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From wood to supercapacitor electrode material via fast pyrolysis

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ABSTRACT

Adding high-value products, such as carbon-based electrode materials for electrochemical energy storage, to the value chain of biorefinery may increase the profits of the whole concept. In this work, carbon-based supercapacitor electrode materials were produced by chemical activation (using KOH) of two fractions of bio-oil (aerosol and condensed) as well as bio-char precursors, all of them originally made from fast pyrolysis of stem wood from pine and spruce. The produced materials show a hierarchical porous structure, a high surface area (1300–1500 m² g⁻¹) and, almost double the specific capacitance (149–152 F g⁻¹ @ 50 mA g⁻¹) compared to commercially available activated carbon (79 F g⁻¹ @ 50 mA g⁻¹). The benefit of using bio-oils compared to biochar is having an electrode material almost free from metal impurities alongside marginally higher energy storage performance. Together with the material yield in the production chain (fast pyrolysis and activation), a normalized energy storage value was presented for each material that may be used in the future to select the best techno-economic route for the whole concept.

1. Introduction

The electrochemical (EC) energy storage market has risen significantly in the last decade to complement the increasing renewable energy generation [1,2]. Batteries are the predominant choice for large-scale EC energy storage owing to their high energy densities [3], but they lack usability for certain high-power applications due to their low power densities, ~1 kW kg⁻¹ [4]. The nature of charge storage in batteries involves diffusion-limited chemical reactions between electrolyte and electrode [5] that limit how quickly charge can be dispersed. Supercapacitors (SCs) based on electric double-layer charge storage can store charge physically along the electrode surface. Since this process is not diffusion limited, SCs exhibit fast charging and discharging [5] and have 10 to 1000 times higher power densities than batteries [3,4]. Additionally, they can withstand over 10⁵ charge/discharge cycles without losing performance significantly [5]. Therefore, SCs are used in high-power applications such as pitch control in wind turbines [6], cordless power tools [7], harvesting energy from regenerative braking in electric cars [8], power backup in circuits [9], and electronic devices [10].

Most widely used SCs, also known as electric double-layer capacitors (EDLCs) derive their capacitance from the electric double layer that forms along the electrode-electrolyte interface upon charging. Electrode materials with high specific surface area (SSA) and electrical conductivity are needed for this application. Activated carbon is the most widely used material in SCs because it is cheap, abundant, easily synthetizable, and has a high electrical conductivity as well as a high SSA [4]. Generally, activated carbon is obtained from a carbon-rich precursor via physical or chemical activation [4,11] of wood [12], pitch [13], coconut shells [14], human hair [15], rice husk [16], dead leaves [17], etc.

Bio-oils are crude mixtures of oxygenated hydrocarbons and water, having low amounts of ash or metal impurities [18]. Bio-oils are typically employed as a substitute for diesel or heating oil [19], converted to synthetic fuels [20], and other useful commodity chemicals [21] via catalytic upgrading. Recently there have also been studies that use bio-oils as a precursor to prepare activated carbon [22–25], employing a lab-scale fixed bed reactor for pyrolysis with a capacity of 500 g of wood and 41 % yield of bio-oil [22], adding to the list of applications for bio-oils.

Fast pyrolysis technologies based on ablative-, fluid bed-, or transport bed technologies, can convert large volumes of biomass into bio-oils [26,27]. Among various fast pyrolysis methods, the cyclone pyrolysis concept first suggested by Lede et al. [28] provides a means of quenching and separating extremely clean bio-oils in a timescale of seconds. Unlike conventional pyrolysis techniques based on fluidized beds, the cyclone does not use sand for heat transfer or char for combustion, thus prohibiting any impurities [29,30]. The cyclone concept
has been further scaled up to ~20 kg h\(^{-1}\) feedstock of wood-based biomass with a yield of ~54 % bio-oils and ~15 % bio-char \([31]\). Furthermore, the operating parameters can be adjusted to obtain different compositions \([32]\) and yields \([33]\) of the products. Fast pyrolysis using a cyclone pyrolyzer and a forest-based feedstock may therefore provide a favorable means of producing large volumes of varying yields of bio-char and clean bio-oils that can be activated to produce high SSA activated carbon materials.

Chemical activation using KOH is a common method to produce activated carbons since it can generate a high SSA (1000–3000 m\(^2\) g\(^{-1}\)) with hierarchical pores at relatively low activation temperatures (700–900 °C) compared to most other methods \([34–36]\). KOH dehydrates to K\(_2\)O and reacts with carbon to form K\(_2\)CO\(_3\) around 400–500 °C forming a layered network with the carbon matrix. Upon activation at 700–900 °C, pores are generated by the release of gases \([36]\), leaving behind a hierarchically porous turbostratic carbon – a carbon lattice with a crystal structure between crystalline graphite and amorphous carbon.

In this study, a simple two-step chemical activation technique using potassium hydroxide (KOH) adapted from Qian et al. \([15]\) and Wang et al. \([36]\) was used to activate bio-oils and bio-char produced from fast pyrolysis. The structure, morphology, and porosity of these materials were investigated. Lab-scale SCs fabricated with these materials show promising electrochemical performance, opening a new frontier for energy storage with activated carbon produced from the products of fast pyrolysis, i.e., bio-oils and bio-char, originating from sawdust of stem wood from pine and spruce, thus expanding the domain of applications of products of fast pyrolysis (Fig. 1). Compared to the vast number of results using a different kind of biomass-derived carbon as electrode material for supercapacitors published in the literature, see for example the recent review by Saini et al. \([37]\), the novelties in the work are: Firstly, the biomass used originates from lignocellulosic biomass from the Northern hemisphere boreal forest, which is the world’s largest terrestrial biome dominated by conifers like spruce and pine \([38]\). Thereby, the source of biomass is abounded, and the results presented here can therefore lead to large-scale production, which is one of the critical factors pointed out by Saini et al. \([37]\) in the future development chain for biobased derived electrode material. Secondly, as outlined in Fig. 1, fast pyrolysis of biomass is a very flexible production technique for commodity chemicals, and as was demonstrated here, also as a precursor material (i.e., the bio-char and the bio-oil) for supercapacitor electrode material. To our best knowledge, there are no previous results in the literature, demonstrating the production of supercapacitor electrode material from simultaneously fast pyrolysis production of bio-char and bio-oil using the same reactor. Furthermore, to generate reliable results, the two-electrode setup was used in the testing of the electrochemical performance of the material which is important according to Saini et al. \([37]\). To summarize, the aim of this work is not to produce new fundamental insight into how different material properties of biomass-derived carbon material influence the electrochemical performance. Instead, the novelty is the demonstration of the whole production chain with an abounded biomass feedstock (pine and spruce), a

![Fig. 1. Applications of biomass processed via fast pyrolysis.](image-url)
flexible production technology (fast pyrolysis), and realistic electrochemical characterization (two-electrode method) resulting in the information that can be used by scientists and engineers to evaluate the proposed concept and maybe large-scale production of biomass-derived supercapacitor material in future biorefineries.

2. Experimental section

2.1. Synthesis of bio-oils and bio-char via pyrolysis

Pyrolysis of wood pellets (sawdust consisting of 70–80 % pine and remaining spruce) was carried out in the fast pyrolysis cyclone, the construction of which is described by Wiinikka et al. [31] The raw material was milled twice – first in a granulator (Rapid granulator) and subsequently in a hammer mill (Mafa EU-4B). Particles were then put through a sieve shaker (Fritsch, Analysette 3) for determining particle size distribution. Most of the particles were in the 250–500 μm size range (52 %) and <1 mm (99.5 %).

The pyrolyzer was run at 20 kg h⁻¹ capacity corresponding to 100 kW thermal power. The feed was carried to the pyrolyzer via a Nitrogen stream heated at 100 °C. The biomass capacity over the heated area was 24 kg h⁻¹ m⁻². The wall temperature of the cyclone was maintained at 750 °C. The solid residue was collected at the bottom of the cyclone and labeled as bio-char (BC). The carrier gases were let through a water-cooled heat exchanger maintained at 25 °C to collect bio-oil. The bio-oil collected at this stage was labeled as bio-oil condensed fraction (BOC). The remainder of the gases were let through an oil mist separator, and the bio-oil collected at this stage was labeled as bio-oil aerosol fraction (BOA).

2.2. Chemical activation to prepare electrode material

Each one of these materials - BC, BOC and BOA was activated using 1 g ml⁻¹ solution of KOH (Merck). First, each raw material was mixed with KOH solution in 1:2 ratio by weight and sonicated followed by overnight drying in an oven at 100 °C to reduce water content. All weights of the biomass samples (including oils) in the activation procedure are on as received bases, i.e., the moisture content is included. Activation was done in two steps in a muffle furnace – first at 400 °C for 1 h followed by removing and mixing the char and then activating again at 800 °C for 1 h in alumina crucibles covered with lids. The final product was thoroughly rinsed with HCl (Merck) and distilled water with centrifugation to remove supernatant until a neutral pH was obtained and then dried in an oven. Activated powder produced this way from BC, BOC and BOA were labeled as BCa, BOCa and BOAa, respectively. These would collectively also referred as “in-house synthesized materials”. Additionally, commercial activated carbon (AC) from Merck was used as a benchmark material to compare the materials synthesized in-house.

2.3. Structural and morphological characterization

X-Ray Diffraction (XRD) was performed with Bruker Phaser D2 X-Ray diffractometer that uses Cu Kα radiation. The diffractograms were analyzed using the DiffracEVA software and OriginPro. Analogous to soot turbostratic structure, Scherrer’s formula [39] was used to obtain structural parameters – interlayer spacing (d₀₀₂), nanocrystalline height (Lc), and nanocrystalline width (Lw) according to –

where, Kₐ = 0.9, λ = 1.84 Å (for CuKα), θ₀₀₂ and θ₁₀₀ are the Bragg’s angles, and B₀₀₂ and B₁₀₀ are the full widths at half maximum (FWHM) for (002) and (100) peaks, respectively.

Scanning electron microscopy (SEM) was performed using a Hitachi TM3030 tabletop scanning electron microscope. Energy dispersive X-ray (EDX) spectroscopy was performed with the attached Bruker Quantax 70 EDX detector. High-resolution SEM (HR-SEM) was performed with an FEI Magellan 400 field emission XHR-SEM.

Porosity analysis was performed with an ASAP 2020 porosimeter using Nitrogen adsorption at 78 K. The samples were degassed at 200 °C for 6 h before measurements. Surface area and pore analysis were done by analyzing the adsorption-desorption isotherms using Brunauer–Emmett–Teller (BET) and Barrett-Joyner-Halenda (BJH) methods. The first point in the adsorption-desorption isotherms was at a relative pressure ratio (P/P₀) of 0.01 and it was not possible to reduce this pressure further with the instrumental setup (i.e., the type of the pumps installed). Therefore, the pore size distribution of the micropore presented in this work is less accurate compared to the size distribution of the larger pores (meso-, and macropores).

2.4. EC characterisation

Each material (AC, BCa, BOCa, and BOAa) was thoroughly mixed individually with conductive carbon black (Alfa Aesar) and binder polyvinylidene fluoride (Alfa Aesar) in the weight ratio 7:1:2 in the solvent 1-N-Methyl-2-pyrrolidone (Alfa Aesar) to form a homogenous ink. The ink was spread on a current collector Ni Foil (MTI corp.) using a doctor blade setup to form a film of 20 μm and dried at 75 °C in an oven.

Two circular electrodes of 12 mm diameter were punched out, pressed at 600 psi, and weighed. The mass loading on electrodes was 1.1–1.5 mg cm⁻². For each cell, two electrodes with very close weights (maximum weight difference of 3 %) were chosen. A 14-mm circular piece of glass fiber filter (Whatman) and 6 M KOH solution were used as separator and electrolyte, respectively. CR2032 coin cell components (MTI corp.) were used to fabricate a cell. The cell was assembled and pressed in a hydraulic crimping machine at 750 psi. Each cell was left undisturbed for a day before EC measurements.

EC characterization was performed on the coin cells in a two-electrode setup using a BioLogic potentiostat and EC-Lab software. Cyclic voltammetry (CV) was performed within 0–0.8 V at different scan rates from 5 mV s⁻¹ to 100 mV s⁻¹. Electrochemical impedance spectroscopy (EIS) was performed with a 10 mV amplitude sine wave in the frequency range from 100 kHz to 100 mHz and fitted with an equivalent circuit. Bulk solution resistance (Rₛ) and charge-transfer resistance (Rₜ) are obtained from the fit, while equivalent series resistance (ESR) is obtained by extrapolation of the curve from the low-frequency region of the Z’ axis. Galvanostatic charge-discharge (GCD) with potential limits of 0 V and 1 V was performed at different current densities ranging from 50 mA g⁻¹ to 10 A g⁻¹. Long-time cycling was performed for >10,000 cycles at 5 A g⁻¹.

The specific capacitance, Cₛ (F g⁻¹) was calculated from the galvanostatic discharge curves using –

where I is the current (mA), t is the discharge time (s), ΔV is the voltage difference (V) after the IR drop, and m is the combined mass of active material in both electrodes (mg). The energy density (W h kg⁻¹) was calculated from the discharge curves using –

where Cₛ is the specific capacitance (F g⁻¹) from Eq. (4), ΔV is the voltage difference (V) after IR drop and the factor 3.6 in the denominator accounts for unit conversion. Lastly, the power density (W kg⁻¹)
was calculated from the discharge curves using equation –

\[ P = \frac{E \cdot 3600}{t} \] (6)

where \( E \) is the energy density (W h kg\(^{-1}\)) from Eq. (2) and \( t \) is the discharge time (s). Also, the maximum power density (W kg\(^{-1}\)) possible is given using ESR for the device using equation –

\[ P_{max} = \frac{\Delta V^2}{4 \cdot m \cdot ESR} \] (7)

where \( \Delta V \) is the voltage difference (V), \( m \) is the combined mass of active material in both electrodes (kg) and ESR is the resistance (\( \Omega \)) obtained from Nyquist plots.

3. Result and discussion

3.1. Structural characterization

The turbostratic nature of all activated carbon materials was confirmed using XRD (Fig. 2a) showing broad graphitic peaks near 23° and 44° corresponding to the (002) and (100) planes in graphitic carbon lattice, respectively. XRD diffractogram for BC\(_K\) shows some crystalline impurities suggesting the presence of calcite impurities (Fig. S1). BOA\(_K\) and BOC\(_K\) are free from any crystalline impurities since ash elements are retained in the biochar during pyrolysis [31]. The crystal structure of activated carbons resembles other turbostratic carbon materials like carbon black. Pure crystalline graphite structure gets distorted and

Fig. 2. Structural characterization. (a) XRD patterns for AC, BC\(_K\), BOC\(_K\) and BOA\(_K\). SEM micrographs for (b) AC, (c) BC\(_K\), (d) BOC\(_K\) and (e) BOA\(_K\) at different magnifications.
crystallite sizes for the materials are calculated using Scherrer’s formula \( d_{002} = 0.34 \text{ nm} \) for crystallite graphite [40]). This likely originates from weaker van der Waals forces indicating a higher degree of disorder between the layers [42]. \( L_a \) is indicative of the average crystallite size and the ratio of edge to basal carbon atoms. Higher values indicate a lower number of edge atoms and thus lower reactivity [42], which is the case for activated materials (Table 1). Lower reactivity ensures longer stability in the presence of an electrolyte.

The porous structure of AC, BC\(_K\), BOC\(_K\), and BOA\(_K\) was investigated using HR-SEM (Fig. 2b-e). Pores can be seen at different length scales for BC\(_K\), BOC\(_K\), and BOA\(_K\) confirming a hierarchical network of pores. In contrast, AC lacks large macropores and exhibits pores only at submicron scales indicating a lack of a hierarchical porous network. Additionally, an SEM micrograph of a dried particle from the condensed oil fraction does not show the presence of any hierarchical pores (Fig. S2), suggesting that the porous network is a consequence of adsorption. Semi-quantitative EDX analysis of BC\(_K\), BOC\(_K\), and BOA\(_K\) shows a high carbon content (88–90 %) with some oxygen (~6–10 %) and some impurities (0–3 %) in the samples (Fig. S3). These materials are rich in carbon with some amount of oxygen, which is likely present as functional groups alongside the edge carbon atoms and assists in wetting of the electrode material with aqueous electrolyte when employed in the SCs [43].

Nitrogen adsorption/desorption isotherms and pore size distribution calculated using BET and BJH is shown in Fig. 3. The first point in the adsorption/desorption isotherm located at a \( P/P_0 \) ratio of 0.1 is not zero since a certain amount of nitrogen has already been adsorbed by the micropores in the material. From the first point in the adsorption/desorption isotherm, there is therefore an indication that BOC\(_K\) has higher amounts of micropores compared to BC\(_K\) and BOA\(_K\) and that all of them have significantly more micropores compared to AC. The Specific surface area (SSA) and other porosity parameters were calculated for all the materials (Table 2). BC\(_K\), BOC\(_K\), and BOA\(_K\) show a high SSA (1300–1500 m\(^2\) g\(^{-1}\)) due to their hierarchical porous structure, while AC has a relatively lower SSA (984 m\(^2\) g\(^{-1}\)) since it lacks hierarchical pores. The pore volume for BC\(_K\), BOC\(_K\), and BOA\(_K\) is comparable (0.41–0.43 cm\(^3\) g\(^{-1}\)) and nearly twice that for AC (0.23 cm\(^3\) g\(^{-1}\)). BOA\(_K\) has the lowest pore size at 3 nm, followed by BOC\(_K\) at 3.2 nm and BC\(_K\) at 3.7 nm. AC has a larger average pore size at 4.5 nm. From average pore sizes and pore volumes, we can deduce that all three materials BC\(_K\), BOC\(_K\), and BOA\(_K\) have on average, smaller pores and more numerous pores for the same amounts of material, which translates to a higher SSA and capacitance.

### 3.2. EC characterization

CV at a scan rate of 50 mV s\(^{-1}\) (Fig. 4a), indicates the amount of charge stored. BOC\(_K\) and BOA\(_K\) both store a high amount of charge, with BC\(_K\) only marginally less. All three materials store significantly more charge (by a factor of 2) than AC. This behavior is also observed at different scan rates ranging from 5 mV s\(^{-1}\) to 100 mV s\(^{-1}\) (Fig. S4). The capacitive current (from the positive sweep) is linearly proportional to the scan rate and not to the square root of the scan rate (Fig. S5), suggesting that the reactions are adsorption-controlled and not diffusion-controlled, which is expected in EDLCs [44]. Additionally, all three in-house synthesized materials reach saturation current faster in the charging cycle compared to AC, especially for higher scan rates. This is indicative of a lower resistance for the in-house synthesized materials since the delay in reaching the saturation current is caused by the internal resistance of the material [45].

Galvanostatic charge-discharge (GCD) was performed for an accurate calculation of specific capacitance \( (C_{sp}) \). Fig. 4b shows GCD curves for all the materials. At high current densities (5 and 10 A g\(^{-1}\)), a visible IR drop can be seen at the start of the discharge cycle for each material (Fig. S6). This drop is more prominent in AC than in the in-house materials. \( C_{sp} \) for all materials is calculated using Eq. (4) and \( C_{sp} \) shows the highest \( C_{sp} \). BOC\(_K\) and BOA\(_K\) show a similar range but slightly less than 132.9 F g\(^{-1}\) and 128.7 F g\(^{-1}\), respectively. All three materials outperform AC \( (C_{sp} = 70.8 \text{ F g}^{-1}) \) by at least 80 %.

Fig. 5 shows the Nyquist plots, equivalent circuit, and fits for all materials with calculated impedance values. BOC\(_K\), BOA\(_K\), and BC\(_K\) show a total resistance of 1.40 Ω, 2.29 Ω and 3.45 Ω, respectively, while AC shows a resistance of 4.71 Ω, which is more than three times that of BOA\(_K\) and almost two times that of BC\(_K\) and BOA\(_K\) at 20 % of that of BC\(_K\). The total device resistance is a complex value comprising the resistance of device components, electrolyte, and resistance across interfaces, and bulk electrolyte resistance [46]. With electrode material as the only variable and other contributors to the device resistance, i.e., cell components, binder, electrolyte, and measurement conditions are kept approximately the same, BC\(_K\), BOA\(_K\), and AC show a relatively lower resistance and hence, higher conductivity than AC. This also supports the fast saturation observed in the CVs and a low IR drop at the beginning of the discharge cycle for GCD curves of in-house materials compared to respective observations for AC.

The performance of SC devices across a wide range of current densities, known as rate capacitance, represents different working conditions SC undergoing. This essential parameter for all materials is compared in Fig. 6a. Between the slowest and fastest currents, 50 mA g\(^{-1}\) and 10 A g\(^{-1}\), respectively, BOC\(_K\) and BOA\(_K\) shows a decrease in \( C_{sp} \) of 86 % and 79 %, respectively. BC\(_K\) shows a slightly larger decrease (75 %), also similar to AC (74 %). Overall, BOA\(_K\) shows the best rate capacitance across a wide range of current densities. The cycle life of supercapacitors is one of the most crucial factors since SCs must retain their capacitance over many cycles. All the materials show high retention (>97 %) for over 10,000 charge and discharge cycles (Fig. 6b). SCs are crucial for high-power applications, and it is important to evaluate the power and energy densities of the materials. Fig. 6c shows a Ragone plot with energy density and power density for all the materials as measured at different current densities. At the lowest current density condition (50 mA g\(^{-1}\)), BOA\(_K\) shows the highest energy density among the four materials, 5.28 W h kg\(^{-1}\). BOC\(_K\) and BC\(_K\) show 5.14 W h kg\(^{-1}\) and 5.16 W h kg\(^{-1}\), respectively. All three materials show a higher energy density than that of AC (2.75 W h kg\(^{-1}\)). At the highest current density condition (10 A g\(^{-1}\)), BOA\(_K\) shows the highest energy density 4.07 W h kg\(^{-1}\), while BOC\(_K\) and BC\(_K\) show 3.72 W h kg\(^{-1}\) and 3.24 W h kg\(^{-1}\), respectively, and still outperform AC (1.75 W h kg\(^{-1}\)). As BC\(_K\) shows the least resistance (Fig. 5c), it also has a maximum possible power density of 71.4 kW kg\(^{-1}\), followed by BOA\(_K\) and BC\(_K\) at 40.1 kW kg\(^{-1}\) and 23.3 kW kg\(^{-1}\), respectively. All three materials again outperform AC at 16.0 kW kg\(^{-1}\).

As pore morphology is a crucial factor for an electrode’s charge storage capability, we compare \( C_{sp} \) for all the materials normalized to the BET surface area of each material (Fig. 7). BC\(_K\), BOA\(_K\), and BOA\(_K\) all show a higher \( C_{sp}/BET \) at different condition when compared to AC, even after normalizing against the SSA. The nature of pores, i.e., hierarchical pores lower pore size and greater pore volume for BC\(_K\), BOC\(_K\), and BOA\(_K\) all contribute to their higher \( C_{sp} \) compared to AC.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Crystal parameters</th>
<th>( d_{002} ) (nm)</th>
<th>( L_a ) (nm)</th>
<th>( L_s ) (nm)</th>
<th>( L_v/d_{002} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>AC</td>
<td>0.37</td>
<td>1.24</td>
<td>3.99</td>
<td>3.33</td>
<td></td>
</tr>
<tr>
<td>BC(_K)</td>
<td>0.45</td>
<td>2.03</td>
<td>3.84</td>
<td>4.49</td>
<td></td>
</tr>
<tr>
<td>BOC(_K)</td>
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<td>1.07</td>
<td>4.17</td>
<td>2.63</td>
<td></td>
</tr>
<tr>
<td>BOA(_K)</td>
<td>0.40</td>
<td>0.99</td>
<td>3.98</td>
<td>2.49</td>
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</tbody>
</table>
3.3. Yield analysis and further optimization

Analyzing the yield of the whole production chain, i.e., from the feedstock to the final electrode material, may be useful for the selection of the best production strategy and further techno-economic analysis. Fast-pyrolysis converts the feedstock yields 35.2 wt-% BOC, 19.4 wt-% BOA and 15.2 wt-% BC [31]. Further, KOH activation yields 7.4 wt-% BOC$_K$, 9.8 wt-% BOA$_K$ and 28.6 wt-% BC$_K$.

The carbon yield from raw biomass (dry) to the final carbon-rich electrode material was 6.9 wt-% for BC$_K$, 4.7 wt-% for BOC$_K$, and 3.2 wt-% for BOA$_K$. Taking these yields into account, Fig. 8 illustrates the amounts, $C_{sp}$, energy and power densities at 50 mA g$^{-1}$ and 10 A g$^{-1}$ for all the materials obtained using pyrolysis and activation process, starting with 1 kg biomass as feedstock. We demonstrate that we can convert 1 kg of biomass into three different products and further into activated carbon materials, which combined have a capacitance of over 13.2 kF, can store 0.46 W h of energy, and exhibit 216 W of power.

Bio-oils contain some amount of water in their weight as a part of the process which is 22.6 % for BOC and 7.6 % for BOA [31]. Adjusting for this, the yields for BOC$_K$, and BOA$_K$ are 9.5 % and 10.6 %, respectively. Additionally, both BOC and BOA have less amount of carbon in them (55.1 % and 58.3 % by weight excluding water weight) when compared to BC (68.7 % by weight).

The whole process has probably room for further optimization. The yield and quality of both the bio-char and fast pyrolysis bio-oil depend significantly on the feedstock and process temperature of the cyclone pyrolyzer [32,33]. Other fast pyrolysis techniques also have different yields compared to the cyclone pyrolyzer, for example the yield of bio-oil from fast pyrolysis of wood can be as high as ~75 wt-% [47]. Furthermore, pre-treatment by alkali removal of the raw biomass can also increase the yield of the produced bio-oil [48]. The activation step (i.e. thermal- or chemical activation) producing the porous carbon also affects the yield and quality of the electrode material and the EC characteristics of the final cell [49]. For example, chemical doping of the activated carbon with N, S, or P [50–53], or the introduction of graphitized carbon dots [54] are known to increase the capacitance of the.

### Table 2

<table>
<thead>
<tr>
<th>Sample</th>
<th>Porosity parameters</th>
<th>$S_{BET}$ (m$^2$ g$^{-1}$)</th>
<th>$S_{micro}$ (m$^2$ g$^{-1}$)</th>
<th>V$_{pore}$ (cm$^3$ g$^{-1}$)</th>
<th>D (nm)</th>
</tr>
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<tbody>
<tr>
<td>AC</td>
<td></td>
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<td>594</td>
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<td>1085</td>
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<td>1384</td>
<td>1045</td>
<td>0.41</td>
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</tbody>
</table>

**Fig. 3.** (a) Nitrogen adsorption/desorption isotherms for AC, BC$_K$, BOC$_K$ and BOA$_K$. (b) Pore size distribution for AC, BC$_K$, BOC$_K$ and BOA$_K$. 

**Fig. 4.** (a) Cyclic voltammograms of AC, BC$_K$, BOC$_K$ and BOA$_K$ at 50 mV s$^{-1}$ scan rate. (b) GCD curves of AC, BC$_K$, BOC$_K$ and BOA$_K$ at 1 A g$^{-1}$ current density.
electrode material. However, it is highly dependent on the composition of the precursor before activation and in our case, doping of the precursor would add another step of complexity in preparation. It would be interesting to explore other sources of Nordic biomass already rich in such dopants in the future. As there are many parameters, all the way from the composition of the raw biomass to the production technique of the electrode material that affect the final yield and EC performance of the supercapacitor, optimization of the whole value chain is very complicated and beyond the scope of the present work. However, we believe that these results can give the first insights into this question and encourage us and others to explore the most efficient and optimal production route for environmentally friendly supercapacitors material.

Fig. 5. (a) Nyquist plots for all materials. (b) Equivalent circuit used for the fitting of Nyquist plots. (c) Fitting of each curve with the equivalent circuit. $R_s$ and $R_{ct}$ values are calculated from the fitting of each curve. The ESR values are calculated by extrapolating the low frequency capacitance line to the $Z'$ axis.

Fig. 6. (a) Rate capacitance of AC, BC$_K$, BOC$_K$ and BOA$_K$. (b) Capacitance retention over long cycles for AC, BC$_K$, BOC$_K$ and BOA$_K$ measured at 5 A g$^{-1}$ current density. (c) Energy and power densities of AC, BC$_K$, BOC$_K$ and BOA$_K$ on a Ragone plot calculated at current densities ranging from 50 mA g$^{-1}$ to 10 A g$^{-1}$.
4. Conclusion

We demonstrate the synthesis of activated carbon materials from forest-based biomass (pine and spruce mixture) via fast pyrolysis followed by chemical activation. All three materials show a high SSA, $C_{sp}$, energy as well as power densities than commercially available AC at a range of different conditions. The materials also show a long cycle life of over 97% capacitance retention after 10,000 charge-discharge cycles.

Structurally, the prepared activated carbon materials prepared are highly amorphous carbon materials with a hierarchical porous structure and a high SSA (1300–1500 m² g⁻¹), which translates to a high $C_{sp}$ in lab-scale devices. BOC$_K$ shows a high-rate capacitance (86 % at 10 A g⁻¹ with respect to $C_{sp}$ at 50 mA g⁻¹). BOA$_K$ shows the highest energy density of 5.3 W h kg⁻¹ and power density of 12.8 W kg⁻¹ at the lowest current density, while BOC$_K$ shows the highest energy density of 4.1 W h kg⁻¹ and power density of 2862 W kg⁻¹ at the highest current density (10 A g⁻¹). BOC$_K$ also shows the lowest resistance compared to the other materials.

Analyzing the yield gives information about what route to select for preparing an activated carbon material from the biomass feedstock. Combined, all products show a capacitance of over 13 kF for 1 kg of biomass feed. Each material has its own merit – BOC$_K$ shows overall better rate capacitance, lowest resistance, and highest energy and power densities at high current conditions. BOA$_K$ shows the highest energy and power densities at low current conditions. BC$_K$ has a higher yield of preparation and can be considered a by-product as the goal of fast pyrolysis is to produce bio-oil. The process has room for improvement regarding optimization of yields and as well as tailoring to produce different yields of various products.

CRediT authorship contribution statement

Jaskaran Singh Malhotra: Conceptualization, Investigation, Data curation, Methodology, Writing – original draft.
Roudabeh Valiollahi: Conceptualization, Methodology, Writing – review & editing, Funding acquisition, Supervision.
Henrik Wiinikka: Conceptualization, Writing – review @ editing, Funding acquisition, Supervision, Project administration, Resources.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.
Data availability
Data will be made available on request.

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Appendix A. Supplementary data
Supplementary data to this article can be found online at https://doi.org/10.1016/j.est.2022.106179.

References

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