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Tests on the Application of Various Types of Biomass for Activated Carbon Production

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ABSTRACT

Activated carbon (AC) is one of the best adsorbents for removing trace contaminants from air, soil and water due to its adsorption properties. It is produced from carbon-rich materials, mainly fossil raw materials. However, the price of hard coals has increased significantly in recent years due to the COVID-19 pandemic and the war in Ukraine. The existing eastern markets became blocked for carbon-raw-material sourcing. It is therefore important to find alternative materials or plant-based products. This study investigated the possibility of manufacturing activated carbon from waste biomass such as sugar beet fibers (SBSF), mixed vegetable processing waste (mainly corn) (MVW) and cherry stones (ChS). The raw material was subjected to pyrolysis, milling, granulation, carbonisation and activation at different times and temperatures. However, of the biomass materials tested, only SBSF in the form of marc can be processed into valuable activated carbon in further production steps. MVW and ChS as carbon substrates showed, in addition to high moisture and ash, low efficiency in decolourising molasses and methylene blue MB and also had a lower specific surface area.

Keywords: activated carbon, biomass, carbonization, activation.

INTRODUCTION

Activated carbon (AC) is a carbonaceous material with an irregular structure of microcrystalline carbon. Activated carbon has a porous structure that increases its internal surface area and decreases density. AC is one of the best adsorbents for removing trace contaminants from air, soil and water due to its strong physical adsorption. This is due to the advantages of AC, such as porous properties, high chemical and thermal stability, unique surface area, surface functional groups and the physicochemical nature [Lillo-Ródenas 2004, Pietrzak 2007]. Activated carbons are formulated by physical or chemical activation methods. Physical activation has been found to be more favorable due to its higher surface area, higher yield and strongly developed porous structure [Vilella 2017]. Activated carbon is mainly produced from hard coal or lignite [Pietrzak 2007, Paiva 2014]. For the treatment of drinking water, both in waterworks and in domestic filters, the activated carbon made from coconut fibers is commonly used, which has recently been increasingly replaced by wooden activated carbon [EWCMS Report 2021]. In recent years, due to cost pressures and high environmental standards, the activated carbon industry has significantly reduced the volume of production based on fossil raw materials.

According to the Market Research Report [2022], the price of activated carbons has increased significantly in recent years, even above \notin 1,000/t. This has been influenced by the COV-ID-19 pandemic and the war in Ukraine, which has blocked the existing eastern sourcing markets. Therefore, raw coals are often imported from other continents (Africa, Asia, and America). The market for activated carbon in Europe is estimated to grow from US\$ 559.20 million in

2021 to US\$ 1,049.14 million by 2028; it is estimated to grow at a CAGR (Compound Annual Growth Rate) of 9.4% between 2021 and 2028. [MR Report 2022, EWACMS Report 2021]. Activated carbon is one of the best-known parts of the technology used for air filtration [Aktivkohleeinsatz 2016]. The growing need for air purification is driving the demand for activated carbon in many regions of European Union (EU). The European countries are reviewing the internal law under the European Green Deal's zero pollution targets to create a toxin-free environment [Agbor 2011, Balan 2009]. The market is expected to be driven by high demand from water and air filtration applications as well as the food and beverage industry [Aktivkohleeinsatz 2016]. The product is used as a water and air purification filter and decolouriser in the food and beverage industry. Increased demand for different types of purifiers due to growing awareness of health issues is likely to exponentially increase the AC demand over the next years [Iwanow 2022, Mosier 2005].

Independence from fossil raw materials is becoming increasingly important today due to the problems of raw material acquisition, transport and climate change [Ivanov 2020]. The geopolitical situation and the ongoing war in Europe have reduced the access to imported raw materials from the eastern part of Europe [Malini 2023]. This group of carbonaceous raw materials that are difficult to obtain includes hard coal and brown coal as the base for activated carbon production [Yong 2021]. The production process in Europe is mainly limited to the final creation stages, the compounding of different activated carbons for specific applications and the production of shaped activated carbons (e.g. pellets). Consequently, environmental pollution from emissions of, i.a. carbon monoxide, volatile hydrocarbon compounds and soot particles occurs in the countries of raw coals sourcing. Unfortunately, this is mainly in the countries where European environmental standards do not apply. Moreover, the supply chain is often not transparent to the end customer. The environment and especially the climate are relegated to the shadows [Bubanale 2017, Yong 2021].

It is therefore important to find alternative plant-based materials or products that have beneficial or comparable properties to traditional fossil raw materials. Overcoming functional and techno-economic limitations and the added value of products based on waste materials that result from this can help bring new green solutions to the market [Ivanov 2022]. According to the Market Research Report [2022], more than 50 million tons of green waste is generated each year in the European Union, in urban and rural areas altogether. Despite recovery and recycling efforts, the volumes of these residues do not change or increase even further. Attempts are being made to have these wastes undergo biochemical reactions: aerobic decomposition or anaerobic decomposition through methanisation [Agbor 2011]. They can also be used in agriculture (soil-plant interactions), etc. The management of this waste sector is becoming very costly, so innovations in green waste management have become a necessity, especially since these woody and semi-woody plant wastes can be considered as resources. They are a rich source of carbon and can also be converted into activated carbon [Aktivkohleeinsatz 2016]. At the same time, there are many applications of activated carbon (e.g. from biomass), in activated or non-activated form, for the treatment of various media by adsorption of contaminants contained as particulate matter in liquids, air, gases (biogas, flue gas), water or wastewater [Mohammed 2015, Mohammed 2922].

Activated carbons can be produced from a variety of agricultural residues such as sugar cane, peat, brown coal, wood and coconut shells. To produce one ton of activated carbon, 3.5 to 5 tons of hard coal or 5 to 6.5 tons of brown coal are used [Carvalheiro 2008, Kambo 2015, Burbanale 2017]. It takes 10-13 tons of coconut shells, which are a waste material too, to produce one ton of coconut charcoal [Werther 2000]. The production of carbon from coconut can be largely climate-neutral due to the renewable raw material. A prerequisite, however, is that only CO₂ and no other greenhouse gases are released during carbonisation and activation. Unfortunately, due to the often usually outdated pyrolysis technology used and the lack of standards (in the countries of coconut origin i.e. East-South Asia, Africa), it can be assumed that production is accompanied by emissions of volatile hydrocarbons and soot, which pollute the climate far more than a comparable amount of CO₂ from fossil hard or brown coal. This means that the commercially available coconut coal is not a clean alternative, especially as it is transported to Europe from distant continents [Chandel 2015, Lee 2007].

As an alternative to fossil coals and coconuts, vegetable waste is a good solution that is generated locally in Europe from the agricultural or fruit and vegetable processing sector [El-Sayed 2016, Skoczko 2022]. Sugarcane bagasse (SCB) is represented as an excellent biomass for AC synthesis due to its availability and low cost. Sugarcane bagasse is produced from the bioethanol, sugar, polyethylene and ethanol industries [Manocha 2013, Siipola 2018, Mosier 2005]. The composition of SCB includes lignin (20-25%), haemicelluloses (25-30%) and cellulose (40-50%). Elham [2015] reports that the disposal of large quantities of sugarcane waste has become a major environmental pollutant and therefore a health hazard in the region of origin (Asia, Africa). As a result, converting SCB into AC reduces the amount of agricultural waste while producing a useful adsorbent at a reasonable cost [Hendriks 2009, Fernandes 2011].

Therefore, the aim of the experimental work carried out in this project was to manufacture activated carbon from available vegetable waste raw materials, such as sugar beet fibres (SBSF), mixed vegetable processing waste (mainly corn) (MVW) and cherry stones (ChS). The composition of the raw materials was assessed, the conditions for the production of activated carbon from these raw materials were compared, including the conditions for carbonisation and activation, and the sorption as well as strength parameters of the obtained activated carbons were evaluated.

MATERIAL AND METHODS

The conducted experiments were realized in a professional AC-manufacturing facility located in the Middle-East Europe. The work was carried out to develop technology for the manufacture of activated carbon on a semi-technical scale from vegetable waste from the agri-food industry in order to develop technological guidelines for possible further production. The trial programme included the steps of:

- carbonisation and grinding of processed waste
- laboratory tests on carbonisation and activation of selected types of vegetable waste,
- tests to produce activated carbon from carbonised vegetable waste with the highest sorption and mechanical parameters among investigated types.

Raw materials

Three groups of vegetable waste from the agri-food industry were selected for the study:

- Sugar beet marc and sugar beet fiber (SBSF)

 obtained from sugar production SBSF is a ligno-cellulosic material that is a residue from the industrial use of sugar beet in the sugar industry. In terms of chemical composition and fiber structure, beet pulp can be a raw material for the pulp and paper industry, the plate industry and for the production of activated carbons.
- 2. Mixed vegetable waste from food processing (MVW) – also belongs to the group of lignincellulosic materials. Mixed corn processing waste was used for testing. The corn waste contains long fractions that are fibrous and problematic to store. The high haemicellulose content of sweetcorn waste (approximately 40%) makes it valuable as a raw material for the production of xylose, xylitol and arabinose.
- 3. Cherry stones (ChS) represent a group of waste with similar features to nuts. They were obtained from a fruit processing plant as raw washed material. They can be used in natural medicine, as a fuel material and are suitable for further processing in the food industry into oil.

The proportion of specific fractions in the tested plant materials varied. It was highly dependent on the age, type and part of the plant from which the waste was produced. Beet pulp contained: 41.3% cellulose, 29.4% haemicelluloses,



Figure 1. Agri-food industry plant waste groups selected for study: (a) sugar beet marc, SBSF; mixed vegetable waste, MVW; (c) cherry stones, ChS

14.9% lignin and 14.4% other components. Food industry waste contained 39.3% cellulose, 34.4% haemicelluloses, 14.9% lignin and 11.4% other components. Cherry stones contained: 30.1% cellulose, 28.9% haemicelluloses, 32.3% lignin and 8.7% other constituents All tested wastes were randomly sampled and tested for ash and moisture content. The results are presented in Table 1.

Process phases

Biomass primary carbonisation (pyrolysis) was realized in a laboratory rotary kiln - process was carried out using temperatures: 450°, 500°C and 550°C. The carbonisation times measured from the set temperature parameters were: 1h, 1.5h, and 3h. A port was installed in the furnace lid to drain the vapour-gas mixture. After cooling, the liquid was also collected. After thermolysis was completed, the obtained char was left in the furnace without access to air until it had cooled completely. Grinding of the carbonised waste mass - was carried out in a process line consisting of feeding equipment, a mill, distribution equipment and a fan. The pulverised coal was collected in paper bags of 20-25 kg. Binder preparation using beet molasses - to dilute the molasses, a binder installation was used, with 4 parts by weight of binder added per 1 part by weight of molasses. The diluted molasses had the following properties: coking number - 4.30%, viscosity at 20°C - 22.2 mPa·s, 30°C - 18.0 mPa·s, 40°C -15.9 mPa·s Preparation of charcoal-binder paste - the paste was prepared in a high-speed mixer, to which coal powder was fed from the pulveriser tank, while the molasses solution at 50°C was dosed from the binder tank using a piston dosing pump. Granulating - the carbon-binder pulp was granulated in an industrial granulator with the use of calibrating elements with a diameter of 4.2 mm holes. Drying of the raw granules was carried out in a rotary dryer heated by fumes of chadnic gas at a temperature of approx. 550 °C. Carbonisation - the granules were subjected to a carbonisation process in the same laboratory furnace in which pyrolisis was carried out. Carbonisation at

450-550°C for 1.5-2 h resulted in decomposition of the binder with formation of semi-coke, release of volatiles and physico-chemical and structural changes of the carbonised material. Activation – activation was carried out in a tube furnace heated with silica rods and adapted to the activation process. The laboratory activation parameters were as follows: carbonate charge – 0.4 dm³, temperature – 800–900°C, activation time – 1.5–3 h, steam consumption – 200–220 g/h. Final milling of activated carbon – in the case of using activated carbon in powder form, the activated carbon is subjected to milling after the activation process. The degree of grinding obtained should be in the range of 0.0–0.120 mm.

Analytical methods

Table 2 presents the used analytical procedures and standards of coal-based products.

RESEARCH RESULTS

The work carried out in this study was concerned with assessing the suitability of selected biomass waste as raw materials for the manufacturing of activated carbon. All the analysed waste materials belonged to the group of lignocellulosic compounds. The literature concerning the subject states that lignocellulosic biomass consists of a cell wall, which is composed of cellulose, hemicellulose and lignin [Sun & Cheng 2002] and minority occurring extracts and inorganic compounds, the so-called ash [Zhao 2017]. Cellulose is a linear homopolymer composed of several to hundreds of thousands of β -D-anhydroglucopyranose units, which are linked by β -1,4-glycosidic bonds. Parallel to each other, the cellulose chains are packed into cellulose microfibrils, which are stabilised by intramolecular hydrogen bonds and van der Waals interactions [Lee 2007, Fernandes 2011]. Haemicellulose is a branched heteropolymer that has a lower molecular weight than cellulose. It is composed of pentoses (e.g. xylose and arabinose), haemose (e.g. mannose, galactose) and uronic acid

Table 1. Tested biomass properties

Indicator	Biomass			
	SBSF	MVW	ChS	
Moisture [%]	9.43	51.78	33.77	
Ash [%]	1.24	1.33	1.28	

No	Parameter	Standard	Issue	
1.	Bulk density (BD)			
2.	Water absorbance (WA)	PN-74/C-97554	Formed AC	
3.	Specific surface area (SSA)	- PN-74/C-97554		
4.	Mechanical strength (MS)			
5.	Total volatile compounds (TVC)	DN 75/0 07550	Oh arrea al	
6.	Carbon (C)	– PN-75/C-97553	Charcoal	
7.	Ash (A)	PN-84/C-97555/08	AC Analytical procedures determination of ash content	
8.	Moisture (M)	PN-84/C-97555/09	AC Analytical procedures determination of moisture	
9.	Methylene number (MNo)	PN-82/C-97555.03	AC Analytical procedures determination of MNo.	
10.	lodine number (INo)	PN-83/C-97555.04	AC Analytical procedures determination of INo	
11.	Molasse number (MNo)	PN-86/C-97555.05	AC Analytical procedures determination of MNo	
12.	Sieve analysis	PN-87/C-97555.01	AC Analytical procedures sieve analysis	
23.	Total pore volume and distribution of pore volume by radius range and classification into macro, meso and micro pores	According to porosimeter instruction Series 200 and adsorption porosimeter DHL-3.		

Table 2. Laboratory analytical methods used for experiments on biomass processing

(e.g. glucuronic acid). The presence of branched side chains and amorphous nature make this polymer more susceptible to hydrolysis than cellulose. Haemicelluloses are grouped into xylans, xylo-glucans, mannans and glucomannans [Carvalheiro 2008]. Lignin is an amorphous polymer from the group of aromatic compounds [Correa 2017]. The structure of lignin contains many functional groups, such as hydroxyl and carbonyl groups, giving it high polarity [Zhao 2017]. The structure of lignin contains numerous non-hydrolysable C-C and C-O-C bonds, which hinder delignification [Chandel 2015]. From the point of view of activated carbon formation, the high lignin content of lignocellulosic biomass is a disadvantageous factor.

Biomass is characterised by a different composition to known fossil fuels. The carbon content is significantly lower (typically less than 50%), with a significant proportion of oxygen (around 40-50%). The hydrogen content of coal and biomass is similar at around 6%. This composition results in a lower possibility of obtaining a valuable carbon product from which activated carbon can be produced. In addition, the processing of plant waste is adversely affected by the high moisture content. The proportion of mineral matter, and thus the ash content, is also different from that of hard or brown coals. However, the proportion of individual constituents differs: the content of aluminium and iron oxides (Al_2O_3 and Fe_2O_3) is even significantly lower than in coal, while the proportion of phosphorus and alkali metals (MgO, K_2O) can often be higher (especially in the above-ground parts of plants). In addition, plant waste is characterised by a high chlorine content and low sulphur content [Chen 2017, Correa 2017, Malini 2023].

Biomass pyrolysis in laboratory tests

The aim of the pretreatment of used biomass waste for the activated carbon production is to pre-carbonise the raw material by pyrolysis. Pyrolysis is used as a process of thermal decomposition of plant materials with higher carbon content, and can be carried out under various temperature conditions according to the adopted technological specifications [March 2006]. The course of this process depends primarily on the type of raw material to be converted, the apparatus used, as well as the technological parameters (mainly temperature, rate of increase and decomposition time). Due to the above-mentioned properties of biomass, the pyrolysis of vegetable waste is associated with certain difficulties. The high water content delays ignition and extends the drying time. Thermal decomposition (outgassing) results in very high sample weight loss (up to 60–70%). The small coke residue burns much faster than that obtained by burning hard coal.

The literature reports that when wood and other plant raw materials is heated with little airthe decomposition of substances occurs with the formation of new compounds of lower molecular weight [Zhao 2017, Chen 2017]. The newly formed compounds undergo fragmentation, condensation and polymerisation reactions as a result of further increasing temperatures, with the formation of substances that are more stable at high temperatures. Compared to the combustion process, pyrolysis generates significantly less pollution to the environment and is therefore considered a 'clean' technology. The factors that determine the proper course of pyrolytic reactions include the complete absence or deficiency of oxygen in the reaction chamber [Siipola 2018a, Correa. 2017]. During pyrolysis, a wide variety of reactions take place in the biomass, among them: carbonisation, hydrocarbonisation, dehydration, aromatisation, decarboxylation depolymerisation and isomerisation. It is generally accepted that the pyrolysis of biomass consists of three main steps: moisture removal, primary decomposition and secondary reactions (cracking and repolymerisation) [Williams 2005, Sipolla 2018].

According to Zhao [2017], the following phases of thermal decomposition of ligno-cellulosic materials are identified:

- temperature 120–150°C drying of the raw material, without major changes in chemical composition.
- 150–275°C decomposition of the carbohydrate fraction with the release of gaseous byproducts (CO₂, CO) and also some amounts of acetic acid, methanol and wood tar. In this temperature range there are rapid changes in the chemical composition of the raw material.
- 275–450°C intense release of methanol, acetic acid, hydrocarbons and the initial release of hydrogen. The process is characterised by strong exothermics.
- 450–550°C thermal carbon annealing and release of remaining volatile compounds.

Intense decomposition of cellulose and wooded plant matter occurs at 270–280°C, while lignin decomposes at 350–450°C. The volatile products formed in the temperature range 250–350°C are generated from the carbohydrates contained in the raw material, while the products formed at 350– 450°C, are derived from the decomposition of lignin. Balan [2009], Lee [2007], Mosier [2005] and Werther [2000] studied the yields of individual thermolysis products. They proved that it is determined by a number of factors. The individual biomass components are involved in the formation of carbonisation products to varying degrees. The thermal decomposition yields of cellulose, lignin and haemicelluloses extracted from an example woody material are shown in Table 3.

Chen et al. [2017] reports that combustion of this type, where outgassing and combustion of its products is the dominant process, is characteristic for the fuels with high volatile content, e.g. young coals such as brown coal. Volatile components are generated by the thermal decomposition of hemicellulose, cellulose and lignin. These components decompose at different temperatures: Hemicellulose 220-320°C, Cellulose 320-370°C, Lignin 320-500°C [Chandel 2015, Fernandes 2011, Mosier 2015, Pedersen 2009]. When carrying out pre-treatment of plant materials as part of authors' own research in the laboratory, pre-carbonisation and pyrolysis of biomass was carried out in a steel retort placed in a muffle furnace. The temperature in the muffle furnace and inside the retort was recorded using thermocouples. A port for discharging the vapour-gas mixture was installed in the retort lid. The condensate was collected via a cooler into a receiver. The non-condensable gases, after being taken up by the cooler and filter, were directed to the gas meter, samples were taken for analysis and the remainder was combusted. After thermolysis, the resulting carbon was left in the retort without access to air until completely cooled and then weighed.

Pyrolysis of the tested biomass was carried out using a process temperature of: 450–550°C. The process temperature was established based on individual biomass pre-tested fraction size (lower for MVW with smallest fiber parts and higher for ChS as harder material). Pre-test showed that at a temperature higher than 450°C MVW is burned and on the other hand ChS at a temperature lower than 550°C is not dry enough. The pre-carbonisation time measured from the moment the assumed temperature parameters were reached was 1.5–2h also according to the same assumptions as temperature range. During the pre-carbonisation

Lp.	Product type	Cellulose %	Lignin %	Hemicellulose %	
1.	Charcoal	35-44	41-50	29-37	
2.	Black tar	2-5	6-13	5-11	
3.	Dissolved tar and other organic compounds	° 1.3		1-3	
4.	СН ₃ СООН	1-4	0.5-3	0.1-1.1	
5.	CH ₃ COCH ₃	0.01-0.1	0.1-0.3	0.1-0.5	
6.	СН ₃ ОН	0.1-1	0.5-1.9	0.3-1.2	
7.	H ₂ O	25-40	9-20	23-45	
8.	CO ₂	10-17	7-12	9-12	
9.	СО	1-5	1-5	1-5	
10.	CH ₄	0.1-1	0.1-1	0.1-1	
11.	C ₂ H ₄	0.5-6.2	3-10	1-4.5	
12.	Losses	0.2-1.5	0.01-1	0.05-0.5	

 Table 3. Average concentrations of thermal decomposition products of cellulose, lignin and haemicelluloses in pyrolysed biomass [mass %]

Note: Own elaboration based on: Balan 2009, Lee 2007, Mosier 2005, Werther 2000.

operation, the amount of liquid products was recorded and the pyrolysed product obtained was weighed. Pyrolysis tests were carried out in a retort placed in a muffle furnace. The process parameters characteristics of the coals obtained are shown in Tables 4 and 5.

The literature [Correa et al. 2017, Yahya et al. 2018, Manocha et al. 2013] reports as the condensation of VOCs produces pyrolytic oil also called tar. In authors' study, pyrolysis resulted in the generation of tar with MVW exceeding 40% in the highest quantities. The least amount of liquid products was released from the pre-carbonisation of the ChS- about 30%. The resulting pyrolysis tar is a dark brown organic liquid, which contains significant amounts of water (15–45% by weight, depending on the type of biomass) and numerous organic compounds such as acids, alcohols,

ketones, aldehydes, phenols, ethers, esters, sugars, furans, alkenes, nitrogen compounds, and a small proportion of solids. The water content of pyrolysis oil depends on the initial moisture content of the feedstock and the parameters of the pyrolysis process. In authors' study, the moisture content of the samples after pyrolysis ranged from about 10% for ChS up to 23% for MVW. Pyrolysis tar is characterised by a low pH of 2.0-3.7 and therefore exhibits strong corrosive and caustic properties [Kambo 2017]. The complex composition, poor volatility, high viscosity and high acidity of bio-oil limit its direct use. Low purification efficiency along with complex separation steps limit its widespread use [Karunanithy 2007]. In addition to solid products such as pre-treated carbon and liquids in biomass conversion tests gases were generated. It was confirmed by Torres-Pérez

No.	Parameter	Tested biomass			
	Parameter	BSBF	ChS	MVW	
1.	Temperature [°C]	500	550	450	
2.	Time [h]	1.5	2	2	
3.	Amount of products a) stable [%] b) liquid [%]	33.3 43.0	27.8 34.8	30.1 30.8	
4.	Material productivity in relation to primary dry mass of tested biomass a) carbon [%] b) liquid products [%] c) gases [%]	31.6 35.5 32.9	34.2 39.0 26.8	27.8 37.5 34.7	

Table 4. Process parameters and yields of products obtained by pre-carbonisation

Lp.	Parameter	Tested biomass			
		MVW	BSBF	ChS	
1.	BD [g/dm³]	71	80	83	
2.	TVC [%]	33.5	32.55	23.35	
3.	A [%]	23.7	13.75	19.85	
4.	C [%]	42.8	53.7	56.8	

 Table 5. Pyrolysed carbons properties

[2015] that the gas mixture obtained from pyrolysis mainly contains carbon dioxide (CO₂), carbon monoxide (CO), hydrogen (H_2), methane (CH_4), ethane (C_2H_6) , and ethylene (C_2H_4) , as well as small amounts of gases such as propane (C_2H_2) , ammonia (NH₂), nitrogen oxides (NOx), sulphur oxides (SOx) and low-carbon alcohols. The greatest amount of gas in this study was released with MVW pyrolysis, with the lowest carbon recovery. The least gases was formed in the processing of ChS, which also had the highest carbon recovery. Unfortunately, the disadvantage of this material was its high moisture content. Pyrolitic gas has many potential applications, such as direct use in the production of heat or electricity. In addition, the resulting gases are very often used to feed self-powered pyrolysis reactors, operating in a continuous system to preheat the inert gas in the chamber [Torres-Pérez 2015, Sharma et al. 2015).

In authors' own study, after the pyrolysis process and the evaluation of the specific decomposition products formed, it was estimated that after the BSBF conversion, 9.3% by weight of the sample tar only was collected, MVW – 19.6%, ChS – 24.3%. The acidic water that separated from the liquid products is characterised by 2.95% soluble tar for BSBF and 8.68% acid products per acetic acid. For the other wastes, respectively: 3.5% and 12.3% for MVW and 2.5% and 15.7% for ChS.

Grinding of pyrolised biomass, mixing with binder solution and granulation

The grinding of the pyrolised biomass was carried out in a technological process line consisting of feeding equipment, a mill, separation equipment and a fan. The obtained coal dust had a grain size: grains with a diameter greater than 0.12 mm in a rate of 25%, 0.102–0.12 mm i-5%, 0.088–0.102 mm i-2% and less than 0.088 mm in a rate of 68% on average for all the biomass types tested. The pulverised charcoal was further transferred to a mixing plant with a binder paste

prepared on the basis of beet molasses. The binder mixing plant in place was used to dilute the molasses, with 4 parts by weight of binder added per 1 part by weight of molasses. The diluted molasses had the following properties: coking number -4.30%, viscosity at $20^{\circ}C - 22.2$ mPa·s, for $30^{\circ}C - 18.0$ mPa·s and for $40^{\circ}C - 15.9$ mPa·s.

Granulation was carried out on a pulp briquetting machine adapted for the production of granules with a diameter of 4.2 mm. The paste was prepared in a high-speed mixer to which the pulverised charcoal was fed, while the molasses solution at 50°C was dosed from a binder tank. The process ran smoothly until the previously milled coal dust obtained for the 3 biomass waste groups tested was exhausted. The moisture content of the raw granules was determined about 33.76% for SBSF, 35.24% for MVW and 36.63% for ChS.

Drying

The granules formed in the previous process were addressed directly to a rotary dryer heated with combustion gases from the pyrolysis process at 450–550°C. The drying process allowed the surface to harden and obtain a basic mechanical strength that prevented the material from crumbling and abrading. The residence time of the granules in the dryer was 20–25 minutes. However, after this time, the MVW and ChS biomass remained moisture so the drying time was extended for them. Due to the initial high moisture content of the corn waste and cherry stones, the drying time was eventually 90–120 minutes. The properties of the dried granules are given in Table 6.

The preliminary results obtained for the moisture, ash content and water absorption characteristics of the sample made it possible to select the type of biomass best suited to the initial processes of conversion to activated carbon. It was Sugar Beet Marc (SBM). After the drying stage, the samples of corn pulp and cherry seeds were rejected due to insufficient post-process moisture

Sample	BD [g/dm³]	WA [cm³/g]	M [%]	TVC [%]	A [%]	Mech. strenght [%]
SBSF	455	0.762	0.00	11.15	10.25	77
MVW	417	0.798	2.29	17.86	10.90	35
ChS	481	0.757	2.57	15.49	826	51

Table 6. Properties of the dried granules

content, too long drying time and low mechanical strength of the granules, which disintegrated after removal from the dryer.

Ivanov [2018] and Kambo [2015] report that during carbonisation, micropores in the structure of the carbonised biomass start to expand, leading to the deposition of tarry substances, as mentioned in 3.1. This phenomenon leads to the formation of mesopores (2-50 nm) and macropores (> 50 nm). For this reason, pore volumes were measured for the SBSF sample. The pore volume above 7500 nm was 0.0251 cm³/g, in the macro pore range 7500–1500 nm it was 0.1855 cm³/g, in the mesopore range 1500-150 nm it was 0.5207 cm³/g, and the lowest micro pore range 150-15 nm it was 0.0597 cm³/g. For the samples of the other materials tested, it was not possible to perform a porosity test because the samples underwent self-disintegration.

Process and results of SBM activation under laboratory conditions

The most commonly used activation method involves the reaction of carbonaceous material at high temperature with oxidising gases, i.e. water vapour, carbon dioxide or oxygen. When using the physical activation method, the high-temperature pyrolysis and activation used in the first stage of biomass processing are usually two individual stages [Dawood 2014, Han 2014, Torres-Pérez 2015]. As mentioned earlier in the pyrolysis stage, the raw materials were carbonised in an neutral gas atmosphere at 400-550°C, and the resulting biomass charcoal has a defined pore structure with low porosity usually [Sipola et al. 2018]. It can be compared to charcoal. The second step is the obtained carbonisate is the activation of the biomass charcoal with an activate agent in a suitable manner at high temperatures. This procedure aims to increase the pore number of the processed pyrolysed biomass. What is important is that it enables to obtain activated carbon that meets the expectations of high efficiency of adsorption of pollutants from gases or liquids. As a result of the reaction with the activator, further gasification of the carbonaceous material takes place. The porous surface corresponding to the sorption properties of the material is formed as well. The rate of oxidation is limited by the reactivity of the carbon material and activator [Marsh 2006, Yahya 2018]. The type and quality of raw materials are of fundamental importance in the technology of activated carbon production. Of the raw materials with a general low degree of carbonisation, beside hard and brown coal, peat, raw materials of wood origin (wood, wood waste, pomace, waste wood processing products) and plastics are of the greatest importance. Of particular importance are waste materials, which can be a fully-functional raw material for the production of activated carbons [Yong 2021]. This type of material also includes SBSF, but the form of this raw material and the ash content present difficulties in technical decisions for the production of activated carbons. In order to produce the activated carbons that achieve high sorption and mechanical parameters, the organic feedstock must be selected appropriately. The carbons derived from different types of biomass have different properties, which are usually eventually are shaped by the activation process [Manocha et al. 2012, Sopola et al. 2018]. Authors' own investigation was therefore performed to check if SBSF and other possible biomass may be sufficient raw material for AC manufacturing.

In the study, biomass only in the form of SBSF all fractions individually, 2-step process at the beginning was tested including pyrolysis under laboratory conditions and then activation. The charcoal used for testing was subjected to pre-carbonisation, milling, granulation and drying. During pyrolysis, carried out at temperature of 550°C and a time of 1.5–3 h, decomposition of the binder with formation of semi-coke, separation of volatile parts took place. Physical-chemical and structural changes of the carbonised material were also realised. The method of obtaining feedstock for laboratory activation tests, the course and results of their pyrolysis or carbonization, and the properties of the resulting semi-finished products are

presented in Tables 7 and 8. Activation was carried out in a laboratory tube furnace heated with sylvite rods and adapted to the activation process. Laboratory activation parameters were maintained according to literature guidelines [Vilella 2018, Mohamed eta al. 2015, Schramm 2006, Manocha 2013], and the technological procedure used with the plant:

- carbonate feed -0.4 dm^3 ,
- temperature -800-850 °C,
- activation time 1.5–3 h,
- steam consumption 200–220 g/h.

The tested SBSF material was divided into 3 separate groups: fibre, marc and mixture, depending on the fraction in which the raw material was delivered. Table 7 summarises the course and results of the carbonisation and laboratory activation of SBSF of its different parts.

The pyrolysis and activation process for all types of SBSF fractions was carried out under the same conditions, with the same temperature and process duration. The fibre fraction after the carbonisation process was largely converted to volatile fractions and ash, resulting in a small amount of charcoal remaining for further activation. In this process, it was difficult to maintain the correct parameters of the fibrous fraction, which was burned and remained as an activate with a very low bulk density in the range of 70 g/dm³, which is almost 3-4 times lower than the obtained mass of the other fractions tested. The high water absorption and the increased proportion of ash indicated the very low quality of the received carbon. It is also worth noting that the specific surface area of the fibre carbon was only the half of the surface area of other valuable activated carbons. The quality of the coals is also confirmed by the decolourisation indices of molasses and methylene blue. Similarly, in this case, the test results obtained disqualified the fibres as a product to be processed into AC. The mixed raw material and marc allowed achieving better sorption parameters close to the produced other charcoals. The mix had slightly lower molasses decolourisation rates and lower MNo compared to the marc sample material. Other parameters were comparable. However, it can be concluded that the use of single pyrolysis and activation processes does not provide the expected production efficiency or sorption properties of the activated carbons so prepared. Despite the low purchase cost and simplicity of processing SBSF fibres, further trials

and research of this biomass type were not undertaken, as the material in this form (very light mass and fine fibres size after pyrolysis of carbonised bagasse), which is shown in Figure 2, does not qualify sugar beet fibres for activation in technical production units. Therefore, further work was carried out using granulation of pyrolysed and next milled SBSF with a larger fraction.

Quality studies of SBSF activated carbons include the determination of physico-chemical properties, structural properties and adsorption tests from solutions, i.e. the absorption capacity of methylene blue, iodine and molasses. The later indicator, called the molasses number or milligram number, is of particular importance for the application of activated carbon in the sugar industry. As the activated carbons from SBSF will be primarily intended for use in the food industry, e.g. decolourisation of sugar solutions, the molasses number is a fundamental criterion for the quality assessment of the activates. The molasses number (MNo), tested in accordance with PN-84/C-97555.05, is the mass of activated carbon expressed in milligrams required to decolourise 200 ml of a standard molasses solution in such a way that 500 mg of standard carbon is used. A standard molasses solution is prepared, 200 ml of which is decolourised with 500 mg of standard carbon to an extent that corresponds to 32.5 ± 0.5 % light transmittance measured with a spectrocolorimeter at 400 nm and an absorbent layer thickness of 1.0 cm. Qualitative evaluation of activated carbons is carried out using a standard solution of molasses according to the methodology specified by the standard, measuring the transmittance of the decoloured solution after adsorption. On the basis of the obtained transmittance result, the value of the molasses number is read. The higher the transmittance values, the higher the molasses number values and the poorer the quality of the tested carbon in terms of molasses decolourisation. A molasses number above 800 indicates practically no ability to decolourise sugar solutions. Commercially available activated carbons, e.g. CWZ-3 used commonly in the sugar industry, have MNo in the range of 270-370. Due to the size of the molasses particle (2.8 mm), it is necessary to test the molasses number of activated carbons intended for the sugar industry, as positive results for adsorption of methylene blue (1.5 nm) or iodine (1.0 nm) are not sufficient criteria for the quality assessment of these carbons. A simplified system of laboratory



Table 7. Carbonisation and laboratory activation of the separated sugar beet fractions

processing of SBSF (Table 7) involving carbonisation and laboratory activation only did not lead to valuable final products of AC. Only the compact SBSF marc could be accepted for further tests under semi-technical conditions. These tests included the full technological cycle, except for pyrolysis process, which was described before and the results are presented in Tables 4 and 5. In the extended semi-technical laboratory tests, carbonisation was analysed at temperatures of 450, 500 and 550°C (Tests 1, 2 and 3) for times of 1.5 and 3 h. The lowest temperature and the lowest activation rate were found to result in a lower BD and higher WA of final product. Such phenomena are not to be expected for valuable AC manufacturing and allow in the future the migration of such coal during washing process and regeneration and additionally could lead to corrosion of processing equipment used in technological line. The increase in temperature had an impact on the product parameters, which also depended on the process time. An acceptable bulk density of more



Figure 2. Carbonised SBSF: (a) fiber, (b) marc, (c) mix

than 400 g/dm³ was achieved at 450°C for 1.5 h and 550°C for 3 h. In both ranges, low WA was also noted. Due to these similarities, the choice of carbonisation conditions was based on an analysis of the efficiency of the process to obtain the final carbonisate. It turned out that the process efficiency was best in the lower temperature variant (450–500°C). In the higher variant, material losses already appeared and ash content increased over 11% in comparison to the previous process of pyrolysis. The carbonised coal was further subjected to milling, mixing with molasses binder, granulating and drying. The resulting granules with a diameter of 4.1-4.3 mm were subjected to drying (3.2 and 3.3), followed by activation, and the results obtained are shown in Table 8 with supporting graphs and Figure 2.

Activation of the received dry granules was carried out at 800 and 850°C over a period of 2 and 3 h. The tests performed were labelled as Test 1, Test 2-1, Test 2-2, Test 3-1, Test 3-2, Test 3-3, Test 3-4, so that the nomenclature of Test 1 corresponded to the previously conducted carbonisation at the lowest temperature; Test 2 at an intermediate temperature and Test 3 at the highest temperature. Different activation times were tested for the given temperature ranges. The activating agent was climate-neutral water steam. As reported in the literature [Sipola 2018, Yong 2021], the process can also be carried out using carbon dioxide or various compounds or chemical bonds. Sipola [2018] noted clear differences between the studied biocarbon from pine and willow bark in terms of pore size, surface area $(238-3505 \text{ m}^2/\text{g})$ and surface chemistry. His activation with KOH produced highly microporous ACs from all the tested bio-materials, while there was also an increase in meso- and macroporosity with H₂PO₄ and CO₂. In contrast, Vilella [2017] as well as Bubanele [2017] report that steam

ing significant internal structures of up to 1000 m²/g. At the activation temperature, steam reacts with carbon four times faster than CO₂, indicating that steam activation is superior both in terms of producing a large surface area and a shorter activation time [Chen 2017]. Since the biomassbased carbon prepared in this way will be used in the food industry in the study, chemical activation was dropped. For environmental reasons, CO₂ activation was also resigned. The activation of the carbonised products was carried out in such a way that the temperature ranges corresponded with the time for both phases: carbonisation and activation. For lower temperatures and shorter carbonisation times, the activation was also carried out at a lower temperature and shorter time. The efficiency of the process and the quality of the final products were evaluated. Similarly to carbonisation, activation at 800°C for 2 h showed the lowest process performance. The obtained carbons were characterised by a high ash content of approx. 25%, high water absorption and low bulk density, compared to carbons activated under other technological conditions. At the same time, but with an increase in temperature, the coal contained an even higher proportion of ash, up to 28%, while the water absorption decreased significantly to approximately 1 cm³/g. Due to the high proportion of ash, the bulk density of the product decreased. Activation was also observed with increasing temperature. The AC parameters in this case appear to be improved. The use of steam as an activating agent decreased and the ash content decreased as well. Thus, the final stage of the study was conducted for the highest temperature used, 850°C, testing different activation times: 1.5, 2 and 3h (Test 3-1, 3-2, 3-3 and 3-4). The conducted research caused that increasing the activation time to 3h does not increase the process

and CO₂ are ideal oxidisers. They allow obtain-



Table 8. Granulation with binder, carbonisation and laboratory activation of pyrolised SBSF

[cm3/g]



a) Porosity for Tests 1, 2 & 3 (with SBSF marc fraction)



b) Porosity for Tests 3-3 and Test 3-4 (with SBSF marc fraction)



Figure 3. (a) Activated charcoal porosity for Tests #1, 2 & 3 [cm³/g]; (b) Activated charcoal porosity for individual Tests #3-3 and Test #3-4 [cm³/g]

efficiency. Test 3-3 at 850°C and 2h showed the lowest ash content and water absorbance. Porosity, on the other hand, was highest for the longest activation time and highest temperature (Figures 3a, 3b, and 4). Higher values for the Transmittance of molasses decolourisation were recorded for shorter activation times and lower temperatures. Given that higher molasses number values and poorer quality of the investigated carbon in terms of molasses decolourisation occurred for MNo > 800% – these parameters excluded the activation process technologically due to the lack of decolourisation capacity of the sugar solutions. Low MNo occurred for times of 2 and 3 h at 850°C. Similarly, the Iodine Number typical for a good activated carbon (i.e. INo > 1000 mg/g) also occurred for the same samples.

In addition, the adsorption capacity of SBSFbased activated carbon was investigated by assessing the adsorption of Methylene Blue (MB). After equilibrium was achieved, the samples were filtered and the dye concentrations in the solutions were measured spectrometrically. The results showed that the maximum percentage of dye removal ranged from 15 to 35% (removal capacity from 25–63 cm³), thus SBSF is not highly efficient in the adsorption of Methylene Blue from aqueous solution. Hence, it can be confirmed that the prepared activated carbon is mesoporous, as Methylene Blue is used to characterise mesoporous activated carbons. Elham [2015] observed that mesoporous activated carbon from sugarcane is more suitable for MB removal and allows effective adsorption of over 90%. Similarly, corn cob carbon can adsorb MB at 96.2% from aqueous solutions. Other important AC parameters, i.e. sorption capacity and Specific Surface Area were investigated by Williams (2006). The biomass tested by him also was considered as waste and was in the form of fibrous flax textile. The scientist performed physical and chemical activation trials to produce activated carbons obtaining surface areas ranging from 500 m^2/g with physical activation up to 2000 m²/g with chemical activation. On the other hand in authors' own study, the SSA of the produced ACs

3.7699



800 °C 1,5h

850 °C 2h

850 °C 3h

Figure 4. Activated SBSF marc with different technological conditions; (a) 800°C 1.5 h; (b) 850°C 2 h; (c) 850°C 3 h

in Tests #1 and #2 was 500–700 m²/g, while for samples #T3-3 and #T3-4 it was 886 and 971 m²/g, respectively. The created pores were mainly mesoporous in structure.

CONCLUSIONS

The most commonly used raw materials for the production of activated carbon are, besides fossil hard and brown coals, for example coconut shells and wood. The literature [Malini 2023, Manocha 2013, Siipola 2018, Williams 2006, Kambo 2015, Correa 2017] also describes numerous publications on the production of activated carbon from different agricultural waste or biomass. However, in the case of biomass, unlike fossil-based materials, production technologies are dependent on changes in output parameters and, in the case of wet material, are energy consuming [Manocha 2013]. The exploration of a suitable, low-cost, waste-recovered adsorbent can lead to environmental sustainability and bring promising benefits for various applications in gas and aqueous solution purification. The Biomass used in the production of charcoal is suitable as a valuable raw material. The manufacturer of the product tested in the research described in this paper additionally took into account the priority of ensuring clean production, maximising the use of waste gases and reducing costs. Therefore, activation was carried out using steam and waste carbon dioxide from activation and carbonisation furnaces. In addition, the main accent in AC production was not on the largest possible surface areas, but on specific applications of the carbon, i.e. for the food industry not always requires high sorption parameters, but retention of given pollutants mainly in mesopores. The adaptation of the pore structure to specific pore size distributions in the modern production of activated carbons is currently the most valued parameter. The experiments in this work were conducted to determine the optimal technological parameters and guidelines for the production of activated carbons in a professional existing production company. Due to limited access to conventional coals, three types of biomass were tested: SBSF, MVW and ChS as coal-like raw materials. Biomass or post-production waste like SBSF, MVW and ChS represent an inexpensive source material for AC production that can be easily obtained from locally available resources. This would make it possible to convert difficult to exploit residual material into a valuable raw material and significantly improve the climate balance. The composition of the raw material can be adapted by selecting and/or combining suitable biomass materials such as SBSF, MVW and ChS. It is possible to select individual fractions of material for marc, fiber or mix and choose the most favorable option for production. In the case of authors' own research, SBSF pulp was such an option. When processing SBSF, MVW and ChS into activated carbons, a lower energy input is required due to lower temperatures of pyrolysis, carbonization and activation than for hard coal. On the other hand, the disadvantage of lowering process temperatures is the residual moisture remaining. However, in the lower temperatures, process yields for SBSF fibers and MVW fibers were low, yielding a carbonised product that was brittle and not suitable for further processing. In addition, the MVW-based carbonisate contained significant amounts of ash, which disqualified it as a potential raw material for real-scale AC production. Material limitations must be taken into account, involving the significant proportion of post-AC-production ash in all samples tested. Material limitations are also often related to the relevant quality of the raw material: the raw ChS

had a high moisture content and required significant energy input for drying and carbonisation. Although the proportion of elemental carbon was significant. It should be required pre-drying for ChS delivered directly from the farmer or from the plant. Wet seeds are not suitable for industrial processing into activated carbon. Of the biomass materials investigated, only SBSF in the form of marc can be processed further into valuable activated carbon. MVW and ChS as carbon substrates showed, in addition to high moisture and ash, low efficiency in decolourising molasses and MB and also had a low specific surface area.

The tests carried out showed significant limitations due to the production method, which had to be chosen precisely in order to produce the best AC product. The temperature and time of both carbonisation and activation were important. The optimum carbonisation temperature was 450°C and a time of 1.5 h, while the activation temperature was 850°C and a time of 2 h. This made it possible to obtain a final product in the form of activated carbon with sufficient sorption and porosity parameters for use in the food industry.

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