RIGA TECHNICAL UNIVERSITY

Faculty of Materials Science and Applied Chemistry

Jānis RIŽIKOVS

Candidate for a Doctor's degree in the study program „Chemical technology"

ACTIVATED CARBON FROM HYDROTHERMALLY TREATED AND PELLETIZED WOOD

Summary of the Doctoral thesis

Scientific leaders:
Dr. sc. ing.
J.ZANDERSONS
Dr. sc. ing.
J.KAJAKS

Riga 2010

UDK 674.04 (043.2)
Ri 990 a

Rižikovs J. Activated carbon from hydrothermally treated and pelletized wood. Summary of the Doctoral thesis.-R.:RTU, 2010.-27 p.

Printed in accordance with the resolution of 10 June 2010, protocol No. 84.

This work was supported by the European Social Fund within the project „Support for the implementation of Doctoral studies at Riga Technical University”.

EIROPAS SOCIĀLAIS FONDS

ISBN 978-9984-49-184-4

THE DOCTORAL THESIS IS WORKED OUT AT THE RIGA TECHNICAL UNIVERSITY FOR AQUISITION OF A DOCTORAL DEGREE IN ENGINEERING OF CHEMICAL TECHNOLOGY

The Doctoral thesis is openly defended on 21st December 2010 at 15:00 at the Riga Technical University, Faculty of Materials Science and Applied Chemistry, 14/24 Azenes Street, room 271.

The Doctoral thesis is available at the library of the Riga Technical University, 10 Kipsalas Street, Riga, LV-1659 and the National Library of Latvia, 5 Anglikanu Street, Riga, LV-1050.

OFFICIAL REVIEWERS

Professor, Dr.sc.ing. Jurijs Ozoliņš
Riga Technical University

Senior researcher Dr.chem. Bruno Andersons
Latvian State Institute of Wood Chemistry

Professor Dr.sc.ing. Līga Bērziņa-Cimdiņa
Riga Technical University

CONFIRMATION

Hereby I confirm that I have worked out the present Doctoral thesis, which I submitted for consideration at the Riga Technical University for acquisition of a Doctoral degree (or other) in engineering of chemical technology. The present Doctoral thesis is not submitted in other scientific institutions for acquisition of a scientific degree.

Jānis Rižikovs ……………… (signature)

Date: 4.11.2010.

The Doctoral thesis is written in Latvian; it contains Introduction, References review (9 chapters), Experimental (3 chapters), Results and discussion (11 chapters), Conclusions and the used References list. The Doctoral thesis contains 121 pages, 27 figures, 28 tables, 12 equations, 2 attachments and 132 references.

ACKNOWLEDGEMENTS

I am grateful to my Doctoral thesis supervisors Dr. sc. ing. J.Zandersons and Dr. sc. ing. J.Kajaks for the guidance, timely assistance, patience and moral support during the development of the work.

I would like to thank all my colleagues for the moral and practical support they have rendered me during the development of the thesis, for making the necessary analyses and helping to understand the results. Great thanks to the colleagues of the Latvian State Institute of Wood Chemistry: Ausma Tardenaka, Baiba Spince, Aigars Pāže, Aivars Žūriņš, Gaļina Dobele, Vilhelmīne Jurkjāne, Aleksandrs Aršaņica, Vladimirs Jakušins, Dzintra Vilsone, Uldis Stirna, Bruno Andersons, Ingeborga Andersone, Elīna Kapača, Vladimirs Biziks, Anrijs Verovkins and Māris Puķe, as well as Doctor of the Hungarian Academy of Sciences, Institute of Materials and Environmental Chemistry Emma Jakab for making analyses, helping and for useful recommendations in the experimental work.

Sincere thanks to my wife, mother, sisters and friends for their faith and support.

CONTENTS

LIST OF ABBREVIATIONS

AC	Activated carbon
GAC	Granular activated carbon
GA	Grey alder
MW	Modified wood
o.d.	Oven dried
BET	Brunauer-Emmets-Teller
LC	Lignocellulose
TGA	Thermogravimetric analysis
TG/MS	Thermogravimetry /mass-spectrometry
I2	Iodine
MZ	Methylene blue
MV	Methylviolet
SEM	Scanning electron microscope
kG	Force kilograms, measuring unit of the pellets hardness, determined in an Amandus Kahl Hardness tester device.

ESSENCE AND URGENCY OF THE PROBLEM

The world's price of fossil fuels – oil, coal and natural gas – increases, but the amounts in the fields are getting less. More and more terms such as "green energy", "green products" and "sustainable development" emerge, which means that the use of renewable resources will replace the fossil ones. Therefore, vital political processes were started in the 1980s, which marked the development of the understanding of the overall human responsibility for the future of the planet and its environment. In 1987, the United Nation's Brundtland Commission published the report, "Our Common Future", which focuses on sustainable development and the change of politics necessary for achieving that end. The definition of the term "sustainable development" in the report is quite well known and often cited [1].

The Kyoto Protocol, adopted on 11 December 1997 in Kyoto, Japan, was developed to limit the atmospheric pollution by greenhouse gases in order to reduce global warming, which may cause a dangerous world ocean levels to rise dramatically and alter the Earth's climate system. Latvia has joined the Kyoto protocol in 2002; therefore, it is necessary to reduce the release of greenhouse gases. One of the ways is to produce "green products", employing environmentally friendly technologies. Wood has been examined thoroughly trying to obtain products with a high added value.

Urgency of the issue

There is a low production capacity of exportable chemical products in Latvia. The situation could be improved by producing high-quality products – granular activated carbon (GAC) from the fast-growing and low-value grey alder (GA) wood. Activated carbon (AC) unifies the porous carbon materials prepared by processing of chars with oxidative gases or by carbonization of lignocellulosic materials, with simultaneous chemical activation. The aim of activation is to obtain a high-porosity and internal surface area. Huge amounts of application facilities of AC have been reviewed by more than 1500 industrial patents over the world [2].

Water treatment applications will continue to account for the largest share of the global demand for AC. It is influenced by the need for clean drinking water. Other environmental applications for AC with a strong growth potential include the treatment of flue gases from power plants and hazardous waste remediation. Changes in government regulation and enforcement will significantly impact the demand for environmentally driven applications. The world's annual demand for virgin AC is forecasted to expand by 5.2% until 2012 (that is from 890.5 thousand in 2007 up to 1.15 million tons in 2012) due to the continuing intensification of the global environmental movement, as well as the rapid industrialization in the major part of the developing world [3]. To meet the increasing demand for AC and to decrease the environmental pollution, it is necessary to develop and efficiently realize the innovative technologies of its obtaining.

Powdered activated carbon (PAC), which has historically accounted for the largest share of the overall activated carbon demand (due to its dominance in liquid phase applications and lower cost) will register slower gains of GAC through 2012. The main advantage of GAC is its ability to be regenerated. There is a continuous demand for GAC is in southern Europe and in the United States. Wood as a raw material in GAC production has a disadvantage – the obtained AC is characterized by low density and mechanical strength. Therefore, the AC produced from wood is mostly PAC, which has a lower price than GAC.

The aim of the work

The aim of the work is to develop an original and environmentally friendly technology for production of high-quality, dense and mechanically strong microporous GAC from low-grade deciduous wood, employing the previously known and improved hydrothermal and thermochemical wood-processing techniques. GA as a raw material has several advantages: easy available, cheap, fast growing and capable of growing in poor soils, improving it by enriching with nitrogen.

For the development of the thesis, the following goals were set out:

- to choose the appropriate pretreatment and activation methods for converting of deciduous wood into high-quality GAC based on the data available in the literature;
- to elucidate the appropriate hydrothermal pretreatment technology for pelletizing GA wood without binders, taking into account both environmental and energy aspects based on the experiment results;
- to investigate and develop the impact of the technological parameters (temperature, duration and fractional composition) on the mechanical properties of the obtained modified wood (MW) samples after densification, carbonization and activation;
- to choose the most convenient pelletization method to produce MW pellets with high yield and mechanical properties;
- to investigate the impact of the MW moisture content before pelletization on the properties of the obtained pellets, chars and GAC;
- to elucidate the technological parameters of the carbonization and activation process (temperature, duration etc.) according to the yield, strength and pore structure of the obtained GAC;
- to compare the AC obtained from MW with that obtained from high-quality raw materials (coconut shell) experimentally and from the literature;
- to estimate the possibility to realize the developed GAC producing technology in Latvia and to determine the scope of applications.

For defending the thesis:

- GA wood, which contains high amounts of hemicelluloses and pentosans, is appropriate raw material that would meet the requirements of the proposed subject to treat the wood in a steam atmosphere under pressure at a high temperature without the use of inorganic catalysts.
- During the hydrothermal pretreatment process hemicelluloses are degraded providing self-binding properties of MW for pelletizing of GA wood without binders to obtain dense and mechanically strong pellets.
- Optimized pelletization process (moisture content, fractional composition and the content of hot water - soluble substances) ensure that the resulting pellets are suitable for obtaining high-quality GAC.
- The thermal stability of the MW is higher than the raw GA wood, therefore after carbonization and activation the yields of GAC are higher.
- Chosen optimal parameters make possible to obtain dense, mechanically strong and microporous GAC with a high enough yield and adsorption capacity to compare with GAC obtained from coconut shells.
- Developed technology is environmentally friendly, economically beneficial and appropriate to produce GAC in Latvia.

Scientific novelty of the work

The results of the investigation made it possible to elucidate how the process of partial decomposition of GA hemicelluloses without the use of inorganic catalysts impacts the developed structure, submicroscopic contexture and properties of the obtained MW pellets, chars and AC. A new complex and environmentally friendly technology of GAC production from the modified and pelletized GA wood was developed. Based on the results of research, the proposed technology combines the methods of hydrothermal treatment, pelletization and thermolysis that promote the development of novel technologies.

Practical importance of the work:

- The results of the thesis can be used to develop a novel environmentally friendly production unit, appropriate for Latvia, in which high-quality GAC can be produced from the low grade GA wood (or other deciduous wood species).
- The main feature of the developed technology is the improvement of the properties of GA wood (thermal stability, mechanical strength and density) as a raw material for GAC production by hydrothermal pretreatment with subsequent pelletization, as a result of which the obtained adsorbent is more competitive in the market.

- Optimal parameters of the carbonization and activation process were developed to obtain dense microporous GAC with a high yield, and low abrasion and ash content. So, the obtained adsorbents are appropriate not only for purification of gaseous media, but also in liquid phase applications in pharmacy, chemical and food industries, as well as for environmental applications.

Approbation of the results of the work

The main scientific achievements and the results of the thesis were presented at 13 scientific international conferences, with a positive assessment. The thesis theme is published in 18 printed works, including three articles (1, 6 and 8) in scientific citation journals, 12 articles in full conference proceedings (2, 5, 7, 9-11, 14-18), 3 items of abstract summaries (3, 4 and 13) and a book chapter (with the authors' collective) (12):

1. <u>Rizhikovs J.,</u> Zandersons J., Puke M., Vedernikov N., Dobele G., Tardenaka A. Spince B. Granular activated carbon from deciduous wood lignocellulose // Combined and Hybrid Adsorbents. Fundamentals and Applications. Ed. J.M. Loureiro, M.T. Kartel. - 2005.- Heidelberg: Springer Verlag, (ISBN 1872-4668) - 187-193 p.
2. <u>Rizhikovs J.,</u> Puke M., Zandersons J., Vedernikovs N., Dobele G., Tardenaka A., Spince B. Impact of water-soluble substances of birch lignocellulose on the mechanical and sorption properties of granular activated carbon // Environmental Education, Communication and Sustainability. Sustainable Development in the Baltic and Beyond. Ed. W.L.Filho, A.Ubelis, D.Berzina. - 2006. - Heidelberg: Springer Verlag, (ISBN-10: 3631552823) - Vol. 23. - 479-485 p.
3. <u>Rizhikovs J.</u> Carbonaceous microporous sorbents from furfural production by-product. Abstracts of the 2nd Meeting of the Nordic Baltic Network in Wood Material Science & Engineering (WSE), KTH Campus, Stockholm, Sweden, 30-31 October 2006, - 3 p.
4. <u>Rizhikovs J.,</u> Zandersons J., Vederņikovs N., Puke M., Kruma I., Dobele G., Spince B., Tardenaka A. Lignocellulose-based granulated activated carbons bound with water-soluble carbohydrates // Programme Abstracts Resumes, First International Congress on Green Process Engineering, Toulouse, France, 24-26 April 2007, - 201 p.
5. Zandersons J., Tardenaka A., Spince B., <u>Rizhikovs J.</u> Preparation of high density and strength carbon materials from deciduous wood // Proceedings of the 15th European Biomass Conference From Research to Market Development, Berlin, Germany, 7-11 May 2007, - 2112-2117 p.
6. Zandersons J., Dobele G., Tardenaka A., Spince B., <u>Rižikovs J.</u> Alkšņa koksnes glabāšanas ilguma un ekstraktvielu satura iespaids uz termolīzes gaistošo produktu sastāvu // Latvijas Ķīmijas žurnāls. - 2008. - Nr. 3. - 291-302 lpp.
7. <u>Rizhikovs J.,</u> Zandersons J., Tardenaka A., Spince B. Modified grey alder wood as raw material for production of high density activated carbon // Proceedings

Book of the Italic 4 Science & Technology of Biomass Advances and Challenges, Rome, Italy, 8-10 May 2007, - Roma: Grafica e impaginazione, - 62-65 p.

8. Zandersons J., Dobele G., Jurkjane V., Tardenaka A., Spince B., Rizhikovs J., Zhurinsh A. Pyrolysis and smoke formation of grey alder wood depending on the storage time and the content of extractives // Journal of Analytical and Applied Pyrolysis. - 2009. - Vol. 85. - 163-170 p.
9. Zandersons J., Rizhikovs J., Tardenaka A., Spince B. Lignocellulose of soft structure deciduous wood as a raw material for carbon products // Proceedings of the 10th European Workshop on Lignocellulosics and Pulp, Stockholm, Sweden, 25-28 August 2008, - Stockholm: US-AB, - 376-379 p.
10. Rizhikovs J., Dobele G., Zandersons J., Rossinska G., Tardenaka A., Spince B. Impact of extractives and wood pre-treatment on the composition of grey alder wood smoke // Proceedings of the 16th European Biomass Conference and Exhibition, Valencia, Spain, 2-6 June 2008, - 1106-1111 p.
11. Arshanitsa A., Barmina I., Dizhbite T., Telysheva G., Zake M., Rizhikov J. Combustion and emission characteristics of the plant biofuel pellets // Proceedings of the 16th European Biomass Conference and Exhibition, Valencia, Spain, 2-6 June 2008, - 1482-1491 p.
12. Tardenaka A., Rizhikovs J., Spince B., Zandersons J. Environmental problems in production of high-density activated carbon from wood // Chapter in Kozlowski R. and Pudel F. book Renewable Resources: Obtaining, Processing and Applying. - 2009. - New York: Nova Science Publishers, (ISBN:978-1-60692-534-8.) - 273-279 p.
13. Zandersons J., Rižikovs J., Tardenaka A., Spince B. Provisional amount of the effluents and exhaust vapour formed during production of activated carbon from softwood and feasibility of restriction // Abstract Book of International Conference Eco-Balt *2008,* Riga, Latvia, 15-16 May 2008, - 23 p.
14. Rizhikovs J., Spince B., Tardenaka A., Zandersons J. Activated carbon from modified grey alder wood: advantages and disadvantages of several technologies // Proceedings of the 4th Meeting of the Nordic Baltic Network in Wood Material Science & Engineering (WSE), Riga, Latvia, 13-14 November 2008. - Riga: PERSE Ltd., - 69-74 p.
15. Rizhikovs J. Obtaining of high density and mechanically strength activated carbon from fast-growing deciduous soft structure wood // Scientific Proceedings of the Riga TU, Series 1: Material Science and Applied Chemistry, Riga, Latvia, 14-16 October 2008, – Riga: RTU, 2009. - Vol. 18. - 69-75 p.
16. Rizhikovs J., Dobele G., Zandersons J., Tardenaka A., Spince B. Improvement of the plasticity of grey alder wood and its granulating ability by hydrothermal treatment and upgrading of granulation techniques // Proceedings of the 17th European Biomass Conference & Exhibition, Hamburg, Germany, 29 June - 3 July 2009, - 1583-1588 p.
17. Zandersons J., Tardenaka A., Spince B., Rižikovs J. Aktivētās ogles no hidrotermiski apstrādātas un granulētas koksnes // LV pētījumu programmas

2005. – 2009. g. rakstu krājums - Lapu koku audzēšanas un racionālas izmantošanas pamatojums, jauni produkti un tehnoloģijas, Rīga, 2009. - 165-169 lpp.
18. Rizhikovs J., Kajaks J., Zandersons J., Spince B., Pazhe A., and Jakab E. Pyrolysis behavior of modified grey alder wood samples by TG-MS and TGA techniques // Proceedings of the 18th European Biomass Conference & Exhibition, Lyon, France, 3-7 May 2010, - 1988-1993 p.

SHORT SUMMARY OF THE THESIS

In the **Introduction** of the thesis, the actuality of the work is stated, the aims and objectives are formulated and the guidelines are set out.

The **first chapter** is a literature review, which gives the characteristics of activated carbon (AC) and the obtaining methods; raw materials and application are discussed. Grey alder (GA) wood characteristics and chemical composition are given. Suitable wood hydrothermal treatment technologies are analyzed. The pelletization and carbonization process, as well as the influencing factors on the nature and obtained products are described. The information gathered in the literature review enables to choose the most environmentally friendly physical activation method, which uses overheated water steam as an activation agent. As the raw material, cheap and fast-growing GA wood was chosen. It contains a sufficient amount of hemicelluloses, which, after hydrothermal treatment, act as a pelletization binder [4].

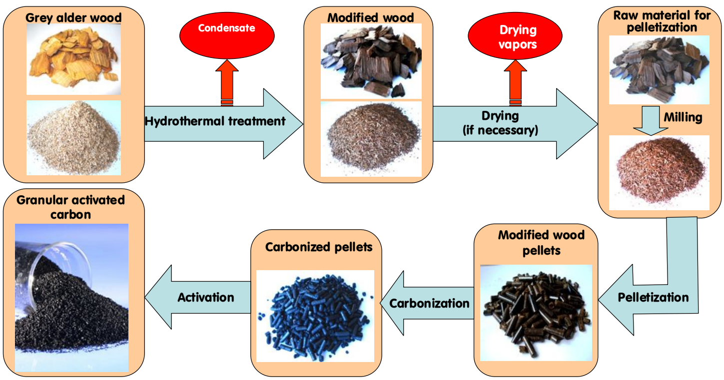


Fig. 1. Experimental scheme for obtaining granular activated carbon from modified grey alder wood

The **second chapter** is the experimental part, which substantiates the choice of GA wood and describes the sample preparation, the materials used in the work, as well as the methods and equipment employed. For development of the new technology, the scheme shown in Fig. 1 was used in the work

The experimental progress and the applied analytical methods are shown in Fig. 2.

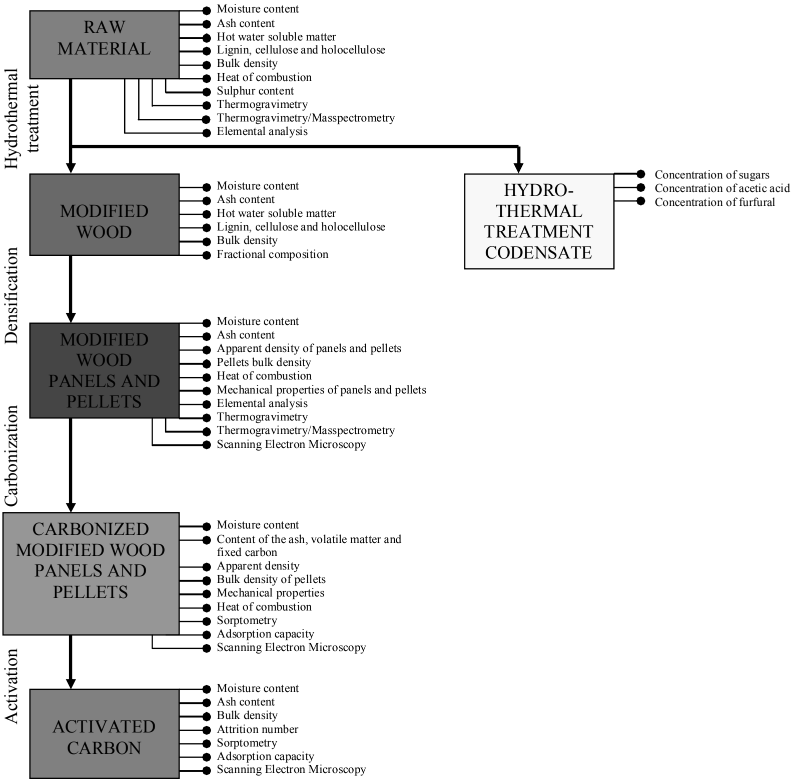


Fig. 2. Progress of the work and applied analytical methods

In the third chapter, the results obtained in chapters 1 and 2 are analyzed, and an assessment is given.

Conclusions consist of the formulation of the obtained results, and the most important solutions are given.

In the References list, the sources used in the work are mentioned, based on which the avenues of research were defined.

RESULTS AND DISCUSSION

Grey alder (*Alnus incana* (L.) Moench) is the second most common deciduous tree species in Latvia. GA wood as a raw material is very appreciative, because it is an excellent pioneer species for re-establishing woodlands on disused farmlands. It is a fast-growing and easy-available tree species, and has a comparatively low price. Due to the high content of hemicelluloses, GA wood is an appreciable material for the hydrothermal pretreatment process.

Hydrothermal treatment

When developing the technology, the minimum quantity of emissions and their pollution degree are taken as one of the parameters of the optimum solution. Therefore, the use of the hydrolysis catalysts was discarded already at the beginning, as they pollute the AC. Also energy consumption is a significant factor, and it is related to the hydrothermal treatment time. In the course of the work, 4 hydrothermal treatment variants were tested:

1) In a laboratory autoclave (water);
2) In a laboratory autoclave with batch supply of saturated steam and blow-off;
3) In a flow reactor;
4) In an autoclave (steam environment).

Heating the water-saturated wood in an autoclave, 5.0-5.6 kg of water should be evaporated during drying in terms of 1 kg of modified wood (MW). It may be concluded that the method is simple; the quality of the MW is good, while the energy consumption is high, and pollution with emissions, especially with furfural, is considerable.

In laboratory conditions, the method is tested with saturated steam, which is supplied and blown-off periodically. The steam consumption and the quantity of the purified emissions to 2.3-4.3 kg/kg oven dry MW are shown in Table 1. It can be seen that this method makes it possible to diminish both energy consumption and the quantity of purifying emissions.

Table 1

Characteristics of emissions of different hydrothermal treatment processes

Treatment type	Moisture of MW, % o.d. mass basis	Quantity of purifying water, kg/kg o.d. MW mass basis	Acetic acid, % o.d. MW mass basis		Furfural, % o.d. MW mass basis	
			Blow-off condensate	Drying exhaust	Blow-off condensate	Drying exhaust
Autoclave	500	5.0–5.6	-	0.1-0.2	-	0.1-0.6
Blow-off autoclave	40-50	2.3–4.3	0.2-1.2	0.3-2.3	0.2-1.1	0.3-3.0
Flow reactor	40-60	1.8–2.4	0.2-1.6		0.2-0.7	
Pilot scale batch autoclave	4-5	0.5-0.6	3.9-6.0		0.2	

If the treatment is carried out in a steam flow reactor, it is possible to reduce the process time from 2 to 1 h, the consumption of saturated or somewhat superheated steam to 1.8-2.4 kg/kg MW, and also the quantity of the condensed wastewater, which contains mostly acetic acid and furfural (Table 1). The concentration of pollutants approximately corresponds to that determined in the previous variant in a blow-off autoclave. The yield of MW is high enough. However, MW, which is obtained in this technology, is wet (w = 40-60%), and drying is connected with energy consumption.

The energy consumption and noxious emissions can be substantially reduced, if the hydrothermal treatment is realized in a pilot scale batch autoclave. The moisture of the MW is about 4-5% (drying is not necessary), and milling of MW chips consumes less energy than milling of wood chips. The quantity of purifying water decreases to 0.5-0.6 kg/kg o.d. MW. The concentration of acetic acid in condensing water increases with decreasing amount of the wastewater, but acetic acid is not the most dangerous pollutant in the wastewater treatment facilities [5]. The yield of the obtained MW is approximately the same as in the previous variants, i.e. 85-91% o.d. wood. It is easy to pelletize, therefore, for the further experiments, the MW obtained in the pilot scale batch autoclave was used.

Pelletizing of the modified wood

The mechanical properties, density and hardness of pellets before and after carbonization depend to a considerable extent on the content of the water-soluble matter in the MW. Water acts as both a binding agent and a lubricant. Water helps to develop van der Waals' forces by increasing the area of contact between particles. Water aids pelleting when water-soluble compounds are present in the raw material such as sugars, sugar polymers, dehydrated carbohydrates, furfural products, lignin and lignin products. Due to the application of high pressures and temperatures, solid bridges may be developed by diffusion of molecules from one particle to another at the points of contact. Solid bridges may also be formed between the particles due to the crystallization of some ingredients, chemical reaction, hardening of binders and solidification of melted components. During the compression process, fibers, flat-shaped particles and bulky particles can interlock or fold about each other, resulting in interlocking bonds. Conventional processes for pressure-assisted densification can be classified into three types: extruding, pelletizing, and briquetting [6].

Two types of pelletizators were employed, namely, extruder type and flat die type. The best results of MW pelletizing were demonstrated on the flat die pellet press, where the pelletized matter yield was higher – from 85 to 94% calculated on the o.d. MW mass. In comparison, 66 to 88% on the o.d. MW mass basis was obtained in an extruder type pellet press. The density of the flat die pellet press MW pellets was 1.362 g/cm^3, and it is by around 36% higher in comparison with 0.886 g/cm^3 of the extruder type pellets density. Almost the same difference was observed in the measurements of bulk density of pellets, respectively, 730-760 g/l and 463-524 g/l (Table 2). The pellets obtained in a flat die pellet press had a significantly higher (around 43%) hardness value, determined using a KAHL hardness tester, in comparison to the pellets made in an extruder type pellet press.

Table 2

Pelletizing of MW

Pellet press type	Yield of pellets, % o.d.b.	Pellet's characteristics		
		Apparent Density, g/cm^3	Bulk density, g/l	Hardness, kG
Flat die	85-94	1.362 ± 0.10	730 – 760	58 ± 8
Extruder	66-88	0.886 ± 0.10	463 – 524	31 ± 8

According to the above mentioned experimental results for further MW pelletizing studies, the flat die pelletizator was used.

Thermal stability of modified wood pellets

Thermal decomposition is strongly influenced by the physical and chemical characteristics of the raw materials. The high oxygen content in the biomass structure, consisting mainly of cellulose, hemicellulose and lignin, is the main reason, why biomass produces high amounts of volatile matter during pyrolysis. In the case of hydrothermal pretreatment, the oxygen content is decreased, and the obtained raw material is thermally more stable than the initial GA wood (Table 3).

Table 3

Results of proximate and ultimate analyses for initial GA wood and modified GA wood samples at separate hydrothermal pretreatment times

Compound	Initial GA wood	Modified GA wood, pretreated at 180 °C		
		1 h	2 h	6 h
Cellulose (wt%)	42.3	50.1	51.9	54.6
Lignin (wt%)	28.7	44.7	47.2	53.5
Hemicelluloses (wt%)	26.9	10.5	8.2	6.3
Ash (wt%)	0.75	1.0	0.82	1.0
C (wt%)	49.94	53.54	54.68	57.34
N (wt%)	0.46	0.40	0.32	0.33
H (wt%)	5.10	4.95	6.38	5.41
O (wt%)	43.45	39.86	37.58	35.72
S (wt%)	0.31	0.25	0.22	0.20

MW has higher cellulose and lignin contents than the initial GA wood. This fact is due to the decomposition of hemicelluloses during the hydrothermal pretreatment. With increasing lignin content, also the elemental carbon content increases from 49.94% for GA wood to 57.35% for MW 6, and the content of elemental oxygen decreases. Hemicelluloses are hydrolyzed; as a result, free sugars are reactive and can be dehydrated under heat into furfural and other decomposition products. These monomers can be further transformed into polymeric substances, which provide a bounding and bulking effect on the obtained lignocellulosic material due to the application of heat and pressure in a pelleting operation. The resulting composite products have a good mechanical strength and an excellent dimensional stability.

To examine the effect of the hydrothermal pretreatment time on the thermal stability and pyrolysis product yields of pelletized modified and initial GA wood, analyses were carried out in a thermogravimetric/mass spectrometric (TG-MS) system and a thermogravimetric analysis apparatus (TGA).

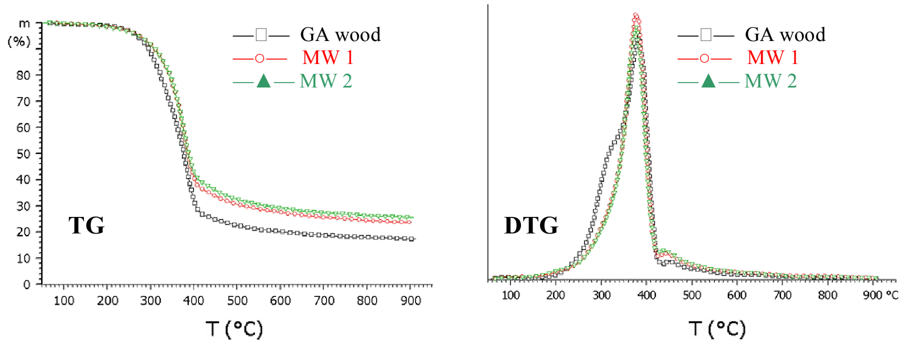


Fig. 3. TG and DTG curves of modified (MW) and non-modified GA wood

The character of the thermal destruction curve (DTG) of the initial GA wood follows the usual shape for lignocellulosic materials [7]. A comparison of the GA wood and MW samples shows that, in the latter case, decomposition starts at higher temperatures, and there is no hemicellulose shoulder because hemicelluloses are degraded in the pretreatment process, obtaining the binder for the pelletization process. The water-soluble matter, which is present in the MW, helps to form a composite material with cellulose and lignin. As a result, stronger chemical bonds are formed (more C-C bonds). During the carbonization, further reactions occur to obtain a stable carbon structure. The TG curve in Fig. 3 shows that the MW samples have higher char yields. This is explained by the higher cellulose and lignin contents. For MW samples, there is no great difference in DTG curves, and the shape is similar to that of fruit stones, which have a naturally developed stable and dense structure [8].

Parameters of the hydrothermal treatment

The MW samples obtained from hydrothermally treated (180^{o}C for 2 h) GA wood chips have a higher content of hot water - soluble substances, milled instantly after the treatment (Table 4). Taking into account the previous results, the amount of hot water - soluble matter is high enough to obtain high-quality pellets.

Table 4

Impact of the fractional composition on the properties MW pellets

Modified wood (2 h, T=180^{o}C)	MW characteristics		Pellets characteristics			
	Yield, %	Hot water soluble matter, %	Yield, %	Density, g/cm^3	Bulk density, g/l	Hardness, kG
Chips, milled ≤ 2.00 mm	84.6	10.28	93.4	1.379	766	50.9
Sawdust, 0.63-2.00 mm	84.2	5.70	93.9	1.300	723	40.2
Sawdust, ≤ 0.63 mm	87.1	7.02	85.3	1.364	746	51.2
Sawdust, ≤ 2.00 mm	84.6	6.31	84.7	1.335	760	45.5

It could be concluded that the optimal GA hydrothermal treatment parameters are the duration 2 h and temperature 180^{o}C, using as a raw fractional composition the chips, which are milled after the treatment through a 2 mm sieve. Milling of MW chips consumes less (around 3-7 times) energy than milling of wood chips [9], and the obtained MW has an optimal fractional composition to prepare dense and mechanically strong pellets.

Carbonization and activation

The influence of the carbonization end temperature on the mechanical properties and adsorption capacity of the obtained granular activated carbon (GAC) was investigated at the same heating rate, i.e. 2^{o}C/min.

Pelletized MW samples were carbonized in a 1l retort inserted in an electric furnace, equipped with an automatic temperature control. To investigate the carbonization temperature, MW 2 (2 h at 180^{o}C) pellets were carbonized up to 300, 400, 500, 600 and 700^{o}C. The relative moisture before carbonization was 2-4%.

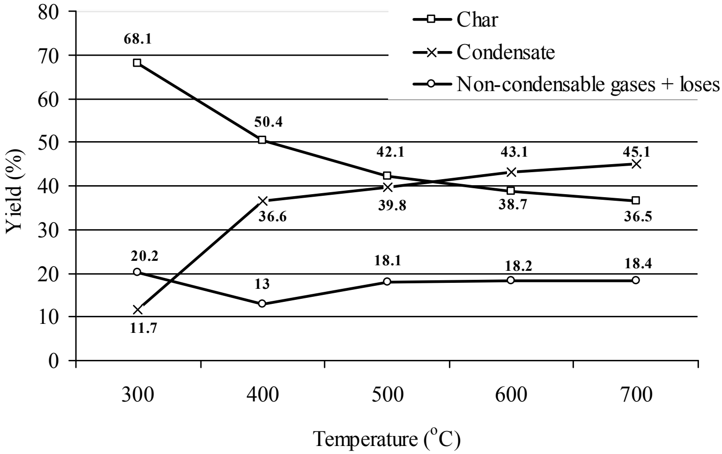


Fig. 4. Yield of carbonization products *vs* temperature

It can be seen from Fig. 4 that the thermal decomposition of MW 2 pellets proceeds in a wide temperature range, but the main amount of volatile products is formed at up to 400°C. With increasing temperature, the amount of pyrolysis gases and fixed carbon increases, but the yield of chars decreases (Table 5). Usually the yield of chars depends on the raw material. For the wood, it is in a range of 20-30% [10]. After the carbonization of MW 2 pellets, however, the yield of chars is comparatively high, namely, up to 40%. This is due to the decomposition of hemicelluloses after modification, which results in a higher fixed carbon content in comparison with the case of the initial GA wood. Carbonized MW pellets have about 3 times higher apparent density than the chars of GA wood [10].

Table 5

Characteristics of carbonized MW 2 pellets

Carbonization temperature, °C	Ash (wt%)	Volatiles (wt%)	Fixed carbon (wt%)	Char yield (wt%)	Bulk density (g/l) ($1<fr\leq3$mm)
300	2.46	51.37	46.17	68.1	557
400	3.13	26.98	69.89	50.4	526
500	3.24	16.23	80.53	42.1	537
600	3.26	8.25	88.49	38.7	538
700	3.52	3.23	93.25	36.5	569
Coconut (500°C)	1.51	11.7	86.79	32.8	609

As a comparative control raw material, coconut shells were chosen, which are widely used for the production of dense and mechanically strong GAC [11]. This is an excellent raw material because of the low ash content and high bulk density (Table 5). The only disadvantage is that the yield of the chars is lower than that of the chars obtained at 500°C from MW 2 pellets, namely, 32.8% and 42.1%, respectively. Mechanical properties are important for GAC, therefore, one of the aims was to obtain GAC similar to that prepared from coconut shells.

Investigating the influence of the carbonization temperature on the properties and yields of AC, activation was performed in a laboratory retort equipped with a steam superheating device. Activation was made in the following conditions: T = 850°C, time 90 min and steam-carbon ratio 3:1. Increased yields of chars at temperatures of 300 and 400°C (Table 5) are deceptive, because these chars are characterized by a low fixed carbon content, which is demonstrated by the obtained yields of activated carbon. Table 6 shows that the highest yields and bulk density results are for the AC prepared from the MW 2 pellets carbonized at 600°C; therefore, it was selected as the optimal one.

Table 6

Yield and bulk density *vs.* carbonization temperature (control sample – coconut shell, $T_{carb.}$= 500°C).

Carbonization			Activation	
Temperature, °C	Yield, %	Bulk density, g/l	Yield, %	Bulk density, g/l
300	68.1	557	13.4	345
400	50.4	526	15.3	352
500	42.1	537	18.1	405
600	38.7	538	18.2	422
700	36.5	569	17.3	420
Coconut (500°C)	32.8	609	15.9	484

Bulk density, in comparison with the control sample – AC obtained from coconut shells, is lower. When studying the effect of the relative moisture content before pelletization, the aim was to achieve the maximum adsorption capacity as well as high enough attrition resistance, bulk density and activated carbon yield.

Optimization of the pelletizing process

Pelletization experiments with MW show that the relative moisture content of the raw material before pelletization is a very important parameter. Water acts as both a binding agent and a lubricant. Water helps to develop van der Waals' forces by increasing the area of contact between the particles. Water aids pelleting, when water-soluble compounds are present in the raw material such as sugars, sugar polymers, dehydrated carbohydrates, furfural products, lignin and lignin products. High-quality soft wood pellets can be obtained, if the moisture content is in the range 6-12% [12]. MW is a new raw material for pelletization. In our case of MW pelletization, the optimum moisture content was 6-8 %, which showed the highest hardness value. High-quality pellets from MW can be made with initial moisture contents of 6-10%, and water contents above or below this range would result in lower quality pellets.

The relative moisture of the raw material also influences the productivity and power consumption of pelletization. It should be admitted that these parameters are related to the corresponding pelletizator, but the trend would be supposedly the same on the industrial scale. Fig. 5 shows that the productivity for this pelletizator reaches its maximum, if the moisture content is 8 wt% (8.45 kg/h), and energy consumption also is the lowest.

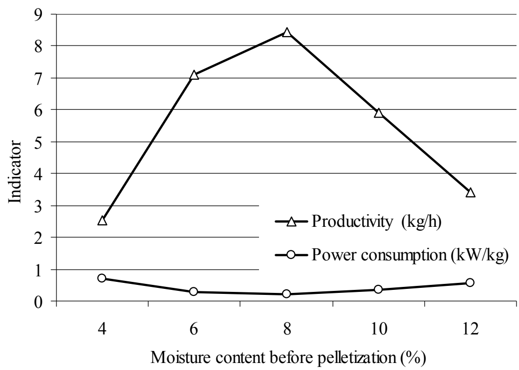


Fig. 5. Effect of the moisture content on the productivity and energy consumption of pelletization

Hence, from the energetic point of view, the best moisture content is 8% (the best productivity and the lowest energy consumption), but the moistures 6 and 10% also show satisfactory results. The influence of moisture content can be observed also after carbonization and activation, because the target product is mechanically strong AC.

The results demonstrate that the best AC yield is gained from the pellets obtained from the raw MW 2 with a moisture content of 8-10%. The yield from the MW 2 of this AC is 20-21%, and the ash content is comparatively low, namely, 4.3-5.3%, which meets the requirements of most standards for the gas cleaning AC. Also bulk density, namely, 457 g/l is closer to that of the AC obtained from coconut shells, namely, 484 g/l (Tables 6 and 7), respectively.

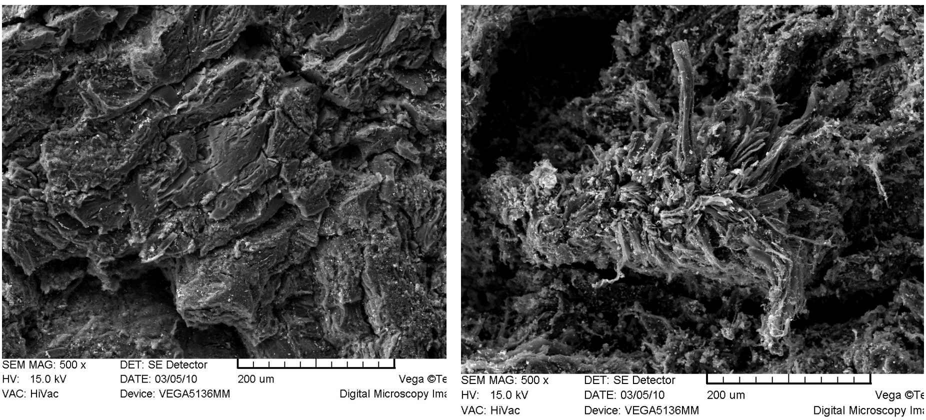
Table 7

Effect of the moisture content of raw MW before pelletization on the properties of carbonized and further steam activated samples

Moisture content, %	4	6	8	10	12
Carbonized specimens (T = 600^{o}C, 2^{o}C/min)					
Ash content, %	3.02	2.15	2.65	2.35	2.2
Bulk density, g/l	570	605	596	602	597
Apparent density, g/cm^3	1.161	1.160	1.157	1.144	1.107
Hardness, kG	18 ± 4	22 ± 4	23 ± 3	20 ± 3	16 ± 4
Steam activated carbon (T = 850^{o}C, time 90 min, Steam/C=3/1)					
Ash content, %	6.29	4.43	5.31	4.45	4.35
Bulk density, g/l	399	436	438	457	439
Yield, % o.d. MW	18.1	20.3	20.2	20.9	20.8
Attrition, %	6.8	5.3	6.0	4.3	4.9

Characterization of the obtained GAC

Images of Scanning Electron Microscopy (SEM) show that the structure of the obtained GAC is loose (Fig. 6 (a)), because of the release of the primary structure by burn-off, and a new – secondary structure is formed. The secondary structure consists of smaller pores – micro- and mesopores, which are not seen in SEM. These pores are characterized by Sorptometer results. It can be seen from Fig. 6 (b) that, after physical activation, the initial raw wood fiber structure elements still remain there, which act as the matrix in the MW pellets.



a b

Fig. 6. GAC SEM surface images at 500 × magnification

Irrespective of the fact that both the pore volume and surface area are significantly raised after activation, the obtained pellets still have high mechanical properties. The AC structure is dense enough to include the obtained GAC in high-quality adsorbents for cleaning of gaseous emissions.

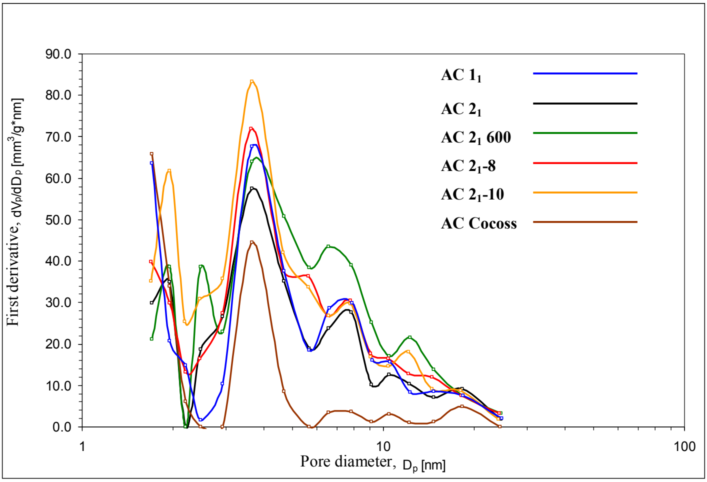


Fig. 7. Pore size distribution of GAC by diameter

Fig. 7 shows the pore size distribution of several GAC obtained experimentally. AC coconut is characterized by a low content of mesopores (between 3 and 5 nm), and the curve is going up to the size under 2 nm. The same trend is for the AC obtained from MW 1 (AC – 1_1). The mechanical properties and yield of the AC are lower. The GAC samples AC 2_1-10 and AC 2_1-8 obtained from pelletized MW 2 (moisture content before pelletization 8 and 10%) have the highest narrow mesopore content. The high content of narrow mesopores relates to the high total pore volume (Table 8), which has a significant indicator in adsorption processes.

The bulk density of the samples obtained from the MW is still lower than that of the AC obtained from coconut shells, but the result is high enough (Table 8, sample 2_1-10) for the adsorbents from biomass. Bulk density for adsorbents from biomass is usually in the range 200-300 g/l. The high bulk density decreases both transportation costs and the dimensions of the adsorption facilities – a higher amount of the adsorbent can be packed in a low volume unit.

Table 8

Properties of GAC obtained from MW 2 pellets and coconut shells

Quality indicators	Raw material					
	Modified wood					Coconut shells
	1_1	2_1	2_1-600	2_1-8	2_1-10	
BET surface, m^2/g	1171.1	950.3	1162	1054	1069.6	1390
Total pore volume, mm^3/g	781.7	669.5	686.5	772.4	780.9	686
Micropore volume, mm^3/g	382.1	298.5	353.3	325.3	304.1	500
Adsorption capacity I_2, mg/g	1069	1028	937	942	973	928
Adsorption capacity MZ, mg/g	101	116	125	69	88	85
Adsorption capacity MV, mg/g	68	48	54	45	41	12
Wet attrition number wt%	32.4	11.7	11.0	6.0	4.3	4.8
Bulk density, g/l	389	405	377	438	457	488
Ash content, %	6.8	7.8	6.0	5.3	4.5	2.1
Yield, %	14.8	17.4	18.2	20.2	20.9	15.9

Development of the technology and production costs

To prepare high-quality GAC from fast-growing and low-grade GA wood, the following equipment and parameters were chosen:

- Hydrothermal pretreatment equipment - autoclave;
- Duration of hydrothermal treatment - 2 h;
- Pelletizator type - flat die;
- Fractional composition before pelletization - modified wood chips milled through a 2 mm sieve;
- Carbonization temperature 600°C;
- Moisture content before pelletization 8-10%;
- Activation temperature 850°C;
- Activation time 90 min;
- Steam - carbon ratio 3 : 1.

In the choice of hydrothermal treatment equipment, both the ecological (potential pollution) aspects and the quality of the obtained MW were taken into account. An autoclave was chosen for hydrothermal treatment. The obtained MW is dry (drying is not necessary) enough to mill and pelletize instantly after the modification. The water consumption for steam production does not exceed 0.6

kg/kg o.d. MW, which means that the obtained wastewater amount will be minimal. Equipment is easy to handle, and the milling of the obtained MW chips consumes 3 times less energy than the milling of freshly cut GA chips. The pelletization alternative is related with certainty better mechanical properties (yield, Hardness value and bulk density) of the MW pellets obtained in a flat die pelletizator. It is chosen as appropriate for pelletization of MW. In the choice of the duration of hydrothermal treatment, the properties of the MW pellets, carbonized pellets and GAC were taken into account to develop the technology.

The GAC prepared in the developed technology can be used as an adsorbent in both gas and liquid phase adsorption processes.

The price of grill charcoal is 350 EUR/t, and from 2.7 m^3 of wood it is possible to obtain 0.28 t of charcoal, which costs 98 EUR. The price of GAC is approximately 4000 EUR/t, therefore, the income from the processed 2.7 m^3 GA wood could be 0.165 × 4000 = 660 EUR or about 7 times higher. If it would be possible to find some special niche, the price of GAC can reach even 12 000 EUR/t. The product cost in the developed technology is from 900 to 1050 EUR/t.

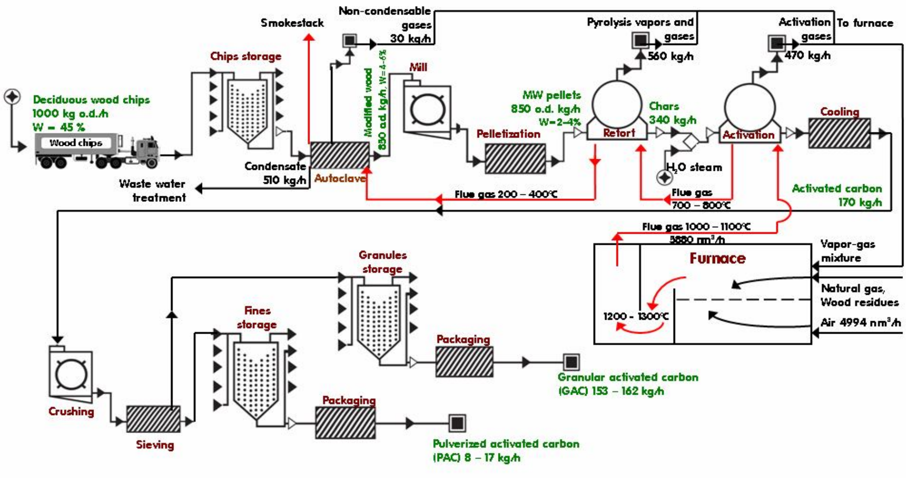


Fig. 8. Flow diagram of the GAC production from GA wood

The proposed GAC production technology is environmentally friendly, because no inorganic catalysts are used in the process, and the carbonization gas-vapour mixture, together with activation gases, can be burned in a furnace, providing the carbonization, activation and hydrothermal treatment processes themselve with heat energy (Fig. 8). In this case, the amount of emissions in the atmosphere will not exceed the European limits. The wastewater formed in the hydrothermal pretreatment process is easy to purify (low concentrations of acetic acid and furfural).

The GAC obtained from the modified GA wood can be used in the following adsorption processes:

1) In wastewater treatment plants to decrease the biological and chemical oxygen demand;
2) As catalysts or catalyst carriers in metallurgy and in gasoline purification;
3) In depuration of swimming pool and soft drinks water from chlorine compounds;
4) In purification of drinking water and industrial exhaust gases;
5) In solvent and gold recovery;
6) In adsorption of dissolved organic compounds from the liquid;
7) In water and gasmasks filters;
8) In refining of beer and other alcohols.

CONCLUSIONS

1. Appropriate methods for obtaining high-quality activated carbon from the fast-growing and cheap grey alder wood, and the effect of the partial degradation of hemicelluloses and other wood components on the resulting pellets' properties were elucidated in the theoretical part of the study.
2. An original technology was developed, in which, before pelletization, grey alder wood is treated at elevated temperature in an environment of steam that ensures the densification of the obtained modified wood without the use of additional binders and additives.
3. Acceptable equipment (an autoclave) was chosen, taking into account both the ecological (the lowest amount of wastewater resulting from up to 0.6 kg/kg o.d. MW) and energy consumption (after treatment - low moisture content 4-6%) aspects.
4. Optimal hydrothermal treatment parameters were developed, and the fractional composition (for 2 h at 180°C processed chips, than milled through a 2 mm sieve) was selected to obtain modified wood with a high enough content of hot water-soluble substances (10%), which act as a binder in the pelletization process.
5. A suitable pelletizator (the flat die) for modified wood pelletizing was chosen, and the optimal moisture content of the raw material (8-10%) was found to obtain pellets with the highest yield (94%), apparent density (1.360 g/cm^3), bulk density (760 g/l) and Kahl hardness number (58 kG).
6. Hydrothermal pretreatment with subsequent pelletization significantly improves the properties of grey alder wood as a raw material for granular activated carbon - the obtained pellets have a dense structure and are mechanically stronger and thermally more stable, which increases the competitiveness of grey alder wood.
7. Optimal carbonization (temperature 600°C, heating rate 2°C/min) and activation (temperature of 850°C, duration 90 min and steam carbon ratio 3:1)

parameters were developed in order to obtain dense activation carbons (bulk density 457 g/l) with a high yield (20.9%), and low abrasion number (4.3%) and ash content (4.5%).

8. The obtained activated carbon has a well-developed pore system (BET surface area 1069.6 m^2/g, total pore volume 780.9 mm^3/g, micropore volume 304.1 mm^3/g) and a high adsorption capacity (Iodine 973 mg/g, Methylene blue 88 mg/g, Methyl violet 41 mg/g) as compared to the activated carbon prepared from coconut shells.
9. The activated carbon obtained in the developed technology acts as a good adsorbent not only in the gas phase but also in the liquid phase, and has a broad range of applications (water and gas purification, catalyst carrier, solvent and gold recovery, refining of beer and other alcohols).
10. It is economically profitable to produce granular activated carbon by the developed technology, because the production costs of such activated carbon are from 900 to 1050 EUR/t, but the market price is about 4000 EUR/t (finding a specific niche applications, the price can increase up to 12 000 EUR/t).
11. The offered technology of granular activated carbon production is environmentally friendly, because no inorganic catalysts are used in the process, and the carbonization gas-vapour mixture, together with the activation gases, can be burned in a furnace, providing the carbonization, activation and hydrothermal treatment processes themselves with heat energy. In this case, the amount of emissions in the atmosphere will not exceed the European limits. The wastewater formed in the hydrothermal pretreatment process is easy to purify (low concentrations of acetic acid and furfural).

REFERENCES

1. Kļaviņa M., Andrušaitis A. Klimata mainība un globālā sasilšana. – Rīga: LU Akadēmiskais apgāds, 2008. - 174. lpp.
2. Rodriguez-Reinoso F. Activated Carbon: Structure, Characterization, Preparation and Applications. Introduction to Carbon Technology. (Marsh H., Heintz E.A., Rodriguez-Reinoso F. Eds). – University of Alicante: Secretariado de Publicaciones, 1997. - 669 p.
3. The Freedonie Group. World Activated Carbon. Industry Study with Forecasts for 2012 & 2017. Study No 2363. – Cleveland, Ohio: Freedonia group inc., 2008. - 364 p.
4. Daugaviete M., Ūsīte A. Baltalksnis Latvijā. – Salaspils: Latvijas Valsts Mežzinātnes institūts „Silava", 2006. -129 lpp.
5. Gangadwala J., Radulescu G., Kienle A., Steyer F., Sundmacher K. New processes for recovery of acetic acid from waste water // Clean Technology Environmental Policy. - Vol. 10. - 2008. - 245-254 p.
6. Kaliyan N., Morey R.V. Factors affecting strength and durability of densified biomass products // Biomass and Bioenergy. - 2009. - Vol. 33. - 337-359 p.

7. Yariv Sh. The role of charcoal on DTA curves of organo-clay complexes: an overview // Applied Clay Science. - 2004. - Vol. 24. - 225-236 p.
8. Sütcü H., Demiral H. Production of granular activated carbons from loquat stones by chemical activation // Journal of Analytical and Applied Pyrolysis. - 2009. - Vol. 84(1). - 47- 52 p.
9. Arias B., Pevida C., Fermoso J. et al. Influence of torrefaction on the grindability and reactivity of woody biomass // Fuel Processing Technology. - 2008. - Vol. 89. - 169-175 p.
10. Кислицын А.Н. Пиролиз древесины: химизм, кинетика, продукты, новые процессы. - Москва: Лесная промышленность, 1990. - 312 с.
11. Heschel W., Klose E. On the suitability of agricultural by-products for the manufacture of granular activated carbon // Fuel.- 1995. - Vol. 74. - 1786-1791 p.
12. Li Y., Liu H. High-pressure densification of wood residues to form an upgraded fuel // Biomass and Bioenergy. - 2000. - Vol. 19. - 177-186 p.