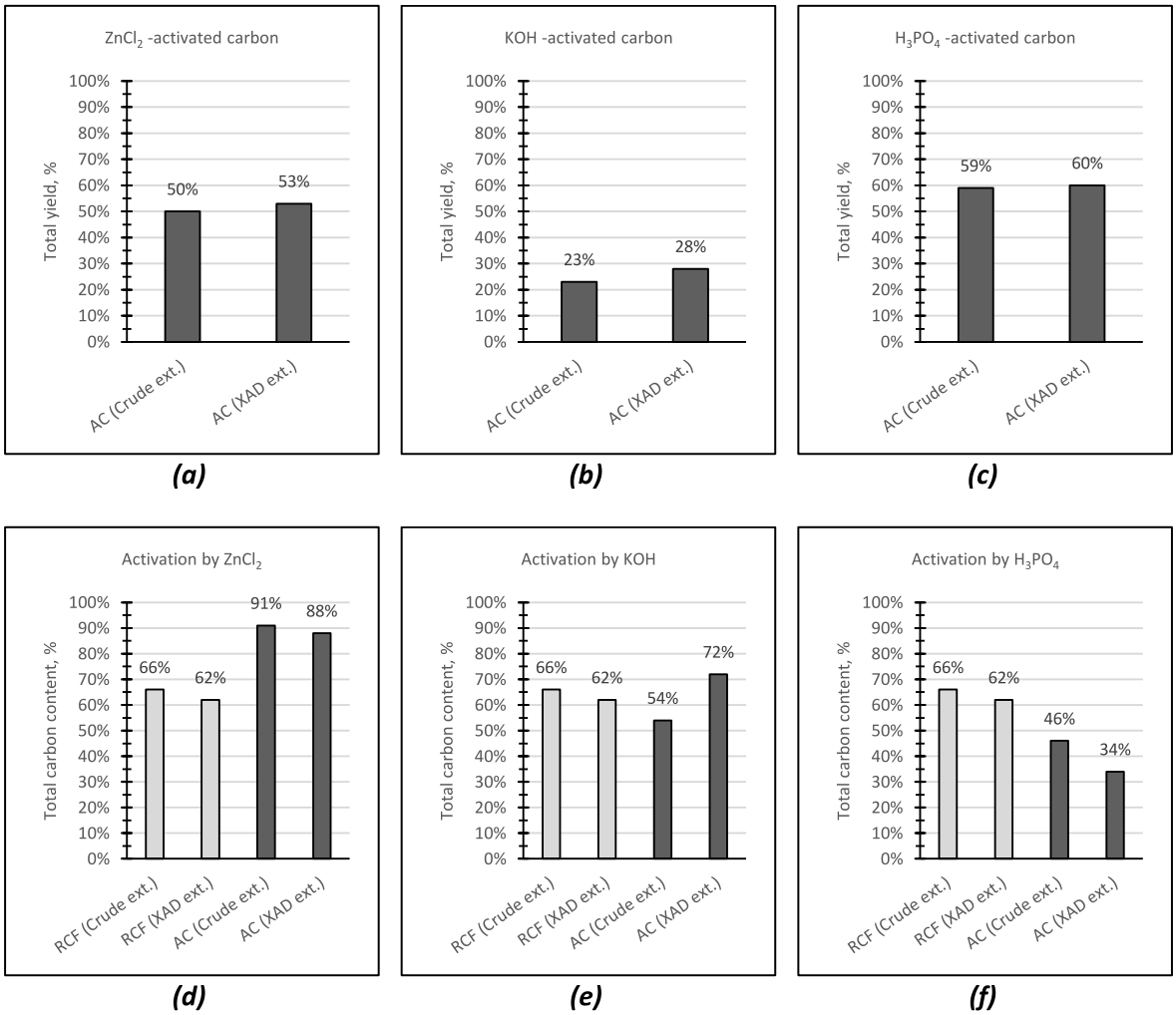

Fig. 7. Effect of XAD treatment of the extract and impregnates used on the total yield of activated carbon (AC) products **(a–c)**; and total carbon contents before and after activation process **(d–f)**. Changes in total carbon contents during the activation process are compared to rigid carbon foam (RCF) made from crude extract (Crude ext.), and XAD-treated extract (XAD ext.), (n = 1).

utilized. The results have been evaluated by laboratory-scale experiments; therefore, the subject requires further investigation by pilot-scale experiments.

4. Conclusions

Populus tremula L. × *P. tremuloides* Michx. bark extract was found to be an excellent precursor in the production of both rigid carbon foam and activated carbon. The dried crude extract separated from the bark can foam satisfactorily without pre-treatments. An XAD treatment of the crude extract was found to have a beneficial effect on the porosity of the carbon foam produced. The positive effect of XAD purification on the quality of rigid carbon foam is speculated to be related to the reduction of interfering substances in the crude extract and the higher concentration of condensed tannins, phenolic substances, and sugars. However, due to the heterogeneous chemical composition of the extracts, further studies are needed to verify the exact compound group-specific effects on foam formation.

XAD treatment of the bark extract has no noteworthy positive advantages in the production of activated carbons. This was the case in all the activation methods studied. Rather, XAD treatment has a disadvantage in the production of activated carbon, as the process results in significantly lower product yields relative to the amount of bark feedstocks used. Based on the results, it can be concluded that if the water-soluble extracts of the bark are to be directed to activated carbon applications, then it is advisable to produce rigid carbon foam as a precursor for activated carbon from the crude extract using $ZnCl_2$ as an impregnating agent. This method produced an activated carbon product with higher quality than its typical commercial counterparts.

Activated carbon yields produced from the bark extractives are low relative to the total weight of the woody biomass feedstock. However, in cases where high-quality activated carbon is one byproduct in the multiproduct recovery of bark side-stream, rigid carbon foam and activated carbon foam are possible options to increase the use value of *Populus tremula* L. × *P. tremuloides* Michx biomass. It should be noted that since the clone trees grown in controlled, scientifically valid experimental plots are valuable and scarce, the experimental results have been carried out from bulk samples of clone tree bark materials and the extracts produced from them. For the same reason, the characterizations of activated carbons and the approximation of the carbon-related atom economy have also had to be conduct without a large sample population. Despite its limitations, this investigation is conducted as a preliminary laboratory-scale experimental study, the results of which will lead to further research on the production of added value from the bark of cloned hybrid aspen trees. The optimization of the methods for pilot-scale biorefinery processes and the statistical examinations of a large sample pool are left for further studies.

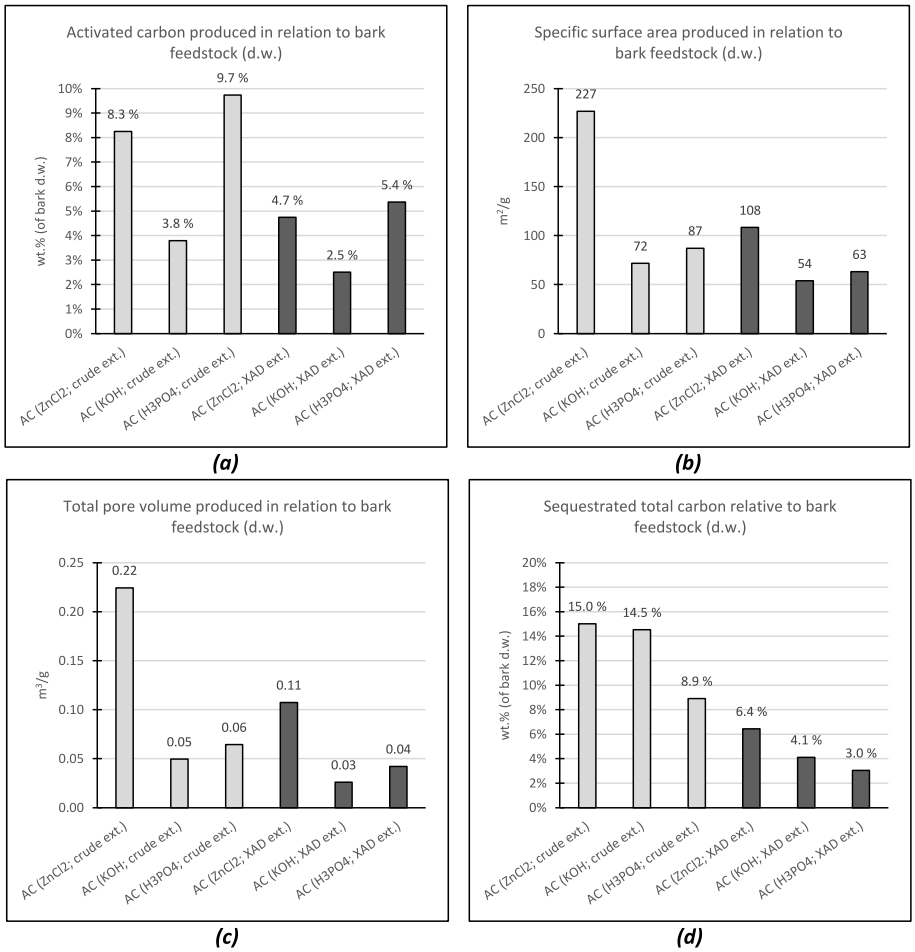

Fig. 8. **(a)** Activated carbon yields; **(b)** Total carbon yield; **(c)** Specific surface area yield; and **(d)** Total pore volume yield produced in relation to bark feedstock volume, (n = 1).

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Author contributions

Pasi Korkalo: Conceptualization, Methodology, Investigation, Writing - Original Draft, Visualization. Toni Varila: Conceptualization, Methodology, Investigation, Writing - Original Draft, Visualization. Hanna Brännström: Conceptualization, Writing - Review & Editing. Jarkko Hellström: Investigation. Tuula Jyske: Project administration, Funding acquisition, Writing - Review & Editing, Supervision. Ulla Lassi: Project administration, Funding acquisition, Writing - Review & Editing, Supervision.

Data availability

Data will be made available on request.

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