Abstract: Porous carbon materials (specific area over 2400 m$^2$ g$^{-1}$) were obtained from birch wood chips, the waste of its thermochemical processing water-insoluble lignocellulosic pyrolysis tar, and their mixture, by thermochemical activation with NaOH at 800 $^\circ$C. Raw materials were carbonized by two methods: pyrolysis (500 $^\circ$C) and hydrothermal (250 $^\circ$C) treatment. The elemental and chemical composition of precursors and the effect of these parameters on the obtained carbon materials' structure and porosity were studied. Results of the study showed that the carbonization method has little effect on the activated carbons’ specific surface area values; however, it allows for the regulation of pore size distribution.

Keywords: biomass; hybrid material; pyrolysis; hydrothermal treatment; alkali activation; mesopores
Carbon materials for the implementation of efficient electrochemical reactions should have varying properties, such as a high surface area, high electrical conductivity, and wettability [15]. The list of necessary properties and features of the porous structure, necessary for use in energy devices, could be continued.

For these purposes, scientists have proposed the production of carbon microporous materials with a high surface area based on thermochemical activation with alkalis using various types of plant biomass, including biomass from processing waste [16–18]. Alkali metal hydroxides and salts are the most effective activators in this regard, with a few cases allowing the production of activated carbon with a surface area (calculated using the BET theory) exceeding 3000 m² g⁻¹, which is higher than the theoretical limit for pure graphene sheets (~2630 m² g⁻¹) [19–21]. Chemical activation for the production of highly porous activated carbon using alkali hydroxides most commonly utilizes KOH, while the utilization of NaOH is less common. However, from the point of view of the cost of the process, the use of NaOH is more profitable, and the efficiency of alkaline activation does not decrease when using biomass as a raw material [22]. The main variables that affect activated carbons’ total porosity and pore distribution are the precursor nature, precursor to activator ratio, impregnation method, heating rate, reaction time, and temperature [23].

The diversity of biomass feedstocks and different carbonization methods allow the use of precursors with different structures and chemical compositions for activation. This approach can expand the possibilities of influencing the formation of a porous structure, in particular changing the pore size distribution. It is economically advantageous to use by-products of primary chemical processing as raw materials since the interaction between the polymeric components of wood (carbohydrates and lignin) in such a material weakens with the simultaneous discovery of new conversion paths during further pyrolysis.

In the production of activated carbons, preliminary carbonized precursors are usually used for the processing, with thermal carbonization (or pyrolysis) being a traditional approach. However, hydrothermal carbonization (HTC) is more economically profitable, allowing for the hydrolysis and transfer into an aqueous medium the least thermally stable component of wood—hemicellulose. HTC is a method which utilizes relatively low temperatures under an autogenous pressure to turn biomass into solid and carbon-rich materials [24–26]. Such carbonization products have specific properties, which include a sphere-like morphology and a core-shell structure comprising a hydrophobic core and hydrophilic shell with high oxygen containing functional group content which makes it an effective precursor for chemical activation [27,28]. Carbonaceous materials originating from HTC and traditional carbonization noticeably differ in their physicochemical properties, which affect further potential applications [29].

The presence of carbohydrate and aromatic polymers in the biomass, as well as the use of residues of chemical processing of wood with a predominance of one or the other component, makes it possible to obtain carbon materials with different structures [1,30,31]. Pore size distribution and the structural ordering of carbon particles are often among the critical parameters for assessing their potential. With an increase in pore size, the electrocatalytic activity also increases, and as a result, mesoporous (pore size from 2 nm to 50 nm) materials demonstrate better catalytic properties compared to microporous (pore size less than 2 nm) materials [32]. When solving the problem of obtaining wide-pore carbon materials, the attention of researchers was attracted by three-dimensional hierarchical porous carbons (3D-HPC), which simultaneously contain pores of different scales (micro- (<2 nm), meso- (2–50 nm) and macro- (>50 nm)) to provide sufficient space for ionic mass transfer. The authors of several studies chose lignin, with its unique structure, as a raw material for obtaining such char [33–35]. It was shown that hydrothermal carbonization was preferable to the traditional method [36].

In this work, wood and the waste of its thermochemical processing, pyrolytic tar, which is formed as a result of pyrolysis of the residues of two successive technological processes, where the target products are furfural and levoglucosan, were used as raw materials. The first process was hydrolysis catalyzed by sulfuric acid, where the target
product was furfural and the residue was lignocellulose. The second process was the pyrolysis of lignocellulose in a stream of superheated steam, followed by crystallization and separation of levoglucosan. The remaining part of the tar after the extraction of levoglucosan, having an increased content of lignin, was used as the second type of raw material. There is practically no market for the further use of the tar, except for proposals for incineration. A composite material of both raw materials was used as the third sample: wood impregnated (1:1) with tar. We have previously shown that charcoal impregnated with black liquor, which is the lignin residue of Kraft pulping, is a promising composite precursor for alkaline activation and the use of activated carbon in energy devices [1].

The aim of the study was to investigate the possibility of expanding the use of waste from thermochemical wood processing for the synthesis of activated alkali (NaOH) carbons with a wide distribution of pore sizes through the thermal and hydrothermal carbonization of precursors.

2. Materials and Methods
2.1. Preparation of Carbon Materials
2.1.1. Materials and Their Carbonization

In this work, 3 types of raw materials were used, namely birch wood chips (Betula pendula, fraction 0.2–0.6 mm), water-insoluble lignocellulosic pyrolysis tar, and a composite mixture of wood chips and tar (1:1). The tar is a by-product from the two successive pilot wood processing processes: catalytic hydrolysis (catalyst is sulphuric acid) where the target product is furfural [37] and pyrolysis (450 °C) of produced lignocellulose residues in a superheated steam, where the target chemical is 1,6-anhydro saccharide—levoglucosan. After the crystallization and isolation of levoglucosan from aqueous condensate pyrolysis tar was obtained [38] (Figure 1).

![Tar production scheme.](image1)

The carbonization of the abovementioned samples of birch chips, tar, and their composite (1:1) was carried out by two methods: thermally and hydrothermally. In the case of thermal carbonization, a 10% ethanol solution of tar was used to impregnate wood chips (1:1 wood chip weight ratio to tar). After drying at 60 °C for 4 h, the samples were heated and treated for 1 h at 500 °C. In the case of hydrothermal carbonization, 200 g of dry birch wood chips and 200 g tar were dispersed in 2.5 L of distilled water, followed by its transfer into a 7.5 L stainless steel PARR-4554 (USA) autoclave. The carbonization process was carried out at 250 °C for 4 h stirring at 140 rpm.

To obtain a carbonizate with an even particle distribution (~10 µm) (Figure S1) all samples were refined for one hour in a Pulverisette 5/4 (Fritsch, Germany) planetary mill equipped with zirconia balls and mortars at 300 rpm.

2.1.2. Activation

Carbonizates were mixed with dry NaOH (ratio of activator to precursor was 3:1) and placed into muffle oven for 2 h at 800 °C in argon atmosphere. After cooling, the samples were washed with water and heated to boiling point for 2 h in a solution of 10% hydrochloric acid, then washed with demineralized water to pH 5–6 and dried at 105 ± 2 °C for 12 h.
2.2. Characterization of Precursors, Carbonisats and Activated Carbons

Analytical pyrolysis (Py-GC/MS) was performed using a Frontier Lab (Japan) Micro Double-shot Pyrolyser Py-2020iD directly coupled with Shimadzu GC/MS—QP 2010 apparatus (Japan) with capillary column RTX-1701 (Restec, USA), 60 m × 0.25 mm × 0.25 μm film (injector temperature 543 K, ion source 523 K with EI of 70 eV, MS scan range m/z 15–350, carrier gas helium at the flow rate of 1 mL min⁻¹ and the split ratio 1:30). The mass of a sample for these tests (residual moisture content < 1%) was 1.00–2.00 mg. The furnace heating program was as follows: isothermal 1 min at 333 K, then 6 K min⁻¹ to 543 K, and finally 543 K for 10 min. The mass spectrometer was operated in the electron impact mode using 70 eV electron energy.

Thermogravimetric analyses were carried out with a Discovery TGA device System in an inert nitrogen atmosphere, heating rate 10 °C min⁻¹ in a temperature range 30–700 °C.

Carbon, nitrogen and hydrogen content was evaluated using the Vario Macro CHNSO (Germany) device. The oxygen content was calculated from the difference from 100%.

Functional group analysis was done by acid-based titration (Boehm’s titration) with Radiometer Analytical Titralab TIM 840 automatic titration station. To approximately 2 g of catalyst 50 mL of a 0.075 M NaOH solution (for acid functional group determination) or 50 mL of a 0.075 M HCl solution (for basic functional group determination) was added and left overnight at room temperature with constant mixing. The solutions were then filtered using a Whatman filter paper, TE 37 (1.0 μm) to remove the hydrochar from the solution. Exactly 5 mL of the filtered sample was taken by pipette and was back-titrated with 0.1 M HCl (for acidic functional group determination) or with 0.1 M NaOH (for basic functional group determination) until the second stoichiometric point. A blank titration (without the hydrochar sample) was performed every time prior to the titration with the sample. For each sample, 3 replicates were done.

The porous structure (specific surface area, the total volume of micro- and mesopores, and the pore sizes) was determined from isotherms of low-temperature adsorption-desorption of nitrogen at 77 K on a Nova 4200e device (Quantachrome, Boynton Beach, FL, USA). The volume of mesopores was determined from the difference $V_{\text{total}} - V_{\text{micro}}$.

3. Results and Discussion

3.1. Characterization of Feedstock and Carbonized Materials

To characterize changes in the structure and chemical composition of the studied samples of wood, tar and their composite (1:1) in the process of two different types of carbonization, differing not only in temperature (500 and 250 °C), but also in their environment, the samples were studied by analytical pyrolysis (Figure 2) and thermogravimetry (Figure 3). The most noticeable differences in the content of volatile products were observed by analytical pyrolysis for the initial samples of wood and tar. In the case of wood, the proportion of the decomposition products of carbohydrates and lignin was typical for hardwoods, which is 56.82% carbohydrates and 17.79% aromatic derivates of lignin. In the case of tar, the content of carbohydrate degradation products was lower—8.87%, but the content of the phenols increased, reaching 62.08%. In a composite with an equal amount of wood and tar, the amount of carbohydrate decomposition products was 41.71%, and the amount of the phenolic products was 34.76%. Accordingly, the ratio of lignin degradation products to carbohydrate derivatives (L/C) was much higher in the case of tar compared to wood and composite. The content of volatile compounds, such as carbon dioxide, water and methanol, was practically unchanged during the pyrolysis of all initial samples, and was about 20%.
Figure 2. Composition of volatile degradation products of: (a) wood, tar, and their composites; (b) hydrothermally carbonized samples (HTC-W, HTC-H and HTC-T); and (c) pyrolyzed samples (PYR-W, PYR-H and PYR-T) determined by Py-GC/MS at 500 °C.

Figure 3. The carbonizates obtaining scheme.

Biomass carbonization is a complex process with many reactions that result in the formation of non-condensable gases, liquid products or bio-oil and a solid residue—
carbonisate (Figure 3). However, the morphology and microstructure of biomass does not change significantly during the pyrolysis process (up to 600 °C) [39]. Compared to pyrolysis, hydrothermal carbonization reactions take place at relatively low temperatures under hydrothermal conditions. Most hemicelluloses are transferred from lignocellulose to water at a hydrothermal process temperature below 180 °C, but cellulose degradation becomes apparent when the hydrothermal temperature reaches 230 °C [40].

As a result of hydrothermal carbonization, the composition of volatile products of all samples changes mainly due to a decrease in the content of carbohydrate degradation products and an increase in the content of lignin derivatives, as well as carbon dioxide, water, and methanol. In the case of the hydrothermally carbonized wood (HTC-W) and hybrid material (HTC-H), the content of phenolic compounds in volatile products increased by 2 and 1.5 times and reached 38.41 and 55.62%, respectively (Table 1). In the case of tar, the increase in aromatic compounds was lower—only 5.83% and the total amount reached 67.91%. Analytical pyrolysis of samples after thermal carbonization showed that the main products in this case, were readily volatile compounds, such as carbon dioxide, water, methanol, and hydrocarbons containing various oxygen-containing groups: carboxyl, hydroxyl and ketone. In this case, there were no volatile products characteristic for wood.

In the case of wood carbonizate, a small amount of phenyl and benzyl derivatives were formed, which, obviously, appeared when the aromatic structure of the carbonizate was fragmented. In the case of pyrolyzed tar, the results were similar to results obtained with the carbonized hybrid material (PYR-H).

### Table 1. Composition of volatile degradation products of wood, tar and their composites, hydrothermally carbonized samples (HTC-W, HTC-H and HTC-T) determined by Py-GC/MS at 500 °C.

<table>
<thead>
<tr>
<th></th>
<th>Wood</th>
<th>Hybrid</th>
<th>Tar</th>
<th>HTC-W</th>
<th>HTC-H</th>
<th>HTC-T</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbohydrates</td>
<td>56.82</td>
<td>41.71</td>
<td>8.87</td>
<td>10.20</td>
<td>5.60</td>
<td>2.44</td>
</tr>
<tr>
<td>derivates</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Acid, Ester</td>
<td>13.58</td>
<td>10.85</td>
<td>0.91</td>
<td>2.99</td>
<td>1.58</td>
<td>0.88</td>
</tr>
<tr>
<td>Alcohol</td>
<td>0.78</td>
<td>0.67</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Aldehyde, Ketone</td>
<td>17.27</td>
<td>12.42</td>
<td>0.47</td>
<td>2.32</td>
<td>1.37</td>
<td>0.40</td>
</tr>
<tr>
<td>Cyclopentane</td>
<td>3.53</td>
<td>2.83</td>
<td>0.38</td>
<td>3.63</td>
<td>1.80</td>
<td>0.70</td>
</tr>
<tr>
<td>derivates</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Furan</td>
<td>9.91</td>
<td>7.27</td>
<td>1.23</td>
<td>1.26</td>
<td>0.85</td>
<td>0.46</td>
</tr>
<tr>
<td>Pyran</td>
<td>3.11</td>
<td>1.71</td>
<td>0.36</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Sugars</td>
<td>8.64</td>
<td>5.96</td>
<td>5.52</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Lignin derivates</td>
<td>17.79</td>
<td>34.76</td>
<td>62.08</td>
<td>38.41</td>
<td>55.62</td>
<td>67.91</td>
</tr>
<tr>
<td>Phenyl and benzyl</td>
<td>0.73</td>
<td>3.15</td>
<td>7.46</td>
<td>6.48</td>
<td>9.59</td>
<td>13.84</td>
</tr>
<tr>
<td>derivates</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Guaiacyl derivates</td>
<td>5.42</td>
<td>11.50</td>
<td>18.67</td>
<td>8.94</td>
<td>13.08</td>
<td>17.56</td>
</tr>
<tr>
<td>Syringyl derivates</td>
<td>11.64</td>
<td>20.11</td>
<td>35.95</td>
<td>22.99</td>
<td>32.95</td>
<td>36.51</td>
</tr>
<tr>
<td>Carbon dioxide,</td>
<td>22.39</td>
<td>22.65</td>
<td>23.78</td>
<td>47.26</td>
<td>35.31</td>
<td>22.72</td>
</tr>
<tr>
<td>Water, Methanol</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Thus, as a result of hydrothermal carbonization (250 °C), three samples were obtained with the preserved hierarchical order and different contents of polyaromatic structures. Under conditions of thermal carbonization (500 °C), due to the reactions of dehydration, destruction and condensation, condensed structures were formed during the rapid pyrolysis of which only hydrocarbon compounds, volatile water, and carbon dioxide were formed (Figure 3).

Comparing the microphotographs of wood carbonizate (Figure 3), it can be concluded that as a result of the hydrothermal carbonization, the products of the hydrolysis of hemicelluloses and regions of weakly oriented cellulose macromolecule pass into an aqueous solution and condense on the surface of wood particles, but that during thermal carbonization, the wood cell walls remain smooth, and the pores fill with carbonization products of pyrolysis products. Since tar is a liquid product and mostly consists of polyaromatic
lignin derivatives, the morphology of its carbonizates is very different from that of wood carbonizates. During thermal carbonization, when volatile products form in the bulk of liquid, they swell and form a foam-like structure, thus creating a material with a scaly surface. Since during hydrothermal carbonization the reactions take place in an aqueous environment, the reaction mechanism is different and the obtained carbonizate has a denser, more condensed morphology.

The thermal stability of the obtained carbonizates was evaluated using thermogravimetric analysis (Figure 4). All the carbonizates obtained as a result of pyrolysis (500 °C) were thermally stable. The weight loss at 700 °C is only 9–14%, with the highest amount of volatiles being formed in the case of wood.

![Figure 4. Thermogravimetric TGA (a) and DTG (b) analyses of wood, tar and their hybrids carbonizates prepared at 500 °C in an inert atmosphere (PYR-W, PYR-H and PYR-T) and at 250 °C in an aqueous medium (HTC-W, HTC-H and HTC-T).](image)

After hydrothermal carbonization the part of the original wood components was preserved in carbon materials, thus the thermal stability of these samples was lower, and the maximum volatile products formation rate was achieved at much lower temperatures (Figure 4a). For the tar carbonizate obtained under the conditions of hydrothermal treatment (HTC-T), the DTG maximum temperature was the lowest—359 °C, and the amount of the volatile products at 700 °C was the highest—63% (Figure 4b). For the hydrothermally treated wood sample (HTC-W) the DTG maximum was higher—417 °C. In this region, the decomposition of highly oriented regions of the cellulose macromolecules is likely to occur. Wood carbonizate obtained as a result of hydrothermal treatment has a less dense structure than carbonizate after thermal carbonization.

The process of transformation of wood components during hydrothermal treatment includes hydrolysis of bonds and intramolecular dehydration with the removal of products into an aqueous solution, which contributes to the aromatization process [41]. Lignin undergoes condensation reactions and polymerizes into hydrochar. Thus, insoluble lignin enters into a solid–solid reaction similar to pyrolysis, which results in the formation of a highly condensed hydrochar with a polyaromatic structure [42].

Comparison of all the carbonizates obtained by hydrothermal treatment shows that most stable of them is based on wood, where the lowest amount of the volatile products is observed at 700 °C—46%. Perhaps this is due to the degradation of not only hemicelluloses, but also amorphous regions of the cellulose macromolecule, as well as partial hydrolysis of lignin and the formation of secondary char on the surface. This is also indicated by the high yield of wood carbonizate obtained under hydrothermal treatment conditions (Table 2). The thermal stability of the hybrid composite occupies an intermediate position: lower than that for wood and higher than that in the case of tar.
Table 2. Yield, elemental composition and as well as the content of carboxyl groups of carbonizates obtained different carbonization the environment.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Precursor</th>
<th>Carbonization Temperature</th>
<th>Yield, %</th>
<th>C, %</th>
<th>O, %</th>
<th>NaOH, mmol g$^{-1}$ (Total Acidic Groups)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PYR-W</td>
<td>Wood</td>
<td>500 °C</td>
<td>27</td>
<td>84.1</td>
<td>12.1</td>
<td>&gt;0.001</td>
</tr>
<tr>
<td>PYR-H</td>
<td>Wood and tar</td>
<td>500 °C</td>
<td>35</td>
<td>88.2</td>
<td>8.1</td>
<td>0.001</td>
</tr>
<tr>
<td>PYR-T</td>
<td>Tar</td>
<td>37</td>
<td>37</td>
<td>82.0</td>
<td>14.3</td>
<td>0.003</td>
</tr>
<tr>
<td>HTC-W</td>
<td>Wood</td>
<td>250 °C, H$_2$O</td>
<td>60</td>
<td>71.1</td>
<td>23.9</td>
<td>0.008</td>
</tr>
<tr>
<td>HTC-H</td>
<td>Wood and tar</td>
<td>250 °C, H$_2$O</td>
<td>44</td>
<td>72.4</td>
<td>22.1</td>
<td>0.011</td>
</tr>
<tr>
<td>HTC-T</td>
<td>Tar</td>
<td>50</td>
<td>50</td>
<td>74.8</td>
<td>19.0</td>
<td>0.010</td>
</tr>
</tbody>
</table>

The chemical composition of the precursor can affect the subsequent activation process (Table 2). The yield of carbonizates obtained under heat treatment conditions is much lower than during hydrothermal carbonization. At the same time, in the composition of thermal carbonizates, the carbon content is 10% higher and the oxygen content is lower (Table 2). The composition of surface functional groups changes as a result of hydrothermal treatment, and the content of oxygen-containing acidic functional groups in the samples increases. Oxygen containing functional groups on the carbon surface influence the surface characteristics such as wettability, polarity, acidity and physico-chemical properties such as catalytic, electrical and chemical reactivity of these materials [43]. More oxygen provides more active sites to react with the alkaline activator.

3.2. Characterization of Activated Carbon Materials

Carbonized samples of wood, tar, and their hybrid material (1:1) obtained after thermal and hydrothermal treatment were chemically activated using sodium hydroxide (NaOH to precursor ratio 3:1) at a temperature of 800 °C and then demineralized. In previous works, we have shown the effectiveness of using NaOH as a chemical biomass activator for the formation of a nanoporous structure of carbon materials [14]. After the activation, all samples had similar carbon and oxygen contents of 91.7 to 93.4% carbon and 4.5 to 6.4% oxygen, respectively.

The carbonization environment and temperature greatly influence the outcome of both carbonization and activation. After hydrothermal carbonization, the yield of the precursor was almost 20% higher. In turn, pyrolyzed samples had a significantly higher yield of activated carbons after activation (Table 3). The carbonization environment affected not only the yield of activated carbon, but also the morphology of the material (Figure 5). After hydrothermal carbonization, activated carbon particles agglomerated to form a flaky structure with a particle size of approximately 50 µm, while after thermal carbonization, particles with an average size of 10 µm with a layered structure were formed. The structure of the carbonizate obtained by hydrothermal carbonization was less dense than the structure of the pyrolysis carbonizate. Therefore, much greater movement of molecules and ions is possible during activation. Reactions of sodium ions and oxygen-containing functional groups in carbonizates lead to the cleavage of bonds between adjacent layers, as well as the formation of new—C-C—bonds. During activation of hydrothermally carbonized, the bonds are broken more easily, and the plates separate from each other. In the case of thermal carbonization, the structure of wood char is denser and the bonds are stronger. In addition, the reduced metallic sodium, formed during the activation process, enters into the system and forms carbonate salts between the crystallite layers, and after the demineralization process, when the Na salts are washed away, pores are formed [44].
Table 3. Yield and elemental composition of activated carbon based on hydrothermally carbonized samples (AHTC-W, AHTC-H and AHTC-T) and pyrolyzed samples (APYR-W, APYR-H and APYR-T).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Yield (after Activation), %</th>
<th>Yield (after Carbonization and Activation), %</th>
<th>N, %</th>
<th>C, %</th>
<th>H, %</th>
<th>O, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>APYR-W</td>
<td>36</td>
<td>10</td>
<td>0.9</td>
<td>92.0</td>
<td>0.6</td>
<td>6.4</td>
</tr>
<tr>
<td>APYR-H</td>
<td>40</td>
<td>14</td>
<td>0.7</td>
<td>92.5</td>
<td>0.7</td>
<td>6.1</td>
</tr>
<tr>
<td>APYR-T</td>
<td>37</td>
<td>14</td>
<td>0.8</td>
<td>93.0</td>
<td>0.7</td>
<td>5.5</td>
</tr>
<tr>
<td>AHTC-W</td>
<td>15</td>
<td>9</td>
<td>1.7</td>
<td>91.7</td>
<td>0.6</td>
<td>6.0</td>
</tr>
<tr>
<td>AHTC-H</td>
<td>16</td>
<td>7</td>
<td>1.2</td>
<td>92.0</td>
<td>0.6</td>
<td>6.1</td>
</tr>
<tr>
<td>AHTC-T</td>
<td>14</td>
<td>7</td>
<td>0.6</td>
<td>93.4</td>
<td>1.3</td>
<td>4.5</td>
</tr>
</tbody>
</table>

Porous structure was studied by the method of low-temperature nitrogen adsorption. Although carbonization environment and temperature did not influence elemental composition and specific surface area, the volume of adsorbed nitrogen varied significantly in the studied samples. Judging by the volume of adsorbed nitrogen and the shape of the isotherms, the hydrothermally carbonized carbon materials are micro-mesoporous and pyrolyzed carbon materials are microporous (Figure 6). According to Dubinin–Radushkevich theory, adsorption in micropores takes place according to the volume-filling mechanism, but in the presence of mesopores at relative nitrogen pressures exceeding 0.4, adsorption takes place according to the polymolecular condensation mechanism and is accompanied with the appearance of hysteresis on the adsorption isotherms [43,45].
Figure 6. N₂ adsorption-desorption isotherms of activated carbon based on hydrothermally carbonized samples (AHTC-W, AHTC-H and AHTC-T) and pyrolyzed samples (APYR-W, APYR-H and APYR-T).

The degree of carbonization, aromatization, and content of oxygen-containing functional groups in the precursor led to high porosity of the activated carbon [46]. In this case, all obtained samples, regardless of the particularities of the structure and properties, had a high specific surface area (S\text{BET})—more than 2400 m² g⁻¹ (Table 4), which indicated that microporosity had been developed.

Table 4. Porous structure parameters of activated carbon.

<table>
<thead>
<tr>
<th>Sample</th>
<th>S\text{BET}, m² g⁻¹</th>
<th>V\text{total}, cm³ g⁻¹</th>
<th>V\text{micro}, cm³ g⁻¹</th>
<th>V\text{meso}, cm³ g⁻¹</th>
<th>V\text{meso from V\text{t}}, %</th>
<th>Average Pore Size, nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>APYR-W</td>
<td>2553</td>
<td>1.4</td>
<td>0.8</td>
<td>0.6</td>
<td>43</td>
<td>2.2</td>
</tr>
<tr>
<td>APYR-H</td>
<td>2494</td>
<td>1.4</td>
<td>0.8</td>
<td>0.6</td>
<td>43</td>
<td>2.3</td>
</tr>
<tr>
<td>APYR-T</td>
<td>2804</td>
<td>1.5</td>
<td>0.9</td>
<td>0.6</td>
<td>40</td>
<td>2.1</td>
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<tr>
<td>AHTC-W</td>
<td>2629</td>
<td>1.9</td>
<td>0.8</td>
<td>1.1</td>
<td>58</td>
<td>2.9</td>
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<tr>
<td>AHTC-H</td>
<td>2919</td>
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<td>0.9</td>
<td>1.3</td>
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<td>AHTC-T</td>
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</table>

The main difference of the porous structure was manifested in different volume of pores depending on the method of carbonization of the precursor. Hydrothermal processing conditions led to a larger total volume of pores (1.9–2.2 cm³ g⁻¹) compared to thermally carbonized samples (1.4–1.5 cm³ g⁻¹). Obviously, this can be explained both by the looser structure of the precursors, which provides accessibility for sodium ions, and by the presence of a larger number of oxygen-containing functional groups in hydrothermally carbonized samples, which increased the activating ability of alkalis. The different proportion of aromatic structures in the precursors, as well as their different thermostability, did not affect the formation of the porous structure.

In addition to the total volume of pores, the activation of precursors obtained by the hydrothermal method leads to high volumes of mesopores with a size of 2.5–4.5 nm (Table 4, Figure 7). The volume of pores wider than 2 nm in the overall volume of pores was 58–59%, while the volume of mesopores for thermally carbonized precursors was only 41–43%.
4. Conclusions

It is shown that, using various carbonization methods, highly efficient micro- and micro-mesoporous carbon materials, which are in demand in various fields for sorption and energy devices, can be obtained using wood and waste from its chemical processing as raw materials.

Depending on the carbonization method, the samples had different chemical and elemental compositions, as well as thermal stability. These carbonizates’ properties did not significantly influence the micropore volume and specific surface area, which is more than 2400 m²g⁻¹, of activated carbon materials.

The main difference in the effect of the carbonization conditions on the porous structure of carbon materials was manifested in the formation of wider pores (more than 2.5 nm) for all hydrothermal carbonized samples. It has been established that after activation, hydrothermally carbonized samples have a micro-mesoporous structure with a mesopore volume from total pore volume of 58–59%, while the mesopore volume for thermally carbonized precursors is only 40–43%. Apparently, hydrothermally carbonized samples, which have a looser structure and contain a greater amount of oxygen-containing functional groups, have more active sites for interaction with NaOH, which leads to the more pronounced formation of mesopores upon activation than in the case of thermally carbonized samples with a denser structure.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/su142315982/s1, Figure S1: SEM analysis of wood, tar and their hybrids carbonizates prepared at 500 °C in an inert atmosphere (a-PYR-W, b-PYR-H and c-PYR-T) and at 250 °C in an aqueous medium (d-HTC-W, e-HTC-H and f-HTC-T). The scale bar is 50 µm.

Author Contributions: Conceptualization, A.P. and G.D.; methodology, A.V. and A.P.; validation and formal analysis, A.P., G.D. and A.V.; resources and data curation, A.P. and G.D.; writing—original draft preparation, A.P.; writing—review and editing, A.V.; visualization, A.P.; supervision, G.D. and A.Z.; project administration and funding acquisition, A.Z. All authors have read and agreed to the published version of the manuscript.

Funding: This study was financially supported by ERAF project Nr. 1.1.1.1/20/A/027 “Improvement of wood-based biorefinery by innovative conversion of residues to nanoporous carbon materials (BiReMa)”.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The data presented in this study are available on request from the corresponding author.
Acknowledgments: The authors would like to thank the Latvian State Institute of Wood Chemistry for the support provided.

Conflicts of Interest: The authors declare no conflict of interest.

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