

RIGA TECHNICAL UNIVERSITY
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Institute of General Chemical Engineering

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**MULTIFUNCTIONAL CARBON MATERIALS ON THE BASE
OF WOOD AND LIGNOCELLULOSE**

Summary of the Doctoral Thesis

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**DOCTORAL THESIS PROPOSED TO RIGA TECHNICAL UNIVERSITY
FOR THE PROMOTION TO THE SCIENTIFIC DEGREE OF DOCTOR OF
CHEMICAL ENGINEERING**

To be granted the scientific degree of Doctor of Chemical Engineering, the present Doctoral Thesis has been submitted for the defence on 6th of December 2017 at 4 p.m. at the Faculty of Materials Science and Applied Chemistry of Riga Technical University, 3/7 Paula Valdena Street, Room 272.

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DECLARATION OF ACADEMIC INTEGRITY

I hereby declare that the Doctoral Thesis submitted for the review to Riga Technical University for the promotion to the scientific degree of Doctor of Chemical Engineering is my own. I confirm that this Doctoral Thesis has not been submitted to any other university for the promotion to a scientific degree.

Aleksandrs Volperts (Signature)

Date:

The Doctoral Thesis has been written in Latvian. It includes 53 illustrations, 20 tables, 23 equations and 3 appendices. The total number of pages is 153. The Bibliography contains 182 titles.

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LIST OF ABBREVIATIONS

Adsorption – the adhesion of atoms, ions, or molecules from gas, liquid, or dissolved solid to a surface. This process creates a film of the adsorbate on the surface of the adsorbent;

Activation – treatment of carbon material with oxidizing agents at elevated temperatures with the aim to obtain activated carbon;

AC – activated carbon;

Carbonization – increase of carbon content in organic precursor;

Carbonizate – carbonaceous product of carbonization;

Carbonizate-P – carbonaceous product of carbonization in the presence of phosphorous acid;

CM – carbon materials;

CS – carbon sorbents;

DFT – density functional theory;

EDL – electric double layer;

EDLC – electric double-layer capacitors or supercapacitor;

K – activator to the precursor ratio;

Capillary condensation – process by which multilayer adsorption from the vapor into a porous medium proceeds to the point at which pore spaces become filled with condensed liquid from the vapor;

Lignocellulose – lignin and cellulose complex present in wood and other plant biomass materials;

L_o – micropore width;

NCM – nanoporous carbon materials;

PCM – porous carbon materials;

S_{BET} – porous surface according to BET theory;

S_{DR} – porous surface according to Dubinin–Radushkevich theory;

S_{DFT} – porous surface according to DFT theory;

SC – supercapacitor;

TG/MS – thermogravimetry/mass spectrometry;

V_{total} – total pore volume;

V_{micro} – micropore volume.

GENERAL DESCRIPTION OF THESIS

Topicality of research

The application of activated carbon (AC) and its various modifications is of significant scientific and practical importance since the use of these materials in various technological areas constantly grows – they can be applied in rare earth metal membrane separation, metallurgy, electronics, aero- and space technologies, as well as nuclear energy development.

New studies are devoted to the possibilities of AC application, which are being used and developed in the framework of nanotechnologies. Specifics of carbon atom electron shell properties make nanoporous carbon materials (NCM) one of the most promising nanomaterials, which can be used in various areas of electronics and energetics. At the current moment investments in nanotechnology account for approximately 9 billion dollars annually, one third of studies being carried out in the USA. Other important investors are the EU and Japan. There are forecasts predicting that in 2017 the number of employees in nanotechnology based industries can reach 2 million, and the total value of goods produced by nanotechnologies can reach 1 trillion dollars.

New energy production and storage technologies are and will be topical and of high priority due to the trends in technical and economic development in the whole world. At the current moment existing energy storage devices have drawbacks and this leads to the necessity for the development of new energy storage devices, which meet the demands of modern energetics.

The development of various types of electrochemical devices using NCM is a prerequisite for long-term ecologically friendly technologies, which, in their own turn, can provide the development of many technical areas with minimal energy and reagent consumption. Taking in the view the above mentioned, nanoporous carbon materials from renewable plant precursors are accounting for their lower costs in comparison to fullerenes, CNT and nanofibers. The discovery of some new carbon structures was not the result of purposeful research but unexpected results of the experiments, and the possible reason for this was the influence of a number of unestimated factors.

The fundamental and technological challenges require studies of porous structure development mechanism and relationships, which can lead to synthesis of materials with the required properties.

Objectives and tasks of thesis

The objectives of this thesis are synthesis of activated carbon from wood and its processing wastes using thermochemical alkali activation for the application as supercapacitor electrodes with proton and aprotion electrolytes, as well as the study of the obtained activated carbon structure and electrochemical properties.

The following tasks were assigned to reach the objectives.

1. Study of the formation of volatile products from wood in the conditions of thermodestruction with activating agents.
2. Evaluation of wood, its processing wastes and charcoal application possibilities for the thermochemical alkali activation.
3. Analysis of influence of pretreatment and activation conditions on porous structure development and properties of the obtained activated carbon.

4. Evaluation of influence of various activation conditions on activated carbon porous structure alteration and relationships between carbon material structure and electrochemical properties, using activated carbons as supercapacitor electrodes.
5. Development of principal technological scheme for the production of nanoporous carbon materials, evaluation of material and power balances.

Scientific significance and novelty

Systematic research work led to the new insights of the influence of the wood alkali thermochemical activation on synthesized activated carbon specific surface and pore volume. For the first time it was demonstrated that the activated carbon obtained by NaOH thermochemical activation can be used as an electrode material in supercapacitors with double electric layer.

It was demonstrated that the use of orthophosphorous acid at the pretreatment stage can substantially increase the yield of activated carbon, however this negatively influences the carbon electrochemical properties – electric double layer formation.

For the first time relationships were demonstrated between porous structure and electrochemical properties of the nanosized activated carbons obtained on the base of charcoal.

Practical significance

The research demonstrated that it is possible to obtain highly effective nanoporous carbons with high added value using NaOH thermochemical activation of wood based materials.

The methodology for the synthesis of activated carbon by the alkali thermochemical activation of wood, its processing residues and charcoal was developed.

The results of the research were used for the development of technology, including the demands for the technological units, material and power balances for the activated carbon production from the Latvian natural resources. The developed methodology and material balance can be used as initial data for the design of activated carbon production in Latvia.

Theses for defense

1. The formation of nanoporous structure of carbon materials is influenced by the parameters of synthesis process and can be controlled;
2. There are relationships between parameters of porous carbon material synthesis and specific capacitance of the capacitors with double electric layer.

Approbation of the research results

The main results of the thesis have been summed up in 15 publications and 19 conference theses. One Latvian Republic and one international patent have been awarded.

SUMMARY OF LITERATURE REVIEW

Literature review is devoted to AC synthesis and study methods, their structure and properties, as well as supercapacitor (SC) construction and operation principles.

Nowadays the total AC production is more than half a million tons per year, which meets approximately 80 % of the current demand, while Asia – Pacific Ocean region provides 60 % of the whole world production. There is an assumption that AC production can be the main factor describing technological, ecological and social protection development of a country. Biomass is a renewable alternative to non-renewable fossil carbon containing materials, and traditionally biomass is used for charcoal as well as carbon materials with highly developed specific surface production – AC. They can be used as catalyst scaffolds and catalysts [1] as well as for liquid purification [2] and in various agricultural and industrial areas.

To obtain carbon materials with developed porous structure, biomass should be carbonized and after that by means of steam or chemical activation, carbonize is being activated in process of pyrolysis. Schematic of physical and chemical activation pathways for the obtaining of AC from lignocellulosic biomass is shown in Fig. 1

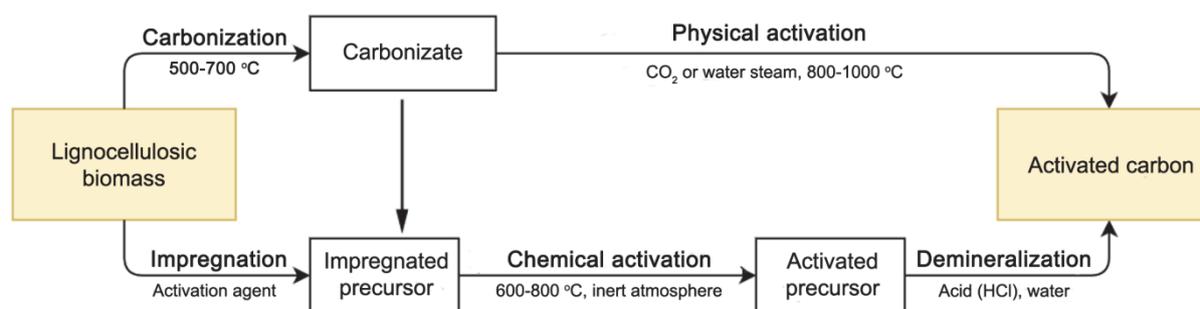


Fig. 1. Two main activation methods.

When the wood is activated, it forms AC with wide spectrum of specific surface and pore size distribution, which are governed by the conditions of activation. AC have macro-, meso- and micropores. The role of macropores in the sorption process is to provide transport pathways for the molecules of the adsorbed substance and to enable them to reach deeper into the sorbent particles. Mesopores are being formed at the stage of carbonization and at the next step – activation. The main property of micropores is that their size is comparable to the size of adsorbed molecules and adsorption energy in these pores is higher, than in macro- and mesopores. Micropores have considerable sorption volumes and play the main role in sorption processes [3].

From the 80s of the last century highly porous CM are being used not only in sorption processes, but also in the areas associated with electric energy accumulation and transfer without using power sources, as well as for leveling energy load peaks. One of the most important devices for this purpose is electrochemical energy accumulation device with double electric layer – supercapacitor [4]. Charge accumulation and preservation in electrochemical capacitors takes place in double electric layer, which forms on the electrode/electrolyte interface, thus electrode material have to meet a number of requirements, such as low density, electric conductivity, and developed porous structure, which should fit ions and molecules of electrolyte (Fig. 2).

The reason of AC application in supercapacitor is their unique properties, namely high conductivity, highly developed specific surface, corrosion resistance, high

temperature tolerance, possibility to control specific surface and porous structure parameters in the process of synthesis, possibility to be used in composites, relatively low cost [5].

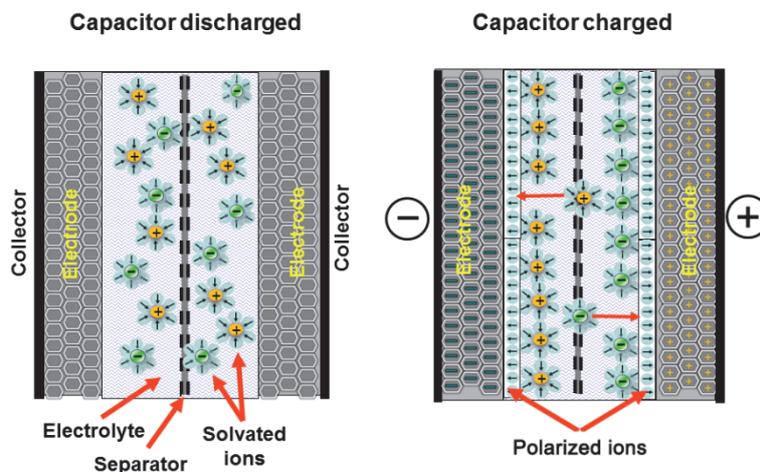


Fig. 2. Operation principles of supercapacitor.

Currently transitions to renewable energetic resources and renewable raw materials are the worldwide trend, and their effective use is also related to AC production. Of the highest interest is the use of renewable plant biomass, and especially its processing residue, as precursors for this purpose. At the same time, methods for obtaining AC from lignocellulosics and wood processing wastes are not fully studied. Taking into account the above mentioned, this thesis is devoted to studies of synthesis of activated carbon from wood and its processing wastes using thermochemical NaOH activation, development of technology for AC production, as well as their application as supercapacitor electrodes with proton and aprotion electrolytes.

EXPERIMENTAL

Experimental workflow, analytical methods and the obtained results are illustrated in Fig. 3.

White alder and birch wood mechanical processing wastes, white alder bark, Kraft cellulose, hydrolysis lignin and charcoal were used as raw materials.

The main stage of AC synthesis from wood and lignocellulosic materials is activation with sodium hydroxide, and the whole process consists of the following steps: 1) carbonization; 2) carbonizate refining; 3) impregnation with alkali; 4) activation; 5) demineralization. Two thermal treatment stages were used for the AC synthesis. The first one (carbonization) includes heating of precursor up to 375 °C to 500 °C and treatment at this temperature for 90 min to 300 min. Several carbonization experiments were performed with preliminary impregnation with phosphorous acid solution (2 %, 4 % and 6 %), filtration and drying. The next step – wood carbonizate impregnation with alkali, was done using two approaches.

1. Carbonized material was mixed with 50 % NaOH solution in polypropylene vessel (K from 4 to 1);
2. Carbonized material was mixed dry NaOH in polypropylene vessel (K from 4 to 1), afterwards water was added and carefully mixed;

The obtained activation mixture was placed into stainless steel crucible with a lid and activated in stream of argon at 600 °C to 800 °C for 60 min to 120 min.

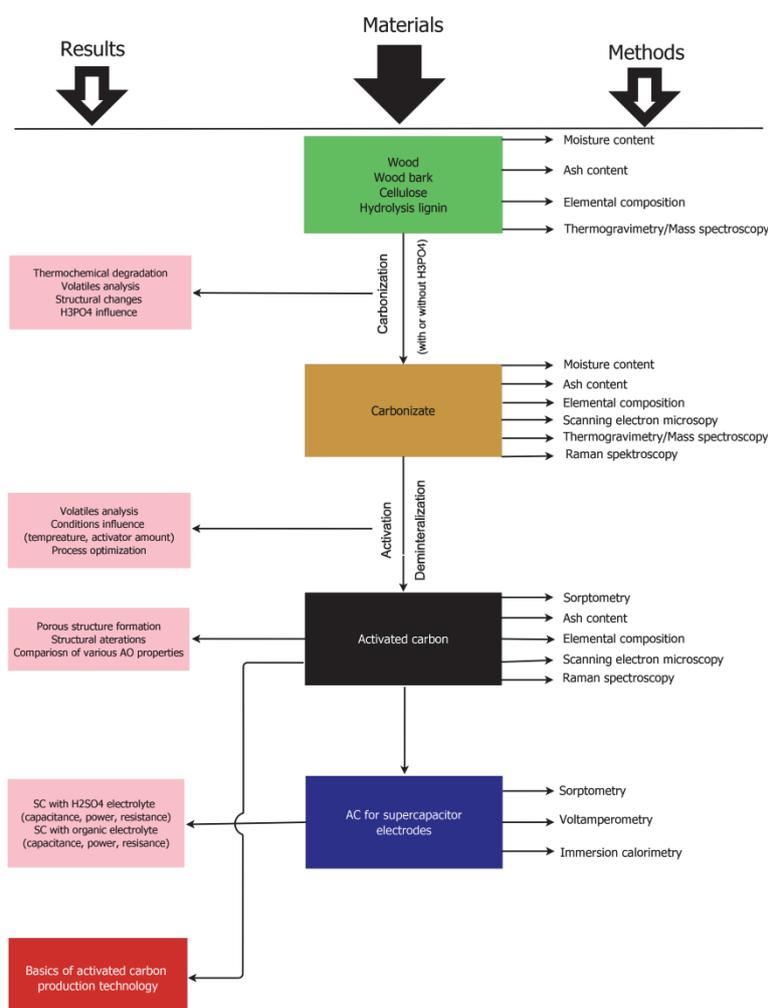


Fig. 3. Experimental workflow, analytical methods and the obtained results.

After activation carbon-salt mixture was cooled down in argon flow and mixed with water. Then samples were demineralized: carbon was mixed with 10 % hydrochloric acid and boiled for 2 hours, after that the flask content was filtered and washed with deionized water until neutral pH.

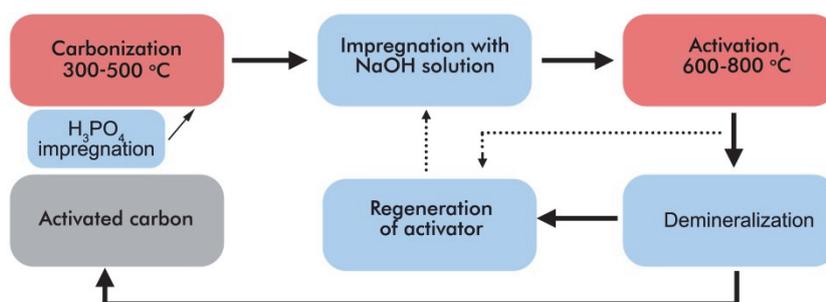


Fig. 4. AC synthesis on the base of plant biomass.

The Experimental part of the thesis provides the description of devices and methods which were used for precursors and AC study. Laser diffraction was used to control

changes of AC particle sizes during the refining process. Specific surface, pore size and volume were calculated using N₂ adsorption isotherms applying BET, DR and DFT theories. Raman spectroscopy was used to study the structural changes of AC. Elemental composition was determined using CHNS elemental analysis. Study of volatiles formation in carbonization and activation processes was performed using TG/MS technique. Determination of thermodynamical interaction (heat evolution) of activated carbons surface functional groups with liquids depending on activation condition was performed using immersion calorimetry. Ash content was determined according with STM D2866 standard. Microstructure of obtained AC was studied with electron scanning microscopy. Supercapacitor testing was performed using galvanostatic charge-discharge method in 2M H₂SO₄ water solution or 1M (C₂H₅)₄NBF₄ solution in acetonitrile or propylene carbonate.

RESULTS AND DISCUSSION

1. The formation of volatiles from wood in thermochemical processes

It was necessary to study volatiles formed in thermochemical processes with NaOH and H₃PO₄ for the elucidation of carbonization and obtained product activation process. The volatile products of the thermal destruction of initial wood, judging from the TG-curve, are formed similarly to the case of samples of other hardwood species [6], with a maximum on the DTG-curve at 388 °C (Fig. 5). The TG-curves of wood after the introduction of 6 % H₃PO₄ are practically similar to the curves, obtained for the wood sample with the additive of NaOH ($K = 1$), despite the different mechanism of action of the acid and alkali (Fig. 5).

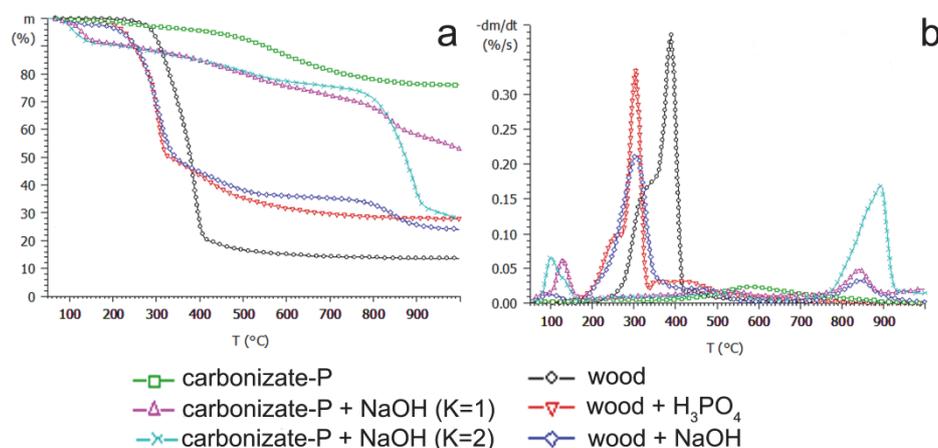


Fig. 5. The TG (a) and DTG (b) curves the samples of wood and carbonizate-P: for initial and with addition of H₃PO₄ (6 %) and NaOH.

The formation of the volatile products during the destruction of carbonizate-P, derived upon the heating of wood with the addition of H₃PO₄, shows that with temperature increase volatile products evolve at a rather low, but relatively constant rate, and the process of their formation is accomplished already at 800 °C. Upon the introduction of NaOH into carbonizate-P, the precursor and alkali reaction releases about 10 % of volatile products in the low-temperature region of up to 170 °C in contrast to the initial carbonizate-P (Fig. 5), (Table 1). With increasing temperature from 170 °C to 780 °C, the formation of volatile products occurs at a low rate similarly in all the three samples of carbonizate-P (Fig. 5).

For wood and carbonizate-P with additives of alkali, typical is the process of the formation of volatile products in the temperature range 800 °C to 900 °C. In this case, the amount of volatile products increases at the increasing content of alkali in the composition, which indicates the reactions connected with the participation of NaOH. The formation of individual volatiles takes place in the temperature range of the main thermal degradation (200 °C to 340 °C), except methane (400 °C to 700 °C) and hydrogen (700 °C to 900 °C) (Fig. 6).

Table 1

Yields of gases and water and mass loss data (TG/MS) of the samples of alder wood and carbonizate-P: for initial and with H₃PO₄ and NaOH addition (%)

Products	T, °C	Yield of volatiles, %					
		Alder wood	Wood + H ₃ PO ₄ (6 %)	Wood + NaOH (K = 1)	Carbonizate -P	Carbonizate -P + NaOH (K = 1)	Carbonizate -P + NaOH (K = 2)
H ₂	450–1000	0.1	0.2	0.3	0.4	0.4	0.3
H ₂ O	30–170	0.0	0.5	2.3	0.5	6.3	8.2
H ₂ O (pyrolytic)	170–900	17.4	30.6	25.0	14.3	8.4	7.8
CO (1 _{st} stage)	150–400	4.8	1.7	6.4			
CO (2 _{nd} stage)	400–950	2.1	5.6	7.3	5.7	9.3	33.2
CO ₂ (inorg.)	50–160					2.0	1.6
CO ₂	160–900	8.9	6.4	13.2	4.6	12.5	11.1
Sum of gases	30–1000	33.3	44.8	54.6	25.6	38.9	62.2
Mass loss	30–1000	86.3	72.1	75.9	24.0	47.0	72.2

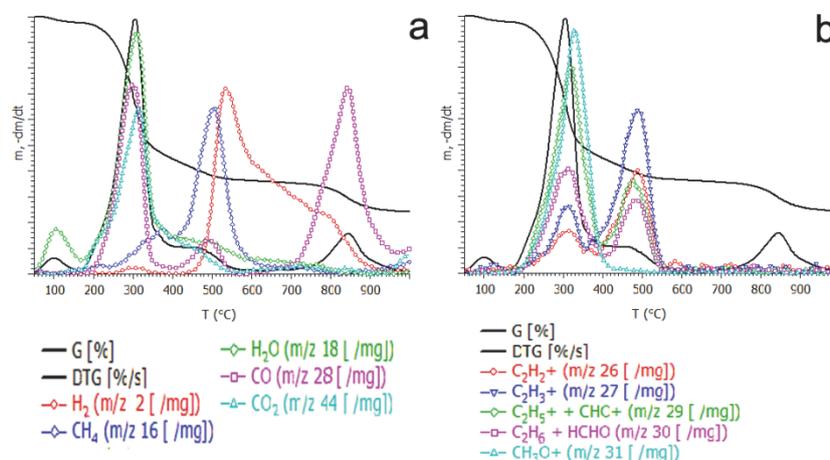


Fig. 6. The TG and DTG curves and the evolution profiles of some fragment ions for the alder wood with NaOH addition (TG/MS method); a – low molar mass volatiles; b – products with molar mass 43 g/mol to 60 g/mol).

The addition of NaOH to wood shows different behavior in the formation of individual volatiles in comparison with raw samples and samples with the addition of H₃PO₄, namely, mass loss occurs in a broader temperature region (Fig. 6). The effect of NaOH manifests itself in the fact that volatile compounds, observed as C₂H₃⁺, C₂H₂⁺, C₂H₅⁺, CHO⁺, C₂H₆⁺, HCHO⁺, CH₃O⁺ fragments, are formed also at higher temperatures with a maximum on the DTG curves at 490 °C (Fig. 6 b). The total amount of gaseous products under the influence of NaOH increases by 20 % in comparison with

that for initial wood, despite the considerable decrease in the share of the organic component in the sample (Table 1). The main changes in the yield of gaseous products occur upon the formation of methane, hydrogen and carbon oxides (Fig. 6 a). The yield of carbon monoxide increases most considerably at both stages of destruction, with maxima at 300 °C and 850 °C (Fig. 6 a). Probably, at the 1st stage, reactions of alkali with the acidic functional groups of wood occur, and the 2nd stage reflects formation of turbostratic carbon structure and, possibly, polyaromatization processes.

The TG/MS analysis of the initial carbonizate-P and carbonizate-P with alkali addition revealed the absence of larger molecules indicating the lack of fragmentation of the structure of the precursor and largely only water and gaseous products such as methane, carbon oxides and hydrogen were formed (Table 1). This testifies a high thermal stability of carbonizate-P, which is explained by the dehydrating effect of H_3PO_4 on the thermal treatment of wood. Besides, as a result of thermal transformations, H_3PO_4 forms at the surface of carbonizate-P a film of polyphosphoric acids, which hamper the thermal oxidation [3].

The interaction of alkali with carbon precursor leads to the one of most important activation reactions. Addition of NaOH to wood leads to evolution of hydrogen in wide temperature region from 480 °C to 900 °C and reaches maximum at 500 °C (Fig. 7 a). In the case of carbonizate-P with NaOH addition range and maximum rate shift to the higher temperatures of 550 °C to 900 °C and 800 °C, respectively (Fig. 7 a). Hydrogen evolution maximum at 800 °C was observed for all samples, including precursor and samples with NaOH and H_3PO_4 addition, and can be connected with polyaromatic structure formation.

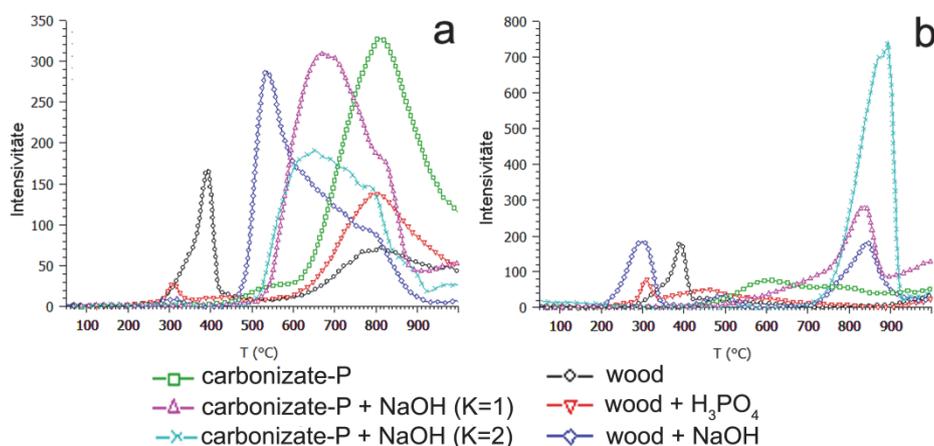


Fig. 7. The TG and DTG curves and the evolution profiles of H_2 (a) and CO (b) for the alder wood and carbonizate-P samples (TG/MS method).

The formation of CO occurs upon the destruction of all the samples under study (Fig. 7 b). The second stage of the formation of CO upon the destruction of wood with the addition of alkali coincides with the formation of maximum of this gas for carbonizate-P with additions of alkali. In this case, with a twofold increase of the amount of the added alkali, the amount of the released CO increases more than threefold (Table 1).

The obtained TG/MS data illustrate that polyaromatic and porous structure formation most actively proceed with H_2 and CO evolution in the samples with NaOH addition.

2. Study of AC structure

It was important to clarify if the precursor nature influences AC porous structure. To elucidate this porous structure tests were performed for activated carbon samples obtained from alder wood and its carbonizate with NaOH addition. Nitrogen adsorption isotherms for all samples belong to Type I isotherms. It is known, that this type of isotherms is characteristic for containing fine micropores [7].

Table 2

Characterization of porous structure of AC based on wood and carbonizate-P with NaOH addition

Sample	Average micropore width, nm	V_{micro} , cm^3/g	V_{kop} , cm^3/g	S_{DR} , m^2/g	S_{BET} , m^2/g
Wood + NaOH, $K = 1$	1.50	0.49	0.53	856	1143
Carbonizate-P + NaOH, $K = 1$	1.12	0.73	0.95	1423	1546
Carbonizate-P + NaOH, $K = 2$	1.22	1.01	1.33	1857	1998

In the case of carbonizate the pore structure was more developed comparing to wood, and the increase of NaOH addition rate intensified this process. In the case of carbonizate activated at $K = 2$ specific surface increases up to 23 % and reaches $1988 \text{ m}^2/\text{g}$ (Table 2). It should be noted that there is a good correlation between specific surfaces calculated from experimental data using BET and Dubinin–Radushkevich theories.

Based on TG/MS experimental data, mechanism of biomass activation in the presence of alkali is suggested and synthesis of AC is schematically represented in Fig. 8. It offers general concept of formation of AC porous structure in the stages of alkali activation process.

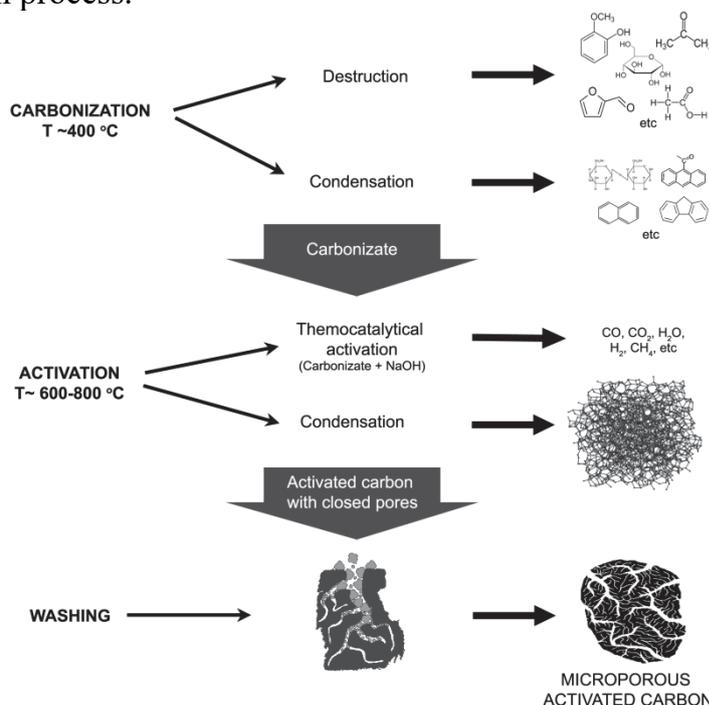


Fig. 8. Thermochemical activation of plant biomass for the synthesis of activated carbon.

The tests of AC structure were performed using Raman spectroscopy. There is a wide spread opinion that solid phase of carbons predominantly consists of polyaromatic graphene clusters (crystallites) [8]. Raman spectra of carbonized wood and AC obtained from carbonized wood at 700 °C in the presence of NaOH are shown in Fig. 9. Raman spectroscopy data allow calculating of crystallites sizes of obtained AC, which is important for stable operation of electrochemical high capacity devices. As the result of Raman spectra deconvolution and numerical integration average sizes of crystallites (~9.8 nm) were calculated for the samples under study.

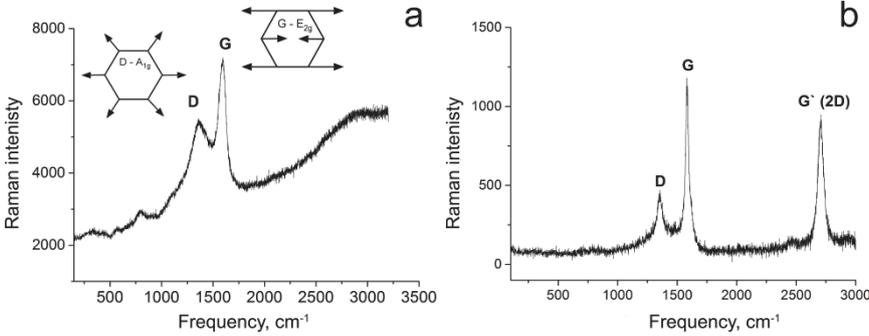


Fig. 9. a – Raman spectra of wood carbonizate; and b – AC (Carbonizate-P + NaOH, $K = 2$, activation temperature 700 °C).
 D – amorphous carbon structure; G – graphite structure;
 G' (or 2D) – two dimensional carbon structures (graphenes).

AC obtained in the pyrolysis process belong to slit pore model [9], where micropores are formed by spaces between carbon layers. There is a number of hypotheses which tend to describe AC pore structure formation.

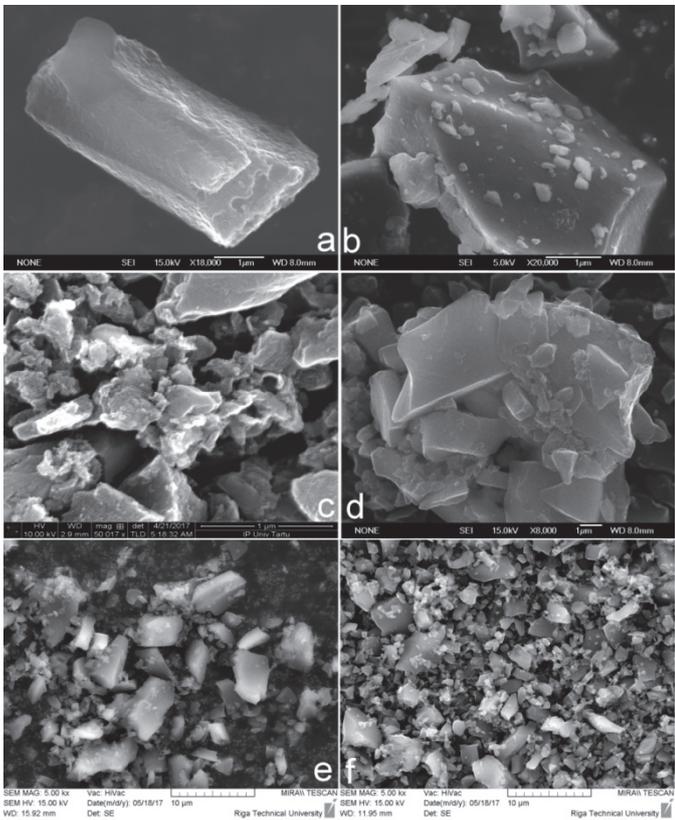


Fig. 10. SEM images of AC samples: a, b, e – carbonizate; c,d,f – AC synthesized at 700 °C and $K = 2$.

According to the hypothesis published in work [10] porous structure forms in the process of lignocellulosic precursor carbonization, which being activated afterwards with elimination of carbon functional groups and carbon atom, stabilize in five-, six- and seven atom cyclic systems. It is generally thought that that these structures are not planar, but rather form cells, which can adsorb adsorbate molecules.

SEM images (Fig. 10) illustrate that the obtained AC particles have a layered structure. The following transformations can take place when carbonize (Fig. 10 a, b) is being thermochemically activated in the presence of alkali: after reaching melting temperature alkali come in contact with the outer surface of carbonize particles and enter into their macropores and cracks; with temperature increase carbon oxidation reactions proceed with volatiles formation at the points where carbon comes in contact with alkali, e.g. at graphenes periphery between edge C-atoms. The above mentioned processes lead to cracking and size decrease of particles (Fig. 10 c, d, e, f). As a result, surface of particles becomes rough and pitted (Fig. 10 c, d), comparing to initial carbonize (Fig. 10 a, b).

The reactions take place at the surface of particles and the non-uniform pore size distribution is possible: the highest number of pores forms at the perimeter of graphene structural edges, where the contact with alkali is most probable. This effect is more pronounced with the particles of larger size and non-uniformity increases with the increase of activator addition ratio.

3. Analysis of various plant biomass precursors applicability for AC synthesis

To further explore options of AC synthesis, various plant biomass precursors were carbonized, activated, demineralized, and their porous structure and properties were investigated. These tests were required to elucidate optimal conditions of AC synthesis and evaluate NaOH and H₃PO₄ influence on their properties – porosity, yield and oxygen content. Besides, precursor and its treatment conditions for application as SC electrodes were assessed. For this purpose 37 samples from Kraft cellulose, hydrolysis lignin, birch wood and bark were tested. First samples were carbonized (375 °C to 550 °C), then impregnated with 50 % NaOH solution (*K* from 0.50 to 2.15), and activated (575 °C to 800 °C). To intensify the dehydration and to reduce oxygen containing groups several samples were impregnated with phosphorous acid and then carbonized and activated.

The highest yield was observed in the case of hydrolysis lignin precursor – 38.5 %. This can be explained by the initial highest content of carbon in the precursor. The lowest oxygen content was found in the case of cellulose sample which was additionally treated after activation (600 °C and *K* = 0.5) at 800 °C – it decreased from 9.3 % to 5.9 %, which can be explained by decomposition of oxygen containing groups.

The synthesized structure of AC samples was tested using N₂ sorption. It was found that NaOH activation in the temperature range 575 °C to 800 °C leads to formation of highly porous carbons. Analysis of nitrogen adsorption isotherms shows that AC porosity is mainly represented by micropores with volume 0.24 cm³/g to 1.15 cm³/g and average width around 1 nm with small addition of mesopores with width lower than 10 nm. Input of the latter into total specific area is insignificant – around 3%. Average specific surface area was from 420 m²/g to 1469 m²/g according to Dubinin–Radushkevich theory and from 402 m²/g to 3358 m²/g using BET theory.

Kraft-cellulose was chosen as the testing subject since this precursor has the most stable and predictable properties comparing to other materials. AC synthesized from

Kraft-cellulose have total specific surface $600 \text{ m}^2/\text{g}$ to $1100 \text{ m}^2/\text{g}$ and pore size 1.0 nm to 1.4 nm . At the same time AC synthesized from hydrolysis lignin, wood chips and bark have porosity higher than $1100 \text{ m}^2/\text{g}$ and pore size close to supermicropores (1.3 nm to 1.7 nm).

Analysis of the results of this work as well as literature data about AC obtained from various precursors in various conditions led to the conclusion, that there is no correlation between AC yield and micropore volume. Obviously micropore volume of AC mainly depends on precursor nature rather than its history and activation conditions. For all samples under analysis correlation between AC micropore volume and width was determined. The obtained comparative data can be used to forecast and utilize application potential of various precursors for AC production.

Response surface methodology was used to assess H_3PO_4 and NaOH influence on thermochemical activation process and AC yield. For this study Kraft-cellulose impregnated with H_3PO_4 and then activated was chosen (Fig. 11). Precursor impregnation with H_3PO_4 before alkali activation leads to AC yield increase (Fig. 11 a). At the same time oxygen content in these samples was substantially lower (Fig. 11 b) – acid reduced it and in the consequent stage of thermal treatment dehydration and condensation reactions take place. These processes decrease volatiles formation and, as a result carbon yield is higher. Figure 11 c illustrates that the porosity development depends linearly on both variables. Whereas H_3PO_4 pre-impregnation appears to hinder the porosity development, increasing amount of NaOH leads to much more porous materials.

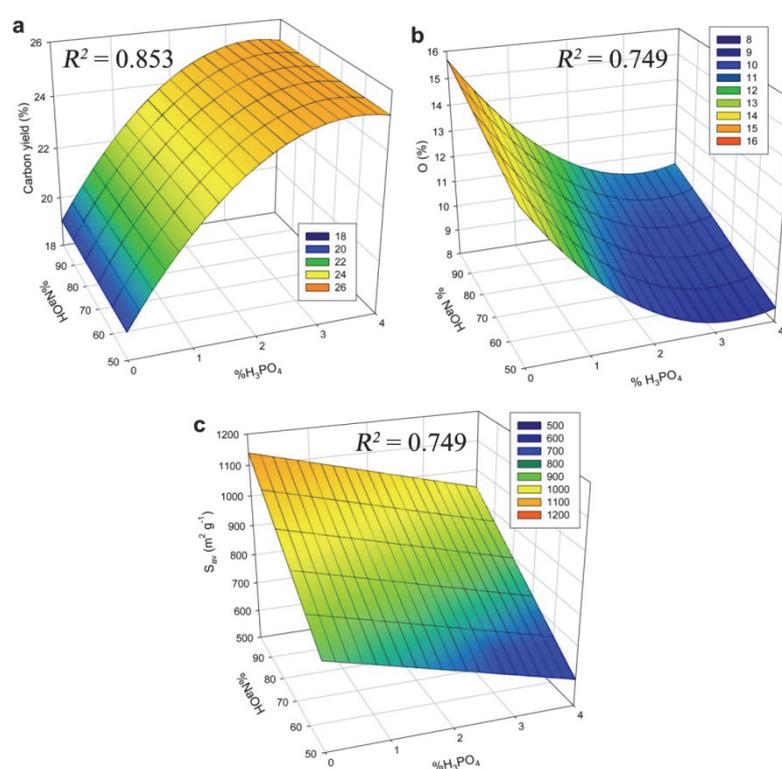


Fig. 11. Response surface of a) carbon yield, b) oxygen content and c) total surface area vs. impregnation ($\% \text{H}_3\text{PO}_4$) and activation ($\% \text{NaOH}$) ratios.

When considering optimal conditions of AC production, it is necessary to consider economical implications and pay attention to oxygen content in AC, which can impact SC properties [11].

4. AC electrochemical properties

Structural and chemical properties of the obtained AC point at their potential use as capacitor electrodes. For the evaluation of the synthesized AC performance as SC electrodes samples with the lowest content of oxygen were chosen. AC synthesized from wood chips and bark showed 308 F/g in sulfuric acid (BM-2) and 200 F/g in $(C_2H_5)_4NBF_4$ /acetonitrile (BK-2) electrolytes, which are promising results comparing to commercial AC (Table 3).

Table 3

SC specific capacitance at current 1 mA/cm

AO	Specific capacitance, F/g		L_o , nm	S_{BET} , m^2/g
	2M H_2SO_4	1M $(C_2H_5)_4NBF_4$ /acetonitrile		
BK-2	258	200	1.13	3358
BK-5	275	173	1.32	2174
BM-2	308	164	1.28	2192
BM-5	211	166	1.52	2596

This, as well as Ragone charts analyses prove the potential of AC synthesized from birch wood as electrode material (Fig. 12) in organic and aqueous electrolytes. The vertical axis in these charts describes how much energy is available, while the horizontal axis shows how quickly that energy can be delivered, otherwise known as power per unit mass. Figure 12 illustrates that SC with electrodes synthesized from wood and wood bark using NaOH at 650 °C to 750 °C compete with commercial AC which is used for SC production (*Arkema-Ceca, Spain*).

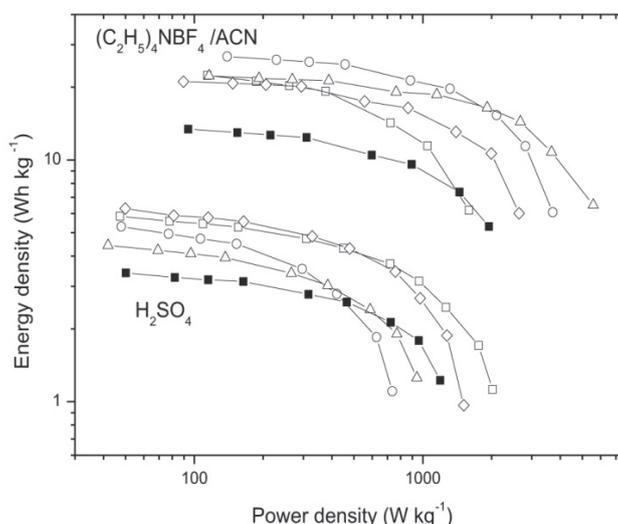


Fig. 12. Energy storage vs. power release of capacitors with birch wood-based carbons as electrodes in aqueous (H_2SO_4) and organic ($(C_2H_5)_4NBF_4$ /acetonitrile) electrolytes. AC from wood chips BK-2 (o), BK-4(\square) and wood bark BM-2 (Δ), BM-5 (\diamond). Commercial activated carbon (SC-10 - \blacksquare) is included for comparison.

The data corresponds to unit mass of carbon in the capacitor.

Contrary to expectations, SC with electrodes synthesized from Kraft-cellulose and hydrolysis lignin did not show impressive results. These SC have exhibited specific capacitance of only around 100 F/g in aqueous electrolyte and did not reach high power in the case of organic electrolyte since energy density decreased with power increase. With the increase of AC pore volume increases surface where electrical double layer

forms, however at the same time thickness of pore walls decreases, which, in its turn, can hinder EDL formation due to interaction of similarly charged particles and consequently slow down the movement of charge in the solid phase. It should be noted, that at the particles borders pore walls can be even thinner due to the processes of volatiles formation which take place when carbon interacts with molten alkali. Obviously, this process is more pronounced with activator addition ratio increase. This can lead to ohmic resistance of AC and electrodes, since the solid phase contact area between carbon particles decreases. Taking in the view the above mentioned hypotheses it can be proposed that the high degree of heterogeneity, which is governed by the number of thin pore walls at the AC particles perimeter, can lead to the situation when EDL does not form in the comparatively deep pores. In other words, AC with large micropore volume can show low energy efficiency when calculating on dry mass of AC and even worse in the case of carbon mass with electrolyte.

Thus, when developing AC synthesis technology using thermochemical alkali activation, the most important tasks are to provide optimal pore volume and the most uniform pore structure formation inside carbon particles. The crucial factors leading to this are optimal carbonizate particle size and, alkali activator addition ratio.

5. Relationship between AC properties and electrochemical characteristics of SC with inorganic electrolyte

In order to evaluate the influence of AC properties on SC characteristics a number of experiments was performed in to assess the most promising synthesis conditions which would enable achieving of the highest specific capacitance and power of SC. As it was already mentioned the most viable raw material for this task is wood carbonizate. It already has been shown [12] that AC obtained from birch or white alder wood have practically identical porous structure properties and it can be assumed that both wood types are interchangeable within the scope of this work.

Wood-based AC with different NaOH mass ratio to carbonizate ($K = 3.7$ and $K = 1.25$) were obtained using a two stage thermochemical synthesis (1 – carbonization at $400\text{ }^{\circ}\text{C}$, 2 – activation) (Table 4, samples T-1 and T-2). Sample T-2 was synthesized from commercial charcoal on the base of white alder (SIA “Fille 2000”) and activated in the same conditions as T-1 without additional carbonization. Comparatively cheap commercial charcoal was taken for three reasons: first, it allows synthesizing AC in one stage, secondly – local readily available feedstock can be used to synthesize material with high added value, thirdly – this material has stable properties, and is produced in Latvia in large quantities.

All three samples have high specific surfaces (S_{BET} T-1 – $3297\text{ m}^2/\text{g}$, T-2 – $3304\text{ m}^2/\text{g}$ and T-3 – $1659\text{ m}^2/\text{g}$) and similar micropore volumes (V_{mikro} T-1 – $823\text{ m}^3/\text{g}$, T-2 – $828\text{ m}^3/\text{g}$ and T-3 – $791\text{ m}^3/\text{g}$) despite differences in surface areas. This is indication of prominent presence of mesoporosity in the structure samples activated at $700\text{ }^{\circ}\text{C}$ and $K = 3.7$.

All samples are good candidates for SC or as highly effective sorbents regardless of their differences in porosity. It was found that structural parameters for samples T-1 and T-2 are similar. This is an indication of possibility to use commercial charcoals as precursor in further experiments.

Samples T-1 and T-2 and commercial AC from various countries were tested as electrodes in SC with H_2SO_4 electrolyte. For T-1 and T-2 specific capacitances were, 310 F/g and 318 F/g , respectively (Table 4).

However, probably due to high synthesized AC pore volume, electrodes had low density and, respectively electrolyte volume was high and inefficient. The high capacity of SC was prominent only based on dry mass calculation and it was less meaningful if calculated based on whole cell weight (Table 4).

Table 4

Comparison of characteristics of SC with electrodes made from synthesized and commercial AC and carbon fiber cloth (2M H₂SO₄ electrolyte)

Sample	Specific capacitance F/g (at 0.3 A/g)	Specific resistance, Ω/cm	Pore volume (width < 10 nm), mm ³ /g	Electrolyte volume, mm ³ /g	Cell specific power, Wh/kg
T-1 (700 °C, $K = 3.70$)	310	4.5	1550	2311	2.16
T-2 (700 °C, $K = 3.70$)	318	4.3	1290	2202	2.23
T-3 (600 °C, $K = 1.25$)	390	4.6	799	1401	3.06
YP-50F Kuraray (Japan)	182	4	800	1350	1.81
V2 EnerG2 (USA)	182	4	800	1290	1.85
XH-001W Shanxi Xinhui (China)	254	4.4	1000	1670	2.4
Carbon fiber cloth UVIS-AK – T 0.41 (Russia)	211	7.5	370	1170	2.35
Maxsorb-3 (Japan)	320	–	–	2800	–

To elucidate the dependence of SC properties from AC porosity the unorthodox approach was taken – AC pore volume reduction varying temperatures and mass K . Results of wood-based AC porous structure tests are presented in Fig. 13.

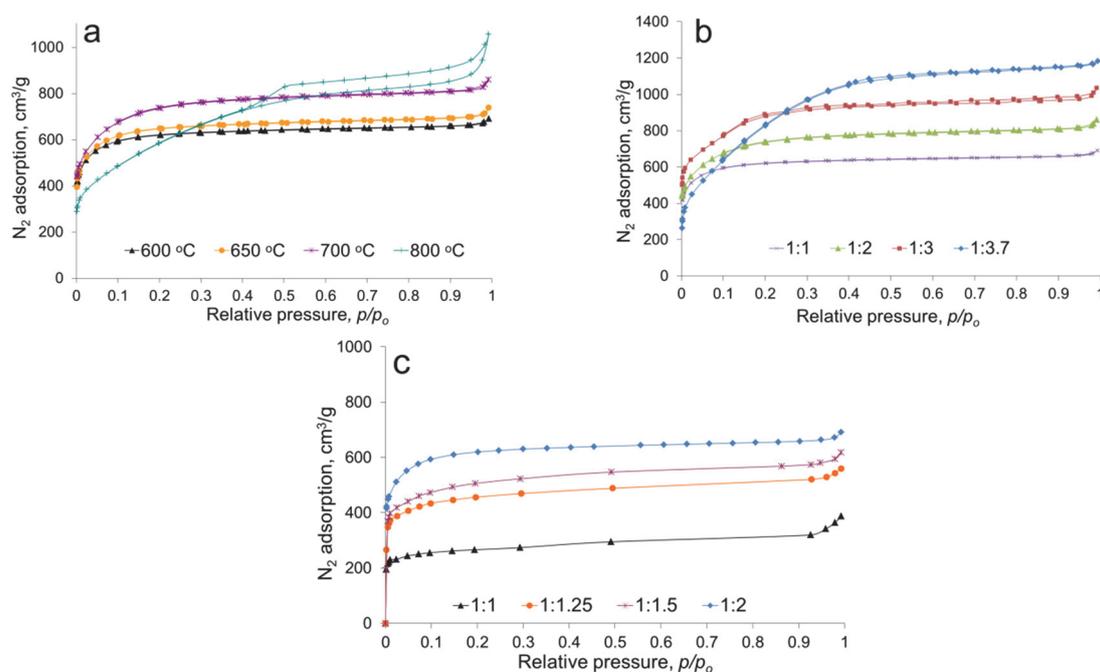


Fig. 13. N₂ adsorption isotherms for AC synthesized in various conditions: a) $K = 2$, activation temperature variation 600 °C to 700 °C; b) activation temperature 700 °C, K variation 1.0 to 3.7; c) activation temperature 600 °C, K variation 1 to 2.

Based on the isotherms of AC synthesized in temperature range 600 °C to 800 °C ($K=2$) (Fig. 13 a), it can be concluded that the adsorbed gas volume increases in activation temperature range from 600 °C to 700 °C at $K=2$ and isotherms belong to Type I, which indicates that AC are microporous. Isotherm of AC activated at 800 °C is different to those of ACs synthesized at lower temperatures and illustrates presence of both micro- and mesopores. The same effect is observed in Fig. 13 b, showing isotherms of AC activated at 700 °C with K values between 1.0 and 3.7. At $K=1$ and 2, isotherms correspond to microporous sorbent (Type I) and with the increase of activator/carbonizate ratio, both isotherms and adsorption mechanisms are changed. At $K=3.7$ the shape of isotherm changes starting at relative pressure 0.1 and up and illustrates that pore filling is governed by both volume filling and capillary condensation and that mesopores are present as well as wider pore size distribution. Isotherms of AC activated at 600 °C and lower K (Fig. 13 c) also illustrate that with increasing K in the range from 1 to 2, the volume of adsorbed nitrogen increases and samples are microporous.

The synthesized AC were used as electrodes in SC cells with sulfuric acid electrolyte. Relationships between porous structure and SC characteristics are shown in Fig. 14.

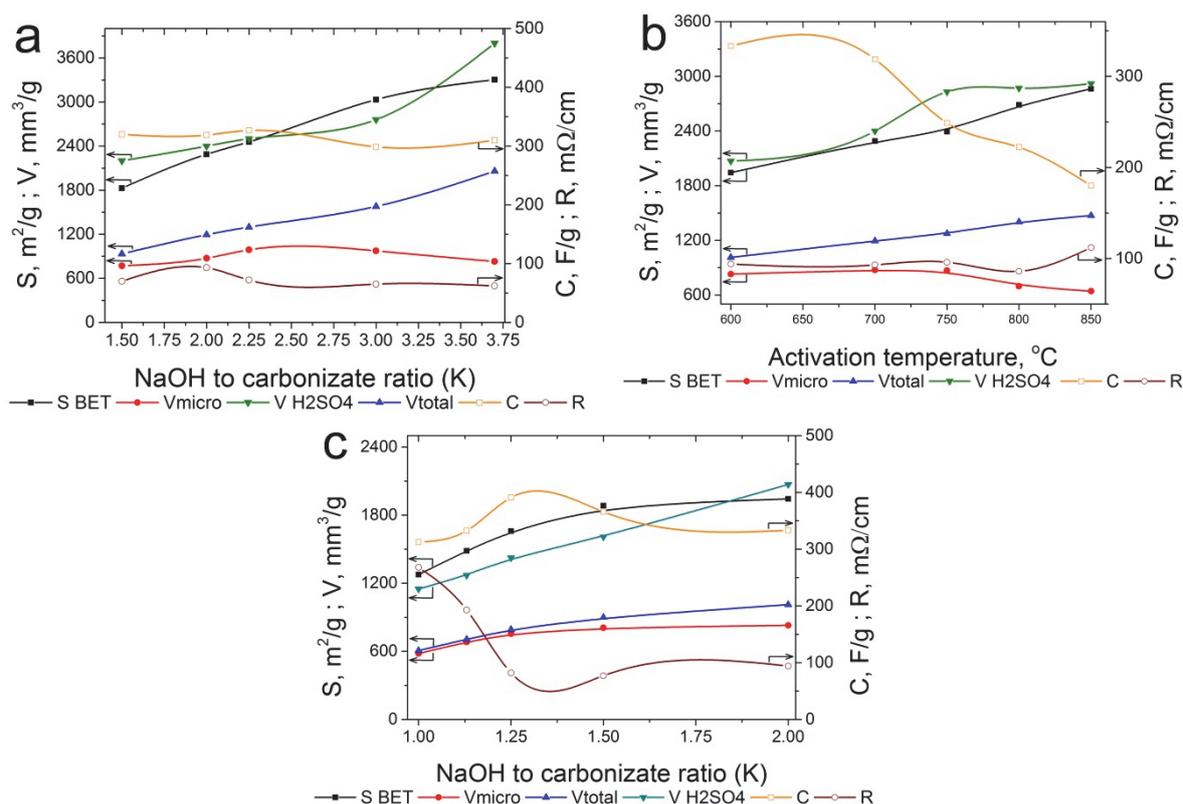


Fig. 14. Dependence of AC porous structure and SC characteristics from: a) K at 700 °C; b) activation temperature at $K=2$; c) K at 600 °C S_{BET} , V_{mikro} , V_{kop} , $V_{H_2SO_4}$ is volume of adsorbed electrolyte, R is resistance and C is specific capacitance.

Calculations based on isotherms data show that activator ratio increase (K varies from 1.5 to 3.7) at 700 °C leads to the development of specific surface (S_{BET}) and total volume (V_{total}), however micropore volume (V_{mikro}) increases until $K=2$ and after that practically does not change (Fig. 14 a). With the increase of pore volume amount of

adsorbed electrolyte ($V_{\text{H}_2\text{SO}_4}$) increases until $K = 2.25$ and does not change until $K = 3$ after that rapidly increasing again. With the alteration of activator ration specific capacitance of SC changes negligibly. It is the same for all samples in the range of K from 1.7 to 3.7 – 310 F/g.

The small influence of K at 700 °C on the capacity (Fig. 14 a) can be explained by the fact that a minimal pore volume is required for the formation of electrical double layer. Probably, there is a factor which counteracts the positive effect of mesoporosity increment – this observation can be interpreted by the change of oxygen-containing functional groups on the surface. These groups can contribute to SC capacitance due to redox reactions (also called the pseudocapacitance effect) and can also elevate the hydrophilicity of surface pores, where EDL is formed. This parameter is evaluated and discussed further.

Another important parameter influencing carbon material properties in the process of synthesis is activation temperature. Characteristics of AC activated at 600 °C to 850 °C and $K = 2$ are presented in Fig. 14 b. With the increasing activation temperature keeping the constant activator ratio, the total pore volume does not change significantly, but the micropore volume reaches its maximum at 700 °C and after that a negative trend can be observed. The same is true for SC capacity, which practically does not change in 600 °C to 700 °C range – it is 330 F/g in case of 600 °C, but it is lowered to 180 F/g in case of 850 °C. This means, that in this case activation temperature and activator ratio decrease positively influences SC electrochemical characteristics as well as AC production expenses.

At higher activation temperatures, the total volume of electrolyte in the electrodes significantly increases. At the same time the intrinsic resistance practically does not change with activation temperature increment in the range from 600 °C to 800 °C (Fig. 14 b). At higher activation temperatures, the resistance increases, probably due to the presence of larger pore volumes. Probably the capacitance decrement with activation temperature increase can be explained by the decrease of C-O groups content on the carbon surface, a parameter, which influences pseudocapacitance.

Thus the activation temperature decrement positively influenced specific properties of SC calculating at cell mass. Experimental data for AC synthesized at lower activator to precursor ratios and 600 °C are presented in Fig. 14 c. Increase of NaOH ratio from 1 to 2 leads to higher values of total and micropore volumes, and in the K range 1.5 to 2.0 the latter does not change. Increase of porosity entails an increase of adsorbed electrolyte volume. With the elevation of K from 1.00 to 1.25, capacitance of SC increases and its resistance rapidly decreases, reaching maximum and minimum, respectively (Table 4, sample T-3). With the further increase of K from 1.25 to 2.00, capacity decreases with practically constant values of electrode resistance.

As the result of alterations of wood activation conditions, specifically the decrease of activation temperature and K , lead to the increase of specific power capacity up to 30 % calculating on elementary cell mass.

Activation temperature or/and activator ratio increment lead to the formation of additional pores, which adsorb electrolyte. Probably with the increase of activation temperature, pore walls become thinner, which can negatively influence EDL formation. This assumption was proven by authors of [13], who found that potential distribution in CM has the main influence on the system capacity compared to potential distribution in the aqueous electrolyte. Solid phase contribution into the SC intrinsic resistance for the electrolytes with high and low ionic conductivity is different. For the water-based

electrolyte with higher ionic conductivity, its effect is more pronounced than that for organic electrolyte. The smaller cell wall thicknesses influence probably negatively the solid phase coherency, which in its turn leads to more ohmic losses due to the diminished contact between carbon particles in electrodes.

Judging from the dependency of SC characteristics from activation temperature, the increase of adsorbed electrolyte volume is not accompanied by intrinsic resistance decrement and specific capacitance increment. This can be explained by two factors. First, deepening of pores can cause difficulties for ion penetration because of gating and uneven charge distribution inside micropores. Secondly – narrower micropores can have positive influence on specific capacitance due to ions solvation shells distortion inside carbon nanostructure, which leads to closer approach of the ion center to the electrode surface and to an improved capacitance.

6. Relationship between AC properties and electrochemical characteristics of SC with organic electrolyte

Operation limits of carbon electrodes in aqueous electrolyte are within 1V range, since higher potentials lead to non-reversible electrochemical reactions, which destroy the structure of fine carbon materials and rapidly decrease SC operation time. SC with aqueous electrolytes gained popularity due to hybrid type power supplies, which can rationally accumulate and recuperate energy in vehicle acceleration and braking processes. The same problems exist in miniature autonomous information storage systems, which operate in pulse mode – these systems require high electrical power supplies.

Transition to organic and other electrolytes makes it possible to increase the potential up to 3V, however this leads to pronounced decrease in electrolyte specific conductivity, increases capacitor intrinsic resistance and decreases specific capacitance.

To study electrochemical properties and applicability of synthesized AC, electrodes were manufactured and SC tests with organic electrolyte were performed. The electrodes were impregnated in vacuum with 1 M solution of tetraethylammonium tetrafluoroborate (TEABF₄). Acetonitrile and propylene carbonate were chosen as solvents. The objective of these tests was to determine the conditions for high specific power, high efficiency and low ohmic losses of SC. In the previous chapter it was shown that AC synthesized from wood at 600 °C and $K = 1.25$ were optimal for electrodes with 4.9M H₂SO₄ electrolyte, however in the case of organic electrolyte application of this AC in SC led to only 100 F/g specific capacitance. Obviously in the case of SC with organic electrolyte the mass ratio K is insufficient to provide the structure necessary for effective EDL formation.

For AC which work well in the case of aqueous electrolytes where ion size is rather low the requirement for the certain degree of mesoporosity is not that important, but it is known that pore size distribution plays the most important role for electrolytes based on ionic liquids because of steric factors related to ion size.

As shown in Fig. 15 a, an increase in K up to 2 positively influenced the electrochemical characteristics of SCs, and specific capacitance reached a value of 160 F/g. After taking into account this observation, $K = 2$ was chosen as the basis for further studies.

Specific volume and area increased as a function of activation temperature from 600 °C to 800 °C at $K = 2$ (Fig. 15 b). Up until 750 °C micropore volume and capacity practically do not change. For the synthesized AC the ratio of micropores to the total

volume decreased probably because of the elimination of pore walls, i.e., by merging of the pores. AC electrodes resistance decreases with the increase of activation temperature from 600 °C, reaches minimum at 700 °C and increases afterwards.

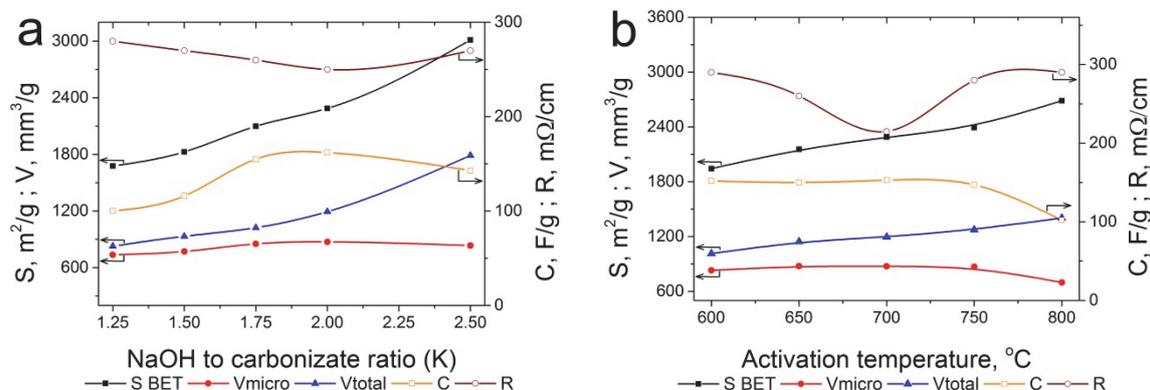


Fig. 15. Dependence of AC porous structure and SC characteristics from: a) K at 700 °C; b) activation temperature at $K = 2$; S_{BET} , V_{micro} , V_{total} , $V_{\text{H}_2\text{SO}_4}$ is volume of adsorbed electrolyte, R is resistance and C is specific capacitance.

Thus the minimal micropore volume and SC specific capacitance were observed for the AC synthesized at 800 °C. The highest capacitance was determined in the case of AC activated at 600 °C to 750 °C and at $K = 2$.

Comparison of SC electrochemical properties made from synthesized and commercial AO is shown in Table 5.

Table 5

Comparisons of characteristics of SC with electrodes made from synthesized and commercial AC (1M (C₂H₅)₄NBF₄/acetonitrile electrolyte)

Sample	Specific capacitance, F/g	Resistance, mΩ/cm	Specific power (dry carbon) Wh/kg Discharge		Specific power (dry carbon + electrolyte) Wh/kg Discharge		Efficiency, % at current		
			170 s to 200 s	8 s to 10 s	170 s to 200 s	8 s to 10 s	150 mA/cm ²	12 mA/cm ²	
DLC SUPRA 30 (Norit, The Netherlands)	86	250	18.3	16.3	8.7	7.7	n. a.	94	
YP 50 (Kuraray, Japan)	102	512	21.9	15.5	10.7	7.6	55	89	
YP 80 (Kuraray, Japan)	102	318	21.8	18.3	9.3	7.8	80	95	
V2 (Energ2, USA)	104	276	22.3	19.6	12.4	10.9	75	99	
P2 (Energ2, USA)	111	264	23	21.1	9.7	8.9	90	98	
XH-001W (China)	143	290	30	23.7	15.2	12.1	82	97	
AC 700 °C	$K = 1.5$	116	334	22.9	17.6	12.6	9.7	67	85
	$K = 2.0$	164	250	33.94	27.59	15.2	12.4	75	96
	$K = 3.0$	156	348	32	19.2	13.1	7.9	60	78

Experiments were made in galvanostatic mode; current was chosen to provide discharge time of 170 s to 200 s and 8 s to 10 s. Variant 8 s to 10 s is related to breaking energy recuperation and 170 s to 200 s to situations, where capacity is not governed by this relatively small current and can be used to assess SC maximum capacitance. It was found that activation at 700 °C and $K = 1.5$ leads to low specific capacitance, high resistance and low efficiency. The highest capacitance was found for AC sample activated at 700 °C and $K = 2$. Application of this AC led to SC characteristics comparable with those for commercial carbons. AC activated at K value higher than two, have promising characteristics calculating on carbon mass. However, due to notable mesoporosity, calculation on carbon + electrolyte mass shows lower efficiency.

7. Influence of other factors on AC and SC properties

Surface oxygen-containing groups. It was already mentioned that oxygen-containing surface groups influence SC properties. Immersion calorimetry was applied to study the concentration of oxygen containing groups on AC surface – data of AC wetting heats in water and benzene was used for this purpose. Benzene has higher affinity to carbon, thus more heat is evolved, and contrary, hydrophobic nature of AC leads to lower wetting heats. Concentration of oxygen containing groups on AC surface is shown in Fig. 16. With activation temperature increment and activator ratio decrement the oxygen content is decreasing (Fig. 16).

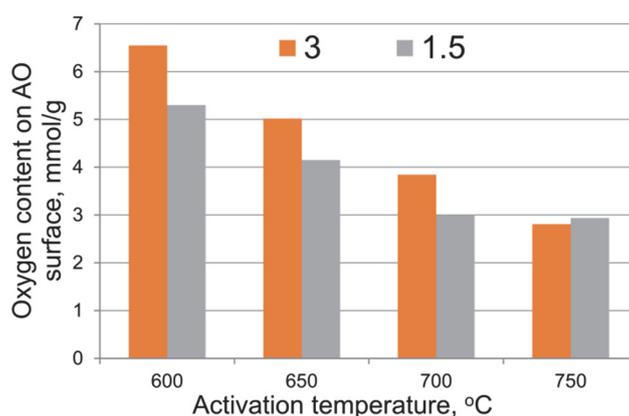


Fig. 16. Concentration of oxygen containing groups on AC surface vs. activation temperature ($K = 1.5$ and $K = 3$).

At $K = 1.5$ and above 700 °C, the oxygen content is nearly constant, and at 750 °C it is the same as in case of $K = 3$. If less NaOH is available, the reactions are finished at lower temperature. Na_2CO_3 formed in these reactions is less active, thus the intensity of reactions is weakening. However, the oxygen content is less relevant than the AC porosity for the elucidation of SC properties in this case.

In the case of sulfuric acid electrolyte oxygen containing groups probably can contribute into pseudocapacitance related reactions and thus increase total SC capacitance. This might be the reason why SC with electrodes from AC synthesized at 600 °C and $K = 1.25$ showed the highest specific capacitance with the lowest resistance. In the case of aprotic electrolyte influence of oxygen containing groups is less pronounced. For this type of SC AC porous structure is an important factor, and oxygen containing groups contribute into intrinsic resistance of cell.

Choice of organic electrolyte. Solutions of TEABF₄ in acetonitrile and propylene carbonate were compared as SC electrolytes. It was found that acetonitrile is a more

effective electrolyte since its application leads to higher specific capacitance 164 F/g and efficiency 96 % with ohmic losses 250 mOhm/cm, when in propylene carbonate case these characteristics were 153 F/g, 85 % and 650 mΩ/cm, respectively. Probable reasons for this were higher density and viscosity of propylene carbonate. These properties can significantly limit electrolyte intercalation into AC pores, decrease ion mobility and hinder EDL formation in SC charge-discharge process. Propylene carbonate also has higher dielectric permeability than acetonitrile (64 vs. 37.5) which increases device resistance and reduces its power and efficiency.

Activation mixture composition. To elucidate the role of water in these reactions, samples were prepared using water-alkali solution for impregnation and using dry mix of carbonizate and alkali powder. It was found that impregnation positively influenced the development of AC porous structure and SC properties. In the case of NaOH water solution, the SC specific capacitance was 164 F/g and only 92 F/g in the case of dry mixing. The efficiency was also positively influenced as it increased up to 2 %. Obviously addition of 50 % NaOH solution leads to more uniform activator distribution among carbonizate particles and reactions are more profound, which is supported by significantly higher porous structure parameter as well as SC properties.

TEHCNOLOGY OF ACTIVATED CARBONS PRODUCTION

Basing on the data obtained in the course of this work the principal schematic of AC production line and material and power balances were developed. Taking into account the demands for AC applied for SC electrodes and for selective gas sorption [14] the technology for the manufacturing of activated carbons for charcoal in the inert, oxygen free atmosphere using NaOH activator at 650 °C to 750 °C with consequent alkali and salt washing and drying is presented. The anticipated volume of production is approx. 100 tons of AC per year. The average volume of production per day is 0.344 tons of AC which will require 0.661 tons of refined charcoal. Total amount of required raw material and lump charcoal per year, taking into account losses in the process of preparation of approx. 0.1 % (burn off, moisture, powdered charcoal losses), was estimated to be 199.9 tons.

The process consists of the following main stages (Fig. 17):

- 1) charcoal refining;
- 2) charcoal mixing with 50 % NaOH;
- 3) activation in the continuous operation kiln;
- 4) cooling down and washing off alkali and mineral compounds;
- 5) drying of product.

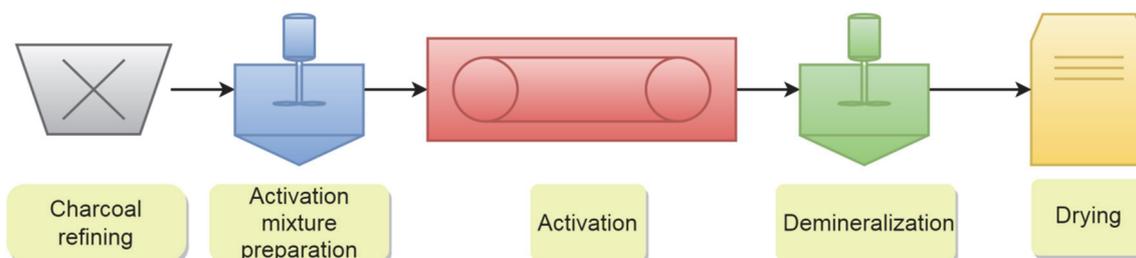


Fig. 17. Main units of AC production from charcoal.

The description of the most important activation and demineralization units and devices is given further.

Activation unit (Fig. 18) is used for a 2 hour long activation of activation mixture at 650 °C with consequent cooling in the stream of inert gas. Activation kiln (3) is a tunnel-type device made of rust-free steel through which the containers filled with activation mixture are rolled or transferred by other means. The heating is provided by electric elements. Kiln consists of three sections separated by elastic metal baffles and provides free movement through three sections.

1. In the heating section the filled containers from activation mixture preparation unit are being heated up to 350 °C and water evaporates. Technical grade argon is supplied at the section end and gas-steam mixture flows in reverse to container movement direction. Gas-steam mixture flows into the heat exchanger (1) and the formed condensate is directed to the purification unit.
2. Activation section provides heating up to 650 °C and 2 hour activation in the stream of technical argon. Gas-steam flow formed in the course of activation is directed into the heat-recovery boiler (2) where natural gas is supplied to ensure complete combustion. The recovered energy is used to heat water for demineralization unit.
3. In the cooling section (4) containers with AC are being cooled down in the stream of technical argon supplied at the section end and then directed into the activation section.

Argon flow should ensure a screen for the atmosphere and prevent its ingress into the activation kiln when containers are being loaded and unloaded. The cooled containers are transported in the demineralization unit.

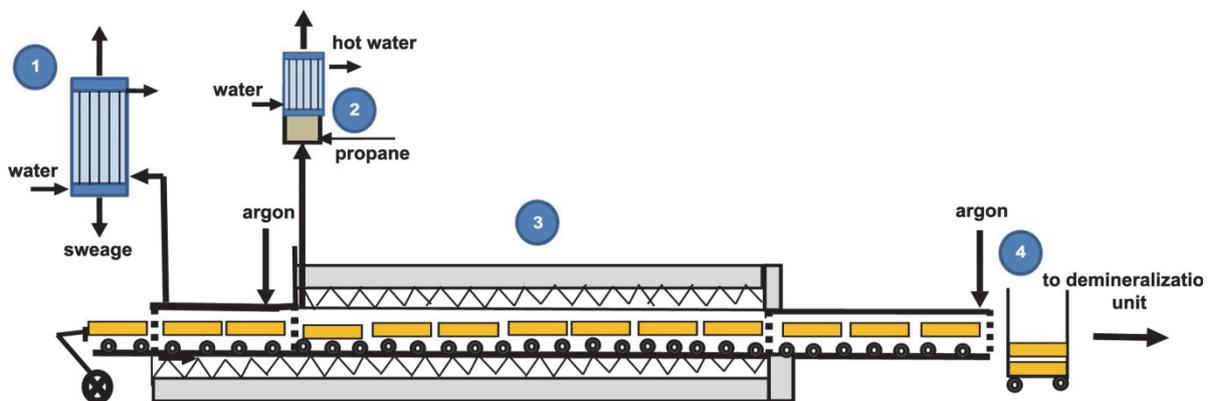


Fig. 18. Technological scheme of activation unit: 1– gas-steam mixture heat exchanger; 2 – recovery boiler for the activation of gas-steam mixture; 3 – activation kiln; 4 – cooling section.

AC demineralization with 10 % hydrochloric acid solution (Fig. 19). After washing from sodium hydroxide and carbonate in the washing unit, AC sediment is directed into reactor (1), which is equipped with agitator, cooling coiler, discharge heat exchanger (2) and stem-heated jacket. 10 % hydrochloric acid solution is being prepared from concentrated technical hydrochloric acid (32.7 %) delivered by vehicles and transferred into the storage (8), connected with scrubber for hydrochloric gas treatment, which also serves as overflow reservoir and is equipped with circulation pump (10). From the storage (8) hydrochloric acid by means of compressed air is being transferred

into the feeder (7) and then the necessary amount is fed into the 10 % hydrochloric acid reservoir, where the required amount of demineralized water, circulating in the closed circle with the aid of pump (4), is added from the feeder (6). The prepared 10 % hydrochloric acid is being directed into the feeder (3) by the pump (4). From the feeder (3) 10 % hydrochloric acid is being fed into the reactor and agitator is switched on. Temperature reaches 100 °C and demineralization process proceeds for 4 hours. Suspension is being cooled down in the reactor by the means of coiler to 60 °C and fed into the nutsche filter (11). Suspension is filtrated with the help of vacuum pump (12) through the receiver (13) and then washed with filtrate from the second nutsche filter (16), which is fed from the feeder (14). Washing proceeds with AC stirring for 15 minutes by means of agitator. The pump (19) transfers filtrate into the neutralization receiver where alkaline solution from sodium hydroxide and carbonate washing unit is being added periodically, then the filtrate from the neutralization unit is transferred to purification units by pump (21). Sediment is being transferred into nutsche filter (16) and for the second time similarly washed with filtrate from the third nutsche filter washing (17), which is stored in the feeder (15), and then for the third time with the filtrate from the fourth washing at nutsche filter (17). After that sediment is transferred into nutsche filter (17) and washed with deionized water from feeder (18) for the fourth and fifth times. The obtained washed AC sediment is being transferred into the trolleys (22) and transported to drying and packaging units.

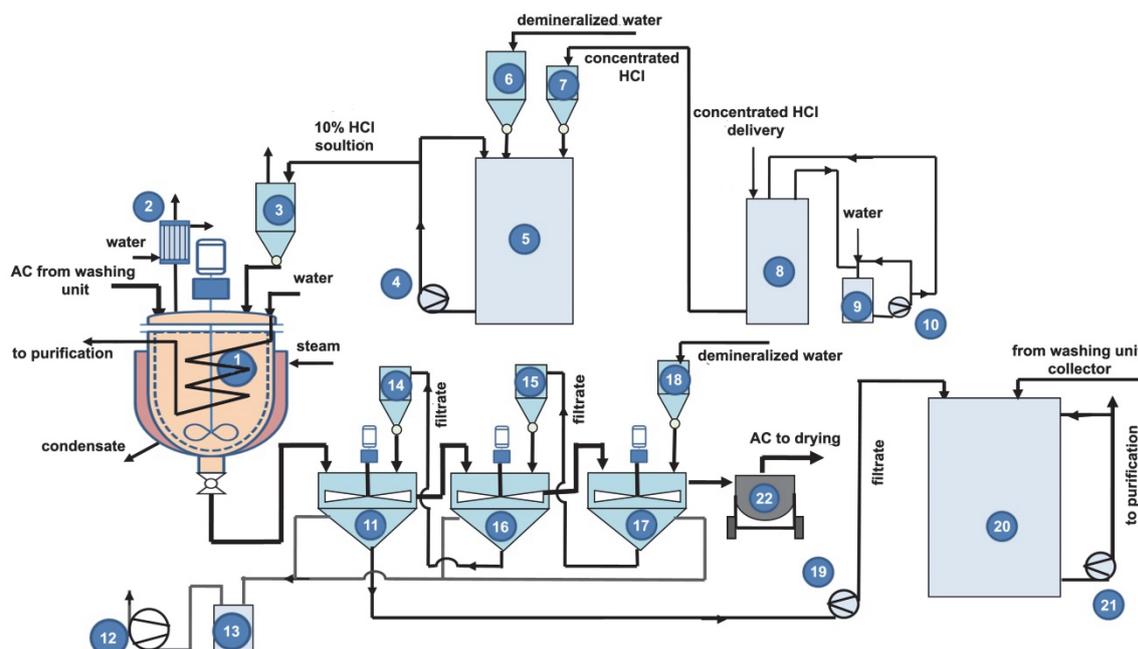


Fig. 19. Principal technological scheme of AC demineralization with 10 % hydrochloric acid.

The total material and power balances calculated per 1 ton of AC are shown in Table 6.

Table 6

Raw materials and power balances

No.	Descriptor	Units	Specific consumption per 1 ton of AC (a. d.)
1	Charcoal	kg	1891.2
2	Sodium alkali	kg	3980.4
3	Hydrochloric acid, 32.7 %	kg	4434.2
4	Argon 4.0	kg	831.7
5	Demineralized water	m ³	79.64
6	Electric power ¹	kWh	17220

¹Electric power consumption is calculated taking into account rated power of units.

CONCLUSION

- The principal possibility for obtaining nanoporous activated carbons from hardwood, its wastes and charcoal using thermochemical activation, as well as development of original technology basics, are studied. Based on this research one international and one Latvian republic patent were awarded.
- It was found that in the course of wood and its carbonizate thermodegradation process activating action of alkali and polyaromatic porous structure formation most profoundly takes place with hydrogen evolution maximum at 550 °C and 700 °C and with carbon oxide evolution maximum at 850 °C.
- It was determined that pretreatment carbonization has positive influence on activation process.
- It was demonstrated that precursor pretreatment with orthophosphorus acid can increase the yield of activated carbon (from 12 % up 36 % in the case of birch wood), total surface area up to 3358 m²/g and decrease oxygen content to 5 %.
- Pretreatment and activation conditions were evaluated and optimized, their influence on activated carbon porous structure, properties and possibility to use in supercapacitors was elucidated. It was shown that micropore volume is mostly governed by precursor nature.
- The optimal properties of wood thermochemical activation for activated carbons porous structure formation and adsorption properties, providing necessary electric double layer formation in supercapacitor electrodes, were established.
- The correlation between activated carbon synthesis parameters, porous structure and properties of supercapacitors with aqueous and organic electrolytes was determined. It was found that in the case of sulfuric acid electrolyte application of activated carbon with pore volume 791 m³/g and specific surface 1659 m²/g led to supercapacitor with specific capacitance 390 F/g and power 3.06 Wh/kg. In the case of TEABF₄/acetonitrile electrolyte application of activated carbon with pore volume 1993 m³/g and specific surface 2289 m²/g led to supercapacitor with specific capacitance 164 F/g and power 15.2 Wh/kg.
- The principal technology and material balance of nanoporous carbon material production from Latvian charcoals were developed based on the experimental data obtained in the course of this work. Total raw materials and power balances for 1 t of AC production were estimated, main AC production stages were developed and resource, energy and technological requirements were assessed.

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APPROBATION OF THE RESEARCH RESULTS

The main results of the thesis have been summed up in 15 publications and 19 conference theses. One Latvian Republic and one international patent have been awarded. A. Volperts' H-index is 7 (SCOPUS).

Publications:

1. G. Dobele, **A. Volperts**, A. Zhurinsh, D. Vervikishko, E. Shkolnikov, J. Ozolinsh, Y. Yang, and J. Ozolinsh, "Wood based activated carbons for supercapacitor electrodes with sulfuric acid electrolyte," *Holzforschung*, Vol 32, No. 4, pp. 661–671, 2017. *SCOPUS*
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