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Valorization of waste biomass towards biochar production - characterization and perspectives for sustainable applications in Serbia

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Abstract

The Republic of Serbia, as a transition country and a candidate to join the European Union, is still facing a variety of challenges to maximize the use of energy potential from its renewable energy sources. The current data indicate that agricultural biomass, followed by the woody biomass are recognized as an alternative energy sources with the highest potential in Serbia. A substantial amount of waste biomass which is generated per year in Serbia represents an excellent feedstock for the production of biochar, an exceptionally rich well-spring of carbon, potentially suitable to address the most important ecological issues of the modern society. This review is focused on the potential directions towards the sustainable utilization of biochar in Serbia with reference to the current state of energy production and consumption in different sectors of the country's economy. Additionally, a relationship between certain properties of biochar produced from different biomass sources originated from Serbia and its potential utilization was proposed. For that purpose, different biomass feedstocks were pyrolyzed into biochar: non-woody samples obtained from agricultural residues, brewer's spent grain as a food industry waste, and oak and beech sawdust as representatives of woody biomass. The composition, structure and texture of the produced biochars were examined by standard characterization techniques. Having in mind that Serbia possesses a significant potential of renewable energy sources, the future implementation of biochar in different sectors can be a contributing factor to the reshaping of the country's economy and accelerating its transition from a linear to circular economy model.

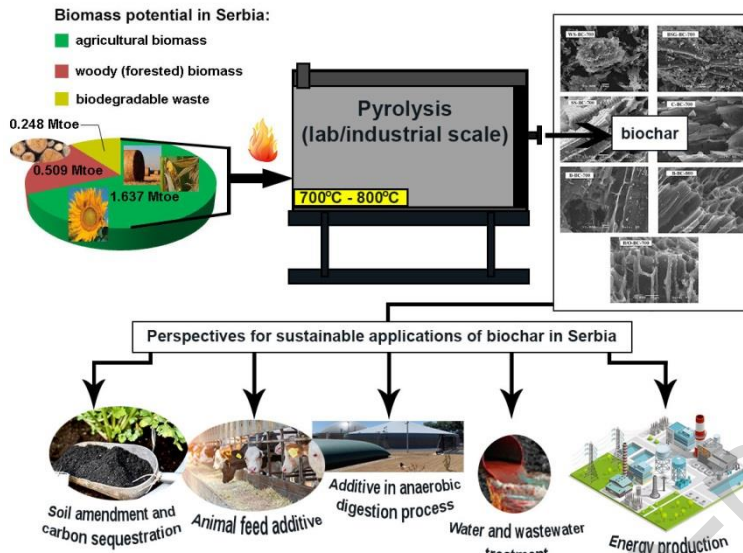
Highlights

- Pyrolytic biochar (BC) was produced from different biomass sources from Serbia
- Composition, structure and texture of BCs were examined by standard techniques
- Current state regarding renewable energy sources in Serbia was surveyed

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- BC structure-potential sustainable application relationship was proposed for directions to sustainable future BC utilization in Serbia

Graphical abstract



Keywords: Biomass feedstocks; Solid waste; Pyrolysis; Biochar properties; Biochar applications; Serbia

Abbreviations

GHGs -	greenhouse gases
RES -	renewable energy sources
BC -	biochar
WS -	wheat straw
C -	corn cob
SS -	soybean straw
BSG -	brewer's spent grain
UNFCCC -	United Nations Framework Convention on Climate Change
INDCs -	Intended National Determined Contributions
AD -	anaerobic digestion
COD -	chemical oxygen demand
GDP -	gross domestic product

Units

Mtoe/ktone - megatons/kilotons of equivalent oil

ha-	hectare
Gg CO ₂ eq -	gigagrams of carbon dioxide equivalent
MW -	megawatt
MWh -	megawatt hour
thous. m ³ -	thousand cubic meters

1. Introduction

By 2050, it is expected that energy consumption will have increased by 50% compared to 2010 (EIA, 2019), while the world population will reach 9.7 billion (UN DESA, 2019). These predictions indicate that it is necessary to pay even more attention to the greatest challenges of human society today – economic progress, energy transition, environmental degradation and climate change mitigation. In order to respond to these global issues, numerous actions all over the world in the form of policies, agreements, etc. have been adopted, highlighting the necessity of profound transition of the fossil fuels dependable energy system to the one that increases the share and effectiveness of renewables (IRENA, 2019). This concept of energy sector decarbonization will diminish the consequences of climate change by reducing the emissions of greenhouse gases (GHGs) and preventing the environmental pollution (Barreto, 2018). Within the scope of the ongoing global energy transition, the recommended strategy has increasingly been incorporated on national levels, in the form of documents with the policy of intensifying the utilization of renewable energy sources (RES). According to the last population census from 2022, the Republic of Serbia has 6.6 million inhabitants (StatOfficeRS, 2022a). Analysis of demographic trends in Serbia indicates the downward trend from the end of 20th century. According to the expected projection scenario, the population of Serbia in 2052 will be 5.2 million, which represents a decrease of about 1.5 million compared to 2022, approximately 22%. The main cause of the expected population decrease in the coming decades will be negative natural growth - 86% on average compared to the effect of negative net migration (StatOfficeRS, 2024). The energy resources and potentials of the Republic of Serbia mainly consist of fossil fuels - coal, oil, natural gas, and oil shales (around 85%), as well as RES (hydropower, biomass, wind, solar, biogas, landfill gas, geothermal energy sources, etc.) (MMERS, 2016). Reserves of more quality energy products, such as oil and gas are symbolic and make less than 1% of geological reserves, while remaining 99% of energy reserves include coals with 95% share of lignite. The Republic of Serbia does not have its own energy sources in the quantity that fully meets its requirements, thus the share of energy consumption comes from imported sources. Despite this import dependence, the energy system of the Republic of Serbia has been characterized by supply stability in the last 20 years. This goal has been largely achieved by utilizing domestic lignite (70%) and large hydropower plants (30%) for electricity

generation, as well as the significant use of firewood as fuel in households. Lignite consistently accounts for over 50% of the total energy sources used in primary consumption. According to the projections of demands of energy sources/fuels in the final consumption in Serbia up to 2040, the largest share in the final energy consumption will have oil derivatives, followed by electricity and wood fuels. The share of oil derivatives would decrease from 31.2% in 2021 to 26.2% in 2040. Electricity would have the largest increase in consumption from 26.8% in 2021 to 33.7% in 2040. This trend of increase in electricity consumption is primarily caused by the foreseen higher consumption in transport, as well as consumption for operation of heat pumps in households and the public and commercial sectors. When it comes to primary energy consumption in the considered period (2021-2040), it increases from 16.508,4 ktoe (2021) to 20.366,1 ktoe (2040). Coal remains the dominantly used primary energy source. Its consumption will increase up to 2040, along with the consumption of oil and natural gas (MERS, 2024).

As a transition country on the way to implement the European integration process, Serbia has to emphasize the maximum use of energy potential from RES. Based on the available data from the Serbian Energy Sector Development Strategy, the potentials of RES in Serbia are significant and estimated at 5.65 Mtoe (tons of equivalent oil) per year (MMERS, 2016). The country is already using around 35% of the total available technical potential of RES. The National Action Plan for Use of Renewable Energy Sources, with a target set for 2020 of 27% of energy provided from RES (MERS, 2013; MMERS, 2016) was not achieved as RES participated with 20% in the structure of the total domestic production of primary energy in 2020 (RSGov, 2022). On the other hand, the data from the Ministry of Mining and Energy support the fact that the country is gradually increasing its renewable energy capacities. Namely, the total planned production of primary energy from RES in 2022 was 2.65 Mtoe. The largest share (61%) in this structure corresponds to solid biomass, hydro potential and wind energy account for 33% and 4%, respectively, while biogas, solar energy and geothermal energy participate with 2% (RSGov, 2021a).

Within an estimated total potential of RES in Serbia per year (5.65 Mtoe), more than 60% is biomass potential amounting to approximately 3.4 Mtoe per year, with only 1.1 Mtoe per year already in use (MERS, 2013). Figure 1 represents the total available and used/unused potential of biomass in Serbia adopted from the Energy Sector Development Strategy of the Republic of Serbia for the period by 2025 with projections by 2030 (MMERS, 2016).

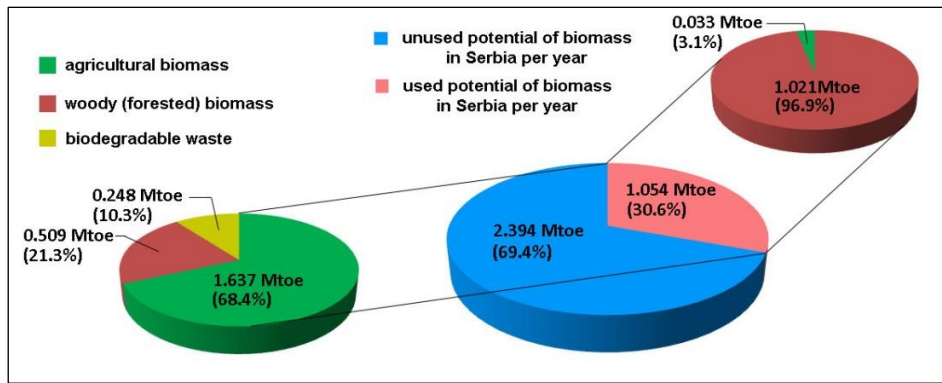


Fig. 1. Schematic overview of the technical usable potential of biomass in Serbia (source adapted from (MMERS, 2016))

These data indicate that agricultural biomass, followed by the woody (forested) biomass are recognized as an alternative energy source with the highest potential. Other types of biomasses are given far less attention. This is in line with the fact that agriculture represents a key sector for the Serbian economy with approximately 5 million ha of agricultural land, which is around 55% of the territory of Serbia (Figure 2a). The production of cereals and crops, as well as related food industry is predominantly present in Vojvodina, the autonomous province in the north of the country (ETIP, 2020). In Serbia, the average annual production of agricultural biomass is around 12.5 million tons (residues of agricultural crops, residues in fruit growing, viticulture and fruit processing, liquid manure), with around 9 million generated in Vojvodina (“Obnovljivi izvori energije,” n.d.). The largest part of the post-harvest residues is generated from corn and wheat productions, accounting for around 26% and 55% respectively of the total annual quantities of the post-harvest residues in Vojvodina. This is followed by sunflower residues (~12%), barley (3%) and soybean (3%) (Dodić et al., 2010). Thus, the Province of Vojvodina can be regarded as the part of the country with the highest quantities of harvest residues, diversely distributed in its 43 municipalities (Figure 2b).

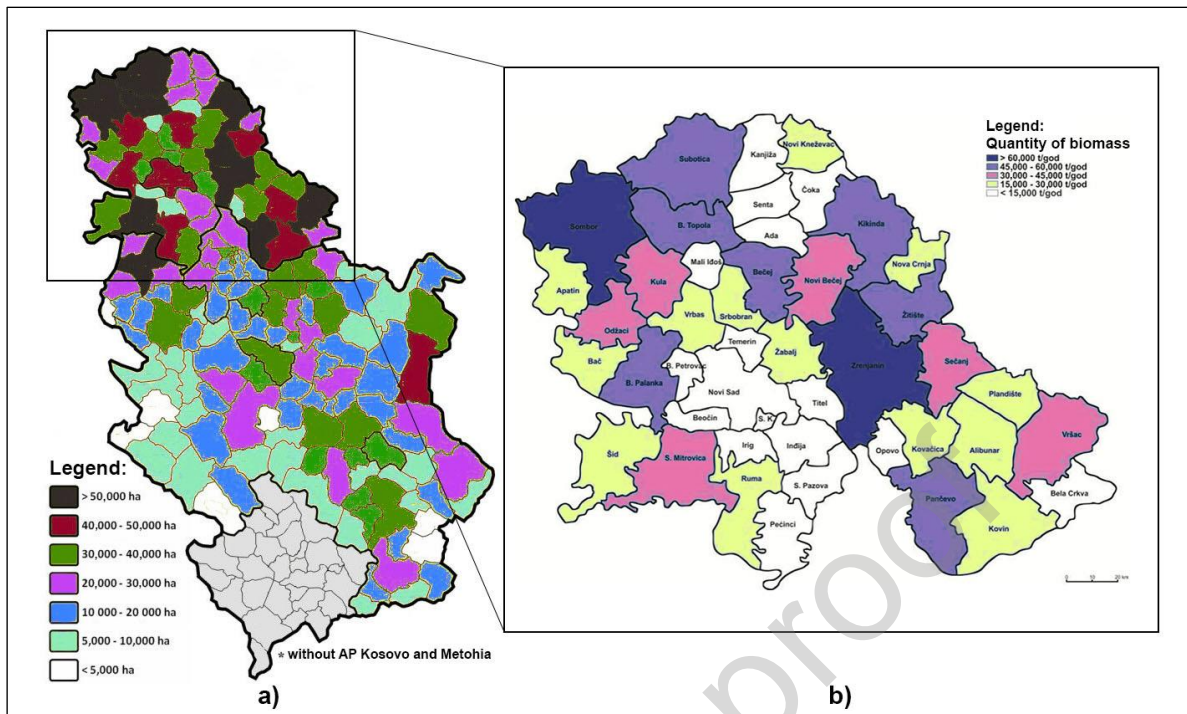


Fig. 2. The arable land on the territory of Serbia (a) (source adapted from (Dragovic et al., 2019)) with the quantities of harvest residues distributed in 43 municipalities in Vojvodina Province (b) (source adapted from (Martinov, M. et al., 2016))

When it comes to woody biomass in Serbia, forests cover around 2.3 million hectares or one third of the total surface area of the country (StatOfficeRS, 2017). The total amount of wood residues after forestry logging operations is estimated at 1.1 million m³. Out of this amount, 0.6 million m³ is estimated as unused forest waste (Energy Saving Group, 2007). The current usage of biomass in Serbia mostly refers to a traditional way of its utilization for heating and electricity generation (MMERS, 2016). The planned production of solid biomass in 2022 was 1.616 Mtoe. Out of this amount, only 0.01 Mtoe was consumed in heating plants. Furthermore, the planned final consumption of biomass amounted to 1.561 Mtoe. In the structure of this consumption, industry participated with 12%, households with 87%, and other sectors with 1%. It is evident that the consumption of solid biomass takes place predominantly within the household sector for heating purposes (RSGov, 2022). One of the possible directions towards the transition from a linear to circular economy in Serbia and, therefore, the greater utilization of biomass potential, is the generation of biochar (BC) from various biomass feedstocks, including the biomass waste. This is of great importance since the country is still facing a variety of challenges in solid waste management (Vujovic et al., 2020). So far, according to the officially available data, the utilization of BC has not been implemented in any sector of the Serbian economy.

Biochar is a multifunctional bioproduct with a huge utilization potential. It is a porous, carbon rich material produced by thermochemical conversion of biomass in an oxygen-free or

oxygen limited environment (Hamid et al., 2022; Uday et al., 2022; Yaashikaa et al., 2022). The thermochemical production of BC involves several different treatments, such as pyrolysis, hydrothermal carbonization, gasification, torrefaction and flash carbonization (Amalina et al., 2022; Libra et al., 2011; Liu et al., 2015; Waters et al., 2017; Yaashikaa et al., 2020). Being a low-cost material, BC has gained attention of many researchers as a material important for soil nutrient enrichment and fertility improvement, contaminated or waste water and gas treatment, production of bioenergy or synthesis gas, to name a few. Its application on soil has been suggested as a means of abating climate change by sequestering carbon: "of the possible strategies to remove carbon dioxide from the atmosphere, BC is notable, if not unique, in this regard" (Woolf et al., 2010). If used as an additive to polymeric and concrete materials due to its low bulk density, high hardness, and porous nature (Shanmugam et al., 2022), it can also be considered as a carbon long-term storage medium. Polymeric composites reinforced with BC have showed enhanced water resistance, as well as mechanical properties, such as strength, hardness, and stiffness. The integration of BC improves the filler-matrix interaction by enhancing adhesion consequently boosting the structural integrity of the composite (Rajendran et al., 2024a, 2024b). The addition of a flame retardant to polymeric materials is one effective way to increase their fire resistance property, but, on the other hand, it could be detrimental to their mechanical strength. BC can be used to host the flame retardant in polymeric composite materials and simultaneously improve fire resistance and conserve mechanical strength (Mensah et al., 2022; Perroud et al., 2022). Due to a high carbon footprint caused by the traditional concrete production, more sustainable solutions have to be found. In this regard, the addition of BC to cement can enhance its resilience to high temperature and maintain its strength under certain fire conditions (Mensah et al., 2024). Owing to its valuable role for the fabrication of sustainable materials, utilization of BC promotes circular economy and could be suggested as a win-win strategy for long-term decarbonisation (Kapoor et al., 2024). The rapidness, simplicity, and wide scale of its production, which is usually both sustainable and cost-effective, make its application acceptable to a variety of socioeconomic situations (Shanmugam et al., 2022).

There is a huge availability of feedstocks for BC production, among which agro-industrial residues and waste are the most important ones due to the huge quantities generated all over the world, especially in developing countries (Gabhane et al., 2020). Agro-industrial residues and waste originate from the agricultural practices and different processes of agricultural produce processing plants, including food and beverages industries. At present, a large amount of agricultural waste is burned or left to decompose in the field, releasing considerable quantities of greenhouse gases such as CO₂ and CH₄ into the atmosphere (Song et al., 2022). Converting such waste into BC can reduce the emission of GHGs if compared to the emission during its burning or microbiological decomposition (Woolf et al., 2010).

A vast amount of waste biomass which is generated per year in Serbia can provide an excellent feedstock for BC production. This is the first paper to demonstrate the properties of the BC produced by lab/industrial scale pyrolysis of the most abundant waste biomass types generated in Serbia. These include non-woody (agricultural and beverages industry waste originating from the Province of Vojvodina) and woody-based waste (originating from different parts of Serbia). The detailed physicochemical characterization of the prepared BC samples aimed to highlight the properties that distinguished BCs obtained from a particular feedstock and/or a feedstock group. Additionally, within the scope of the considerable interest in BC application in various fields, and in order to address the most important environmental issues, a part of this study is devoted to the assessment of potential directions towards BC utilization in Serbia with reference to the current state of energy production and consumption from fossil/renewable energy sources in different sectors. Some environmental concerns regarding the potential BC applications are also discussed.

2. Characterization of the prepared BC samples from Serbia

The potential future implementation of biochar in different sectors of the Serbian economy implies a detailed characterization of BC samples obtained from various types of biomass feedstocks. In this regard, representative samples of biomass residues were collected and transformed into biochar followed by a detailed physicochemical characterization in order to propose directions towards its successful utilization in appropriate economy sectors.

2.1. Feedstock collection

Two groups of BC samples were investigated taking into account the production method: lab-scale produced BC from non-woody biomass sources, and wood-based BC obtained at industrial-scale plants. Table 1 shows an overview of all BC samples used in this research with the relevant markings that are used throughout this study.

Non-woody biomass samples for lab-scale production of BC comprised of wheat straw (WS), corn cob (C), and soybean straw (SS), representing agricultural residues, and brewer's spent grain (BSG) that might be considered as a food industry waste. Samples of wheat straw, corn cob and soybean straw were collected on the territory of the Autonomous Province of Vojvodina. After having been thoroughly rinsed with distilled water, the samples were dried at room temperature for 48 h, finely chopped in a blender and a planetary ball mill (300 rpm, 1 h), and then passed through a sieve with 500 μm mesh size. A sample of brewer's spent grain was obtained from a local brewery and it was treated in the above-described manner. The selection of the brewer's spent grain as a representative of the food industry waste is justified when the quantity of beer produced annually in Serbia is taken into account. Namely, according to the Statistical Yearbook of the Republic of

Serbia from 2022, beer production in the country in 2021 was 5.556.000 hl (StatOfficeRS, 2022b) indicating that around 110.000 t of brewer's spent grain was generated (Mussatto et al., 2006).

2.2. *BC synthesis and characterization*

The processed feedstock samples were used to synthesize BC by slow pyrolysis method. The synthesis procedure and methods used for the characterization of the obtained BC samples are described in detail in the Supplementary Material.

Table 1. Overview of BC samples synthesized from non-woody and woody biomass

Biomass type	Biomass source	Slow pyrolysis temperature/scale	BC marking
Non-woody	wheat straw	700 °C/lab	WS-BC-700
	brewer's spent grain		BSG-BC-700
	soybean straw		SS-BC-700
	corn cob		C-BC-700
Woody	beech	700 °C/industrial	B-BC-700
	beech	800 °C/industrial	B-BC-800
	beech and oak mixture	700 °C/industrial	B/O-BC-700

3. **Results and discussion**

The general composition of the BC feedstock is presented in Table S1 of the Supplementary Material in the form of the literature-based average values (Huang et al., 2016; Phyllis, 1999). The average elementary composition of the brewer's spent grain differs markedly from the other feedstocks with regards to its higher contents of C, N, S, and fixed C, as well as the lower levels of oxygen and volatiles. Non-woody based biomass is characterized by much higher content of ash than the woody-based biomass. Expectedly, the highest lignin content is in woody-based biomass. According to the available data, the main ash component in wheat straw and corn cob is SiO₂, while in beech and oak wood is CaO.

3.1. *Properties of BC samples from Serbia*

Table 2 shows BC yield along with the results of proximate and ultimate analysis of the synthesized BC samples. The achieved yield of BC was in the range from 27.5 wt% to 39.6 wt%, implying that the amount of the produced char is quite similar regardless of the starting biowaste material. Woody-based BCs have lower moisture and ash content, but higher amount of fixed carbon than non-woody ones. The increased ash content in the samples produced from wheat straw, brewer's spent grain, and soybean straw is the consequence of the increased ash content in the

feedstock material (Table S1). The highest amount of volatile matter and the lowest amount of fixed carbon were recorded for SS-BC-700 and C-BC-700 samples. The examined pyrolytic process of beech at 800°C can be successfully applied in order to achieve remarkably high degree of carbonization (94.45 wt% C). The utilization of beech/oak mixture and corn cob was also beneficial in this sense, while the other non-woody samples yielded chars with lower C amount. The H content was pretty low in all the chars, while WS-BC-700 and SS-BC-700 samples contained slightly higher O amounts than other BCs. In addition, a higher content of N was recorded in the BC derived from brewer's spent grain and soybean straw.

The obtained results of the characterization of the examined biochar samples are in accordance with the current literature data, as well as the data present in the Phyllis2 database containing information on the composition of biomass, macro- and micro-algae, feedstocks for biogas production, biochar and torrefied biomass (Phyllis, 1999). Additionally, the presented data can significantly contribute to the enrichment of the existing database, especially in the case of biochar produced from the brewer's spent grain, soybean straw and corncob.

Table 2. Yield, proximate and ultimate analysis of BC samples (in wt%)

BC marking	Yield	Moisture	Volatile matter	Fixed carbon	Ash	C	H	O	N	S
WS-BC-700	27.5	4.0	45.2	31.9	18.9	67.03	2.13	10.85	0.75	0.34
BSG-BC-700	28.0	5.4	30.7	49.5	14.4	70.88	2.26	6.84	5.54	0.08
SS-BC-700	31.2	2.9	62.2	21.7	13.2	67.43	2.61	15.62	1.07	0.07
C-BC-700	30.8	3.0	59.9	31.2	5.9	82.50	2.37	8.33	0.85	0.05
B-BC-700	35.2	1.2	44.5	52.2	2.1	89.79	1.48	6.32	0.25	0.06
B-BC-800	32.8	1.1	39.7	56.9	2.3	94.45	0.99	2.03	0.16	0.07
B/O-BC-700	39.6	1.6	28.9	63.3	6.2	82.55	1.64	9.28	0.29	0.04

All examined BC samples exhibit remarkably low H/C ratio and relatively low O/C ratio, thus indicating high degree of carbonization and aromaticity, as well as low polarity of the produced chars (Figure S1) (Wantaneeyakul et al., 2021). The H/C ratio displayed a decreasing trend from non-woody- BCs towards their woody- counterparts, with the lowest value recorded for the B-BC-800. It can be concluded that this sample possesses the highest structural stability due to its increased aromaticity. Additionally, the same sample has the lowest O/C ratio, which suggests its lowest polarity – lesser hydrophilic surfaces caused by the loss of polar functional groups. The higher H/C ratio associated with the BCs derived from the non-woody based biomass is related to the higher content of inorganic compounds in the feedstock materials acting as catalysts during the pyrolysis (Smith and Ross, 2016).

All BCs have a characteristic heterogeneous surface and a developed macroporous structure (Figure 3). The morphology of the samples originating from wheat straw and brewer's spent grain is characterized by the presence of platelet structures in combination with particles of different shapes and sizes. On the other hand, the BCs from soybean straw and corn cob consist of significantly better-arranged channel-like structural units with sharp edges. These morphological shapes are characterized by exceptionally developed mesoporous and, in particular, macroporous structure. The BCs derived from woody biomass contain a large share of well arranged, mostly macroporous, specific structures in the shape of honeycomb. The application of 100°C increase in temperature had no impact on the morphological characteristics of the produced BC. The elemental composition (wt%) of all BC samples obtained by EDS is shown in Table S2 of the Supplementary Material.

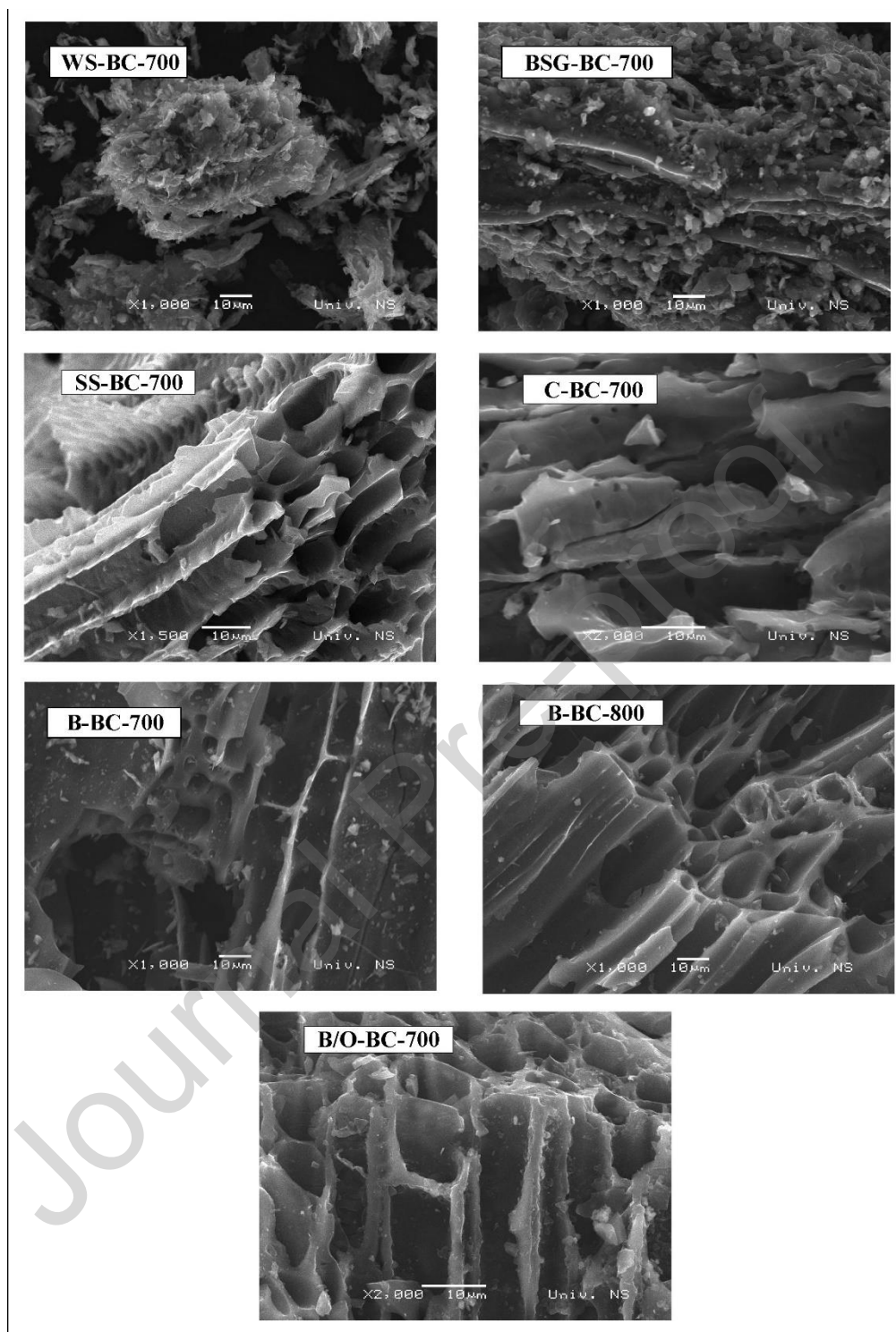


Fig. 3. SEM images of BC samples

The diffractograms of all BCs (Figure S2) can be characterized by basic peaks of turbostratic phase: C(002) (15° - 30° 2θ) and C(100) (40° - 50° 2θ) (PCPDFWIN database, CAS number: 75-1621). The biochars derived from woody biomass are characterized by higher intensity of (002) peak in comparison to the non-woody-based ones, indicating the presence of a turbostratic

phase of a higher degree of crystallinity (Dawodu et al., 2014; Pusceddu et al., 2017; Zeng et al., 2014). The (100) peak intensity is also higher for the woody-BCs, which might be the consequence of the lateral growth of carbonaceous structures created by linking the aromatic sheets to each other. Mineral calcite (CaCO_3) (COD database code: 7022027, Reference code 96-702-2028) and quartz (SiO_2) (COD database code: 5000035, Reference code 96-500-0036) were identified in the SS-BC-700 sample, while all woody-based BCs contain calcite (CaCO_3).

The adsorption-desorption isotherms of BCs (Figure S3, Table S3) from non-woody biomass are characterized by H4 type of hysteresis loop, suggesting the presence of a certain portion of micropores. The same type of hysteresis also appears for woody-based BCs produced at 700°C, while the H3 type is observed for the sample produced at 800°C, indicating the presence of mesopores in the shape of cracks and splits (Lowell et al., 2004). The non-woody BCs have lower specific surface area in comparison to the woody-based BCs, while their pore diameter distribution can be characterized by bimodal profile with the highest portion of pores in the meso-domain with diameter reaching the micro-range (3–5 nm). The C-BC-700 sample has a very low total pore volume, so its high specific surface area (217.2 m^2/g) is due to a high portion of micropores. Pyrolysis of woody biomass leads to BCs with a monomodal profile of pore diameter distribution (3–5 nm); the increase of pyrolysis temperature by 100°C increased the total pore volume by more than tenfold. The textural characterization of the BC obtained from brewer's spent grain could not be performed due to its low value of BET.

The basic peaks in Raman spectra of BCs are D and G bands (Figure S4), where the D band indicates the presence of aromatic systems with a number of linked rings greater than six (Paris et al., 2005). G' (around 1530 cm^{-1}) and V (around 1400 cm^{-1}) bands, obtained after deconvolution in addition to the main vibrations of alkyl functional groups, also originate from the vibrations of the carbon atom in the aromatic systems that contain 3-5 condensed benzene rings (Li et al., 2006). The intensity of these bands gradually decreases with an increase of aromatic systems by condensation of benzene rings. Another important band present in Raman spectrum of all BCs is the S band (around 1170 cm^{-1}), which is related to sp^3 -hybridized carbon atoms (alkyl-aryl C-C structures and methyl groups attached to aromatic ring) (Pusceddu et al., 2017; Yang et al., 2018).

The produced BCs may be further characterized by the ratio of deconvoluted Raman bands areas (Figure S5). The woody-based BCs are characterized by higher A_D/A_G values than the non-woody ones, pointing out to an increased content of larger aromatic systems in their matrix (6 or more condensed benzene rings). It can be assumed that the formation of larger aromatic systems is a consequence of higher content of cellulose and/or lignin in woody biomass (Pusceddu et al., 2017). The A_D/A_G value also increases with the increase of pyrolysis temperature due to the dehydrogenation of hydroaromatic compounds followed by enhanced growth of aromatic systems at higher temperature (Yang et al., 2018). The $A_D/A_{(G+V)}$ ratio is a measure of the content of larger

aromatic systems (≥ 6 condensed benzene rings) relative to the aromatic systems typical for amorphous carbon (several condensed benzene rings). The C-BC-700 sample is characterized by the highest value of this ratio indicating the absence of small aromatic systems. Moreover, this sample can be distinguished from the others by exceptionally low value of the A_S/A_G ratio, suggesting that this matrix possesses mostly individual large aromatic structures with sp^2 -hybridized carbon atoms.

The FTIR absorption spectra of BCs are shown in Figures S6 and S7, while the positions of vibrational bands, as well as their identification based on the data from the existing literature (Singh et al., 2016) are shown in Table S4. All BCs are characterized by a broad and intensive vibrational peak around 3400 cm^{-1} , assigned to the stretching vibrations of $-\text{OH}$ groups. The $-\text{CH}_2$ and $-\text{CH}_3$ stretching vibrations are also present in all samples, with the highest intensity peak at 2851 cm^{-1} in B-BC-800. The WS-BC-700 sample also contains $-\text{OH}$ groups directly attached to the aromatic ring. The FTIR results are in accordance with the results of the XRD analysis also in terms of the presence of calcite mineral. In line with the appropriate intensities of vibrational bands at around 1400 cm^{-1} , 1080 cm^{-1} and 880 cm^{-1} , it can be assumed that this mineral is present in a higher fraction in SS-BC-700 and B/O-BC-700 samples compared to other BCs. The FTIR results also confirmed the presence of some silicate materials in the BCs derived from non-woody biomass, as well as in the B-BC-700 sample.

3.2. *Perspectives for sustainable applications of BC in Serbia*

Biochar is an ongoing area of interest among many researchers due to its eco-friendliness, abundant resources for its production and simple and low-cost synthesis procedures. Since the utilization of BC can address a wide variety of environmental issues, this carbon rich material seems like an ideal approach to improvements in circular bioeconomy. The Republic of Serbia, as a developing country, has numerous prerequisites to become a part of this framework, since the majority of its potential renewable energy sources lie precisely in biomass, due to its availability, biodiversity and distribution. However, although the estimated total biomass technical potential in Serbia accounts for 3.4 Mtoe per year, its utilization rate is quite low (Energetski portal, 2013). Moreover, in some parts of the country the wood mass is primarily and uncontrollably used as wood for heating. When it comes to the production and application of BC in Serbia, the available data are quite scarce, indicating that the current situation is still substandard. However, the fact that there are many ongoing research studies is encouraging. According to the data available to the authors, there are only two manufacturers in Serbia producing BC and/or charcoal from agricultural and wood residuals, mostly to be used for building materials, composting, anaerobic digesters and as animal feed additive. Furthermore, even when it is produced as an energy source, most of the BC is intended for the export market, which proves that it has not been properly introduced into the

Serbian market. Hence, regarding the development of industrial and agricultural sectors in Serbia, the areas in which BC has a high potential of utilization are to be further discussed.

3.2.1. *Soil amendment and carbon sequestration*

Due to the rapid decrease of soil quality caused by ever-increasing population and an excessive addition of chemical fertilizers, sustainable approaches need to be implemented in agricultural crop production. Although many practices have already been proven to increase soil health and fertility, BC, as an emerging soil amendment, is gaining attention as a sustainable product that may lead to a decrease in the need for fertilizers, as well as reduction of carbon emissions. Furthermore, the soil amendment by BC can be considered as an effective method of restoring the soil contaminated with heavy metals, pesticides and hydrocarbons, consequently achieving higher crop yields without harming the natural environment (Placek et al., 2016). As a result of its specific structure and surface features, as well as the presence of organic compounds and various nutrients, the beneficial aspects of BC addition can be reflected in the increase of soil pH, organic carbon, total nitrogen, available phosphorus and the cation-exchange capacity (Dume et al., 2016). Additionally, BC can promote the carbon sequestration, mitigate the effects of GHGs, increase the productivity of crops by retaining water, reduce soil density and enhance microbial development in soil (Amalina et al., 2022).

The Republic of Serbia has around 5 million hectares of agricultural land, of which 71% is intensively used (in the form of arable land, orchards and vineyards), while 29% of its agricultural land consists of natural grasslands (meadows and pastures). The dominant part of agricultural land, 3.3 million hectares, i.e. 65%, is used as arable land (MAEPRS, 2014). There is a large area of agricultural land specialized in crop production in the northern part of the Republic of Serbia (Province of Vojvodina). Its central and southern areas have smaller landholdings, mostly orchards, vineyards and vegetable farms (MAFWMRS, 2010). According to the extent and structure of available agricultural land, Serbia belongs to the ranks of European countries with favorable land resources, since it has 0.7 ha of agricultural land or 0.46 ha of arable land per inhabitant (MAFWMRS, 2010). The data related to the quality of soil in Serbia were published in the Report on the state of soil in the Republic of Serbia for 2018 and 2019 by the Environmental Protection Agency, Ministry of Environmental Protection (Vidojević and Damnjanović, 2020). The soil analyses revealed that the area of central Serbia is dominated by slightly acidic and acidic soils, non-carbonate and slightly carbonated, with low content of phosphorus and high content of potassium. On the other hand, the territory of the Autonomous Province of Vojvodina has weakly alkaline soils, differently provided with carbonates and phosphorus, while the content of potassium is also high. Another very important issue related to the quality of soil in Serbia is pollution. Therefore, the presence of potentially toxic elements (heavy metals) and various organic

contaminants is regularly monitored. Based on the obtained data (Vidojević and Damnjanović, 2020), the situation in Serbia in this regard is not very unfavorable. In general, the soils in Serbia do not have an elevated content of potentially toxic elements (heavy metals). However, the main form of soil degradation in Serbia is the constant loss of organic matter due to the intensification of agricultural production, lack of application of organic fertilizers, as well as other intensive agrotechnical practices. This problem is becoming more complex and intensified every year due to the long-term lack of utilization of organic fertilizers (manure), which is the consequence of the destruction of livestock production. Taking into account the previously mentioned quality indicators of soils in Serbia, the application of BC as a soil additive can be designated as quite promising, as long as the choice of biochar type, according to its specific properties, is adjusted to the quality requirements of a specific soil. The results of physicochemical characterization of the aforementioned BCs indicate that all the samples could be utilized to enhance the quality of the soil by balancing its pH (Yaashikaa et al., 2020). The hydroxyl and phenolic functional groups present in BCs could react with H^+ ions, thus increasing the soil pH, which, in turn, is beneficial as most of the land in Serbia is acidic. Carbonates and silicates could have the same role suggesting the advantage of the application of all woody-originated BCs in relation to their non-woody-originated counterparts. Although Serbia has no great problem with the soil pollution, some polluted micro areas could be treated with woody-originated BCs since they possess higher specific surface area and pore volume than the non-woody-based ones. These properties are prerequisites for increasing the capacity of BCs for adsorbing various harmful contaminants (Amalina et al., 2022). Additionally, the B-BC-800 sample synthesized at higher temperature exhibits increased aromaticity, and consequently the highest structural stability and it could remain in the soil for longer period of time compared to other BCs. Taking into account the elemental composition of the produced chars, the beneficial aspect of the soil supplemented by non-woody-based BC samples could be reflected in the increase of the soil's pH and its subsequent cation exchange capacity due to the enrichment by various cations (K, Ca, Si, Mg, Na). Furthermore, the higher concentrations of Ca, K, N and P present in these chars could contribute to the amount of nutrients and act as a source of minerals for microbial population (Table S2). This could be especially important for the land in central and south Serbia with prevailing acidic soil. Brewer's spent grain proved to be an excellent raw waste material for the production of nitrogen-rich BC that could be used for soils lacking in nitrogen. However, if the ongoing situation regarding the soil quality in Serbia is taken into account, the positive aspects of the application of BC might be best considered in terms of increasing the amount of humus and organic matter, as this is currently the biggest problem and the main form of soil degradation in Serbia.

Soil plays a crucial role in the global carbon cycle. In order to mitigate climate change by reducing the emissions of CO_2 and other GHGs, there is a constant need to enhance carbon

sequestration in soil. Many studies have already reported that BC represents a promising material for carbon sequestration in soil owing to its highly condensed aromatic structure that is resistant to biodegradation (Méndez et al., 2012). However, since the negative effects in terms of CO₂ emissions upon the addition of BC into soil have also been observed, no definitive conclusion can be reached. The variability of the results regarding the utilization of BC for sequestering carbon in soil is partially the consequence of the two classes of carbon existing in BC – liable and recalcitrant. The liable carbon is available and easily consumable by soil microbes resulting in increased carbon mineralization short after BC application. On the other hand, recalcitrant carbon is persistent and can be present in the soil for an extended period of time (Puga et al., 2015).

The Republic of Serbia has been a member of the United Nations Framework Convention on Climate Change (UNFCCC) since 2001. In June of 2015, the Government of the Republic of Serbia submitted its Intended National Determined Contributions (INDCs), predicting a 9.8% reduction in GHG emissions by 2030 compared to emissions in the base year (1990) (RSGov, 2015). The First Report to UNFCCC Serbia delivered in 2010, while the First biennial updated Report was published and submitted in 2016. The last officially quantified GHG emissions in Serbia were published in 2020 by the Ministry of Environmental Protection in the Draft of the Second biennial updated Report sent to UNFCCC (MEPRS, 2020). According to the available data, the total national GHG emissions in 2016, including removals, amounted to 56,808.74 Gg CO₂ eq. The largest share in total emissions comes from the energy sector (79.1%), followed by 9.5% from the sector of agriculture, forestry and other land use. The contribution of the sector of industrial processes and product use was 7%, while the waste management sector amounted to 4.5%. Based on the updated Nationally Determined Contribution (NDC) for the period 2021-2030, Serbia increased its ambitions in terms of reducing GHG emissions by 13.2% compared to the level of 2010 (or 33.3% compared to 1990) until 2030 (RSGov, 2021b). Within the scope of previously mentioned expectations regarding the reduction of GHG emissions, the utilization of BC in Serbia can be considered as one of the potential measures taken in an attempt to reach the predicted values by keeping the carbon sequestered in the ground for a longer period of time. According to the results presented here, the woody-based BC samples having the higher amount of fixed (recalcitrant) carbon and increased content of large aromatic systems in their matrix compared to their non-woody counterparts, represent excellent candidates for this purpose. However, due to the potential negative effects of this kind of BC application, comprehensive studies must be done before its implementation in real practice.

3.2.2. *Animal feed additive*

The application of BC as an additive to animal feed is another beneficial way of its utilization in agriculture. This field of research is relatively young and studies related to the

incorporation of BC in animal feed are limited. However, the obtained results have shown that applying BC in animal husbandry has almost countless positive effects, including improved growth performance, meat quality and milk production, blood profiles, ability to resist pathogens and a reduction of methane production by ruminant animals, which is an additional effect against climate change (Man et al., 2021). The high sorption capacity of BC efficiently aids the removal of harmful substances (mycotoxins, heavy metals, or other pollutants) from the bodies of animals, as well as from farm environments. Due to its high surface area and porous structure, BC can help retain certain nutrients in the digestive system of animals and also provide a habitat for gut microbiota. The beneficial buffering capacity of BC is the consequence of its high cation exchange capacity enabling the absorption and release of various minerals, such as potassium, calcium, and magnesium. This can help stabilize pH levels in the stomach, improving digestion and preventing acidosis in animals like cattle (Rajpoot et al., 2024). An additional positive consequence of the application of BC as an animal feed additive is the production of manure enriched by plant available nutrients (Hammerschmiedt et al., 2022). Thus, the increased fertilizing and carbon sequestration effects can be accomplished at the same time. Agriculture is a key sector of Serbia's economy and according to the data from the Chamber of Commerce and Industry of Serbia, in 2021, the total value of agricultural production for livestock accounted for 29% (Chamber of Commerce RS, 2022). The initial decline of agricultural production in Serbia during the first half of the transition period particularly affected livestock production. Since the 1980s, livestock in Serbia has declined by 40%, suggesting its real devastation. Available statistical data on the number of livestock, production and consumption of meat, milk, and processed products, indicate that livestock production is still on the road to recovery (StatOfficeRS, 2022c). It was additionally disturbed by the COVID-19 pandemic forcing farmers and the processing industry of Serbia to make additional efforts and investments in food production and processing in order to mitigate the consequences that the pandemic had on the market. Thus, considering the ongoing livestock production recovery trend mentioned, the utilization of BC as a supplement in animal feeding could be a promising way to firstly preserve, and then develop the livestock sector in the coming years.

However, due to the limited knowledge and contrasting findings already reported on this topic, further investigation on the effectiveness of BC in animal production must be performed. Despite its potential benefits, BC must be used cautiously due to certain toxicity concerns. One of the main risks associated with BC is that it can adsorb and retain toxic heavy metals and other contaminants from the feedstock used to produce it (e.g., cadmium, lead, arsenic). Thus, the origin and quality of the biomass used to produce BC must be carefully considered. BC may also contain residual polycyclic aromatic hydrocarbons produced during the pyrolysis process, which are potentially carcinogenic compounds posing animal health risks (De la Rosa et al., 2019). High adsorption capacity of BC might reduce the availability of certain minerals or trace elements in the

animal's diet. Hence, proper dosing and monitoring are necessary to ensure that animals receive balanced nutrition (Osman et al., 2022). Although studies on BC's impact on animal health are promising, the long-term effects are still not fully understood implying that there are imperative challenges that need to be addressed. Careful sourcing, quality control, and monitoring of dosage are critical to minimize risks and ensure that BC is a safe and beneficial supplement to animal diets (Lao and Mbega, 2020).

3.2.3. *BC as an additive in anaerobic digestion process*

In recent years, within the scope of waste valorization into bioenergy, the emerging application of BC as a bulking agent in the anaerobic digestion (AD) process has been intensely studied. Various additive carbonaceous materials have already been widely used to enhance the AD process (Zhang et al., 2018). However, the latest literature assessments on carbon-amended AD processes revealed that BC has enormous prospective to be utilized in AD as an additive and can be designated as the priority material compared to other carbonaceous counterparts due to its cost-effectiveness, improved biogas yield and digestate quality (Kumar et al., 2021). Namely, the addition of BC into the AD process promotes the degradation of organic compounds, increases alkalinity and pH, benefitting the microbial community and enhancing the removal of chemical oxygen demand (COD) (Zhao et al., 2021). Additionally, the high adsorption capability of BC can have a significant role in mitigating the contaminants/by-products inhibition. Consequently, the production of CH₄ is higher, while the emissions of GHGs and total nitrogen loss are reduced (Zhang et al., 2019). The elemental composition of solid digestate (by-product of AD) is improved and can be further processed and used as fertilizer in agriculture. In accordance with the Directive of the European Commission from 2009, the Republic of Serbia obliged to obtain 27% of its energy from renewable sources by 2020 (MERS, 2013; MMERS, 2016). Despite the gradual increase in renewable energy capacities of Serbia in the last couple of years, this target has not yet been reached. In 2018, the European Parliament and the Council of the European Union adopted a new Directive to promote the use of energy from renewable sources, stating that Member States shall collectively ensure that the share of energy from renewable sources in the Union's gross final consumption of energy in 2030 is at least 32% (EU, 2018). In 2021, the European Union reached a 21.8% share of its gross final energy consumption from renewable sources, which is around 0.3% lower than in 2020. This decrease was most likely linked to the lifting of restrictions from the COVID-19 pandemic. Figure 4 shows the available data on the share of renewable energies for the gross final energy consumption in European countries for 2021 (EU, 2023). With more than half of the energy from renewable sources in its gross final consumption of energy, Sweden (62.6%) by far had the highest share among the EU Member States in 2021, ahead of Finland (43.1%) and Latvia

(42.1%). At the opposite end of the scale, the lowest proportions of renewables were registered in Luxembourg (11.7%), followed by Malta (12.2%) and the Netherlands (12.3%).

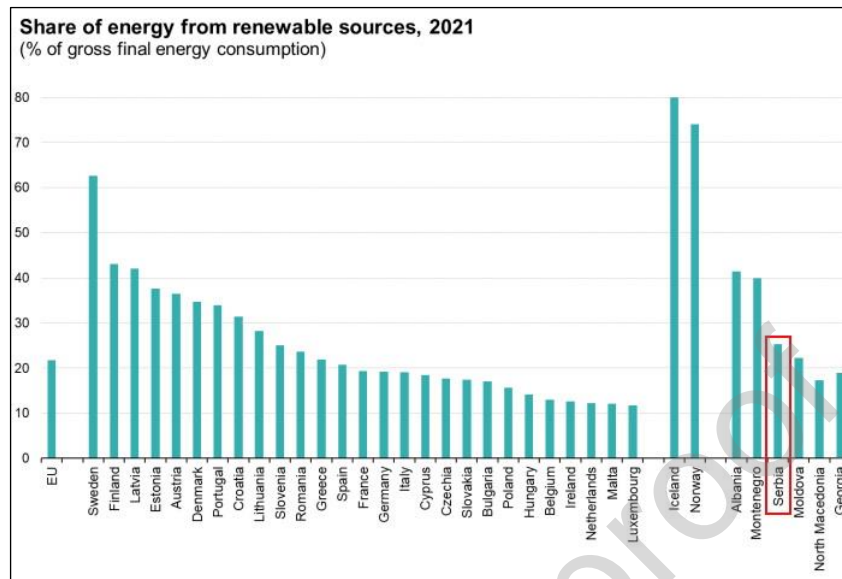


Fig. 4. Share of energy from renewable sources in European countries in 2021 (source adapted from (EU, 2023))

In accordance with the aforementioned recommendation, the Republic of Serbia is obliged to draft and adopt the Integrated National Energy and Climate Plan during the period of 2021 to 2030, including the perspective until 2050 (MMERS, 2022). Parts of this plan are to lower the emission of GHGs by 40% compared to the emissions that were in Serbia in the '90s, to increase the share of renewable energy sources to more than 40% by 2030 in the final consumption and to come across new ways of producing electricity and thermal energy. Therefore, the implementation of BC-amended technology in the biogas production sector could be a promising way to accelerate the achievement of this obliged goal by enhancing the performance of the current AD facilities. In 2010, the Government of the Republic of Serbia adopted the first Decree on the acquisition of the status of privileged electricity producer, which clearly defines the conditions under which this status can be acquired, as well as the price, i.e., feed-in tariff according to which the public company Elektrodistribucija Srbije will buy electricity from producers for a period of 12 years. After the adoption of this Decree, the construction of the first biogas plants in Serbia began. In 2013, Serbia adopted a second Decree regulating the area of renewable energy sources which significantly reduced the feed-in tariff in the field of biogas. The new price was not in line with real costs and did not take into account the value of raw materials as the basic cost of operating biogas plants (Pomoriški, 2020). After the expiration of this Decree, a new one was adopted in 2016, correcting all the shortcomings of the old ones. Consequently, biogas plants began to develop extensively in Serbia, and in 2019, this sector achieved a growth that was three times greater than expected. The

state of the biogas market in 2020 in Serbia includes 28 plants, with an installed capacity of 27.8 MW and an annual production of up to 223,800 MWh, while another 23 with a projected capacity of 24.4 MW are under construction (Ekapija, 2020). Most of the plants are located in the territory of the Autonomous Province of Vojvodina. At the beginning of 2020, the Decree on incentive measures for electricity production adopted in 2016 expired. However, by signing the Green Agenda for the Western Balkans (Regional Cooperation Council, 2021), further growth of investor interest in biogas cogeneration plants can be expected as a positive implementation of the closed chain of the circular economy in the domestic market. Thus, the policy of market drivers has been shifted from incentive tariffs for produced electricity to benefits of decarbonization through decreased costs due to reduced GHG emissions. In Serbia, most of the substrates used for biogas production come from corn and livestock production residues. Nevertheless, there is still a lot of potential to improve the performance of current facilities, as well as to implement new technologies using those or other substrates enriched by BC. Furthermore, by engineering synthesis conditions, the properties of BC can be tailored for the sake of this specific application. Some of the properties of BC that play a vital role in the AD process are its porosity, specific surface area, elemental composition, cation exchange capacity, electrical conductivity, redox properties, pH and surface functional groups (Kumar et al., 2021). The properties of BC samples presented in this study speak in favor of their potential application as a bulking agent for enhancing biogas production and the overall efficiency of AD. The high specific surface area, porosity and stability of woody-based BC samples can be recognized as crucial properties for potentially boosting the microbial functionality in the AD process (Chen et al., 2021; Zhu et al., 2017). The surface functionality identified in both non-woody and woody-originated BCs can contribute to nutrient retention, contaminant removal, and methane yield enhancement via direct or indirect electron transfer mechanism among anaerobic microbes (Chiappero et al., 2020). Additionally, the present functional groups could be the key points for buffering capacity maintenance, since the acidic/alkaline shock is frequently detected in AD systems (Zhao et al., 2021). However, the alkali-buffering ability could be more related to non-woody-based BC samples due to its higher content of alkali (Na, K) and alkaline-earth metals (Ca, Mg) (Table S2). On the other hand, BC samples obtained from agricultural residues contain additional important nutrients (N, P) essential for the syntrophic metabolic functions between different microorganisms (Teklit Gebregiorgis Ambaye et al., 2021), which is another important aspect leading to a more efficient operation of biogas plants. Based on all the above mentioned, the characterized BC samples can be considered as excellent candidates to be implemented in the biogas production technologies in Serbia contributing to the faster development of the circular economy model. However, before the practical application of BC for this purpose, it should be primarily introduced into the Serbian market followed by a thorough investigation on existing facilities.

3.2.4. BC for water and wastewater treatment

Recent studies regarding BC applications focus on its utilization as an adsorbent for organic and inorganic contaminants in water and wastewater treatment technologies. The adsorption capability of BC is highly dependent on the type of pollutant, as well as the physicochemical characteristics of BC (Vasić et al., 2023; Amalina et al., 2022). The specific surface area, porous structure and abundance of surface functional groups can be considered as properties with significant impact on the adsorption capacity of BC. Depending on the type of pollutant that must be eliminated from the water matrix, specific properties of BC can be tailored by varying the pyrolysis parameters. Namely, BC produced at higher pyrolysis temperatures usually possesses a higher specific surface area and porosity which is a prominent prerequisite for the uptake of organic contaminants (Petronijević et al., 2021). Furthermore, by selecting the appropriate temperature of biomass treatment, the bulk properties of carbonized (crystalline, graphene-like fractions) and non-carbonized (non-crystalline, amorphous fractions) fractions in BC can be altered, which is another important aspect within the scope of organic pollutant elimination from wastewater (Inyang and Dickenson, 2015). On the other hand, inorganic contaminants, like heavy metals, have strong interactions with the surface functional groups of BC (mainly oxygen-containing groups) indicating that, in this case, the BC surface functionality has superior impact over other properties (Tan et al., 2015). The enhanced BC surface functionality can be achieved by lowering the pyrolysis temperature (Yaashikaa et al., 2020). Altering the type of feedstock and pyrolysis temperature can also be used to tailor the pH of BC which can range from acidic to alkaline. BC with a low pH (acidic) has the affinity to adsorb positively charged contaminants, while BC with a high pH (alkaline) may adsorb anions (Abbas et al., 2018). A net surface charge of BC is another very important parameter in wastewater treatment processes. At different pH levels, BC can have positive, negative, or neutral surface charges, allowing for selective adsorption of different pollutants. Ash content can also influence BC's adsorption properties. High ash content may reduce its porosity and surface area, but can also provide sites for adsorption of specific pollutants, such as heavy metals (T. G. Ambaye et al., 2021). Bearing in mind the current increasing trend of environmental pollution, BC can be considered as an exceptionally promising solution for addressing the remediation of various contaminants from an aqueous medium. Regardless of its quite successful utilization in this area so far, the possibility of expanding this research field still exists by further development of the methods for BC activation/modification implying that in the future special attention will be focused on fine sharpening/designing BC properties. The engineered/designer BC could be obtained after the production of BC (post-treatment methods) by modifying/improving the original properties of the pristine material. In this regard, different physical and chemical techniques can be used to tailor the physicochemical properties and enhance

the performance of BC for the uptake of various contaminants from the wastewater (Zhang et al., 2022). Physical BC engineering techniques such as ball milling modification, gas/steam activation, microwave irradiation could be efficiently utilized to adjust properties, including porosity, permeability, and functional group diversity and abundance (Li et al., 2020). Chemical methods are designed to activate pristine BC using a variety of chemicals, like strong acids, bases, and other oxidizing agents. Modifications with different acids (e.g., HCl, HNO₃, H₂SO₄, H₃PO₄) can lead to increased availability of surface carboxyl groups and other oxygen-containing functional groups, while alkali treatment (e.g., NaOH and KOH) can form more aromatic groups and other carbon-containing functional groups, optimize surface electrostatic attraction, π stacking, surface precipitation, and/or surface complexation. The surface area and pore size distribution can be tailored using different other oxidizing agents (e.g., Fe(III) and KMnO₄) (Sajjadi et al., 2019). Although many effective modification techniques have already been developed, they may also result in an unstable structure of BC, additional energy consumption, secondary pollution, and/or extra cost. Therefore, the future aspects of BC engineering towards the production of functional BC will have to consider its balanced design which will ensure practicability, sustainable development and effectiveness of this technology (Zhang et al., 2022).

Large amounts of wastewater produced and released untreated in the Republic of Serbia represent a huge environmental problem suppressing the efficient transition from a linear to circular economy model. Thus, in this sense, the application of BC could serve as an opportunity to either overcome this problem or at least come closer to a possible solution. The data related to the quality of water in Serbia from 2021 can be found in the Report of the State of the Environment in the Republic of Serbia published in 2022 (MEP-EPA, 2022). According to this report, the results of surface water quality monitoring in the period of 1998 to 2020 show that the worst situations are in the watercourses and canals of the Autonomous Province of Vojvodina. In this territory, in relation to the total number of analyzed samples, 39% belong to the "bad" and "very bad" class, while taking into account the entire territory of the Republic of Serbia, 66% of the samples from the "very bad" class originate from the Vojvodina Province. The best quality, in the "excellent" category, was recorded in small watercourses in mountainous areas in eastern, southeastern and western Serbia. The current problems related to the quality of surface water, especially in Vojvodina, are the consequence of direct disposal of various wastewaters (industrial and municipal wastewater, water from agricultural areas, etc.) into watercourses without previous treatment. The statistics that follow the field of wastewater in Serbia are not encouraging. Considering the construction of public sewage infrastructure, Serbia belongs to the group of medium developed countries, while in terms of wastewater treatment it is at quite substandard levels due to the utilization of outdated technologies. According to the Statistical Yearbook of the Republic of Serbia from 2022, about 66% of the population was connected to the public sewage system in 2020, while the percentage of

the population covered by wastewater treatment was only 15% in the same year, of which 13.8% was subjected to secondary treatment (StatOfficeRS, 2022b). The total quantity of urban wastewater in 2021 increased by 2.7% relative to 2020 of which the amount of wastewater discharged into wastewater collecting systems increased by 0.6%. The highest share of wastewater discharged into the public sewerage system in 2020 and 2021 still originates from households, followed by other users and the industrial sector (Figure 5). In 2021, the amount of secondary treated wastewater increased by 3.8% compared to 2020.

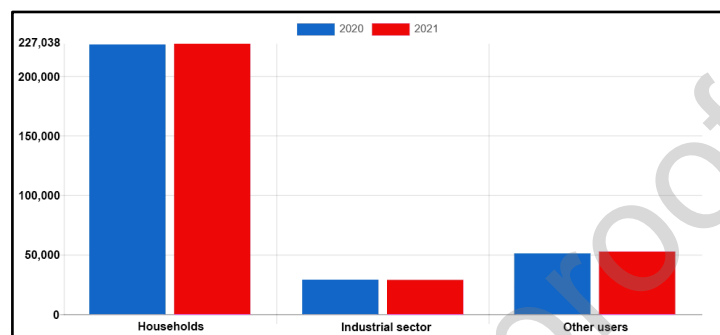


Fig. 5. Wastewater discharged in the wastewater system in the Republic of Serbia, by origin, thous. m³ (source adapted from (StatOfficeRS, 2022d))

In Serbia, 47 cities and municipalities have wastewater treatment plants, but only 26 are in operation (with 2 under construction and 5 in trial operation). Only 5 local self-government units have a facility with tertiary treatment. However, the major environmental problem is related to the absence of wastewater treatment plants in large urban centers, those being, Belgrade as the capital, Novi Sad (administrative center of the Vojvodina Province) and Niš. Consequently, municipal water from Belgrade is discharged directly into the rivers Danube and Sava, from Novi Sad into the Danube, while from Niš, it goes directly to the river Nišava. The dominant pollution of surface water in Serbia with nitrogen and phosphorus originates from municipal and industrial sources that discharge their untreated wastewater into bodies of water through sewage systems (MEP-EPA, 2022). The highest amounts of these nutrients present in industrial wastewater come from facilities within the energy sector, chemical and mineral industry, as well as public utility companies. Heavy metals are introduced into watercourses as a result of erosion and leaching of soil and rocks, but the most important sources of these pollutants come from various human activities including mining, processing or use of metals and/or substances containing traces of these metals (MEP-EPA, 2022). The content of organic matter in wastewater in Serbia is significant and is usually the result of anthropogenic activities. Besides being mostly present in household wastewater, organic matter can also occur as a result of agricultural activities, cutting down forests, and erosion from urban areas. Hospital wastewater and pharmaceutical products from households represent additional pollution. They are predominantly thrown directly into the drain, ending up in the sewage basin, and then in

rivers. The results of BC characterization presented in this study revealed that woody-based BC samples can be regarded as promising candidates for the adsorption of organic contaminants from water matrices due to their higher specific surface area and macroporosity compared to the samples obtained from agricultural residues. Additionally, according to the results of ultimate analysis, XRD, and Raman spectroscopy, these BCs possess a higher degree of crystallinity and increased aromaticity (increased content of larger aromatic systems in their matrix), which are favorable properties in terms of organic pollutant removal. On the other hand, regardless of the biomass origin, all obtained BCs display some degree of surface functionality, but in order to be potentially used for heavy metal adsorption, their surface must be enriched with oxygen-containing functional groups. In this sense, pyrolysis parameters have to be adjusted or further modifications must be performed prior to their utilization for the mentioned purpose. Since the wastewater treatment technologies in Serbia should begin to develop intensively in the future, the implementation of BC in this sector could facilitate the development of cost-effective, safe, less chemically aggressive, less energy-demanding and, above all, sustainable water treatment technology. However, the practical application of BC in this technology will require significant research conducted in the laboratory which will imitate the real requirements due to the complexity of real water samples - cohabitation of various pollutants and competitive adsorption development.

3.2.5. *BC for energy production*

The utilization of renewable bioresources for energy production in substitution of fossil fuels has gained significant attention over the last decade. Numerous studies performed so far have shown that the application of raw biomass for energy supply has several advantages, but also certain drawbacks. Due to the low price of non-woody biomass, its fuels are cheap, adding a high economic potential compared to the expensive woody biomass fuels (Đurišić-Mladenović et al., 2016). Energy production from agricultural and plant residues result in reduced air pollution along with enhanced fuel diversification, but on the other hand, the efficiency of the process is limited due to the high moisture content in biomass, smoke formation during combustion, low heating value and low energy density of biomass, etc. (Waqas et al., 2018). In this regard, the thermochemical conversion of biomass at high temperatures represents a promising way to surpass these issues, since this process provides both energy and value-added products. BC as a solid hydrophobic material is one of the value-added products that is characterized by higher calorific value compared to the biomass used for its synthesis (Tsai et al., 2012). Higher heating value obtained for some BCs is comparable or even higher than the one for good-quality coal and is closely related to the carbon content, along with the types of present volatile compounds and ash content (Kosakowski et al., 2020). Since carbon is the primary energy source during combustion or gasification, its higher content typically results in a higher energy value of BC. On the other hand, lower amount of

volatile matter and ash are prerequisites for the production of more stable, carbon-rich product that is better for long-term energy use (Ahuja et al., 2024). Other elements in BC (e.g., hydrogen, oxygen, nitrogen) also influence its energy content, combustion behavior, and emissions. High oxygen content can lower the calorific value, while nitrogen content can contribute to NO_x emissions during combustion. BC with high surface area and well-developed pore structure is also beneficial for energy production due to its higher reactivity in combustion processes induced by better interaction with gases (Zhu et al., 2024). An optimal design of BC for energy production can be achieved by tailoring its tunable properties. Except for the textural parameters that can be modified by post-treatment strategies, other parameters that dictate how BC behaves during combustion or gasification are mostly related to the type of the used feedstock and pyrolysis conditions. Although current research has showed encouraging results for BC's application for clean energy production, addressing scalability challenges in the future will be critical for revealing its full potential for the implementation in this sector globally.

Energy sector is the largest economic sector in the Republic of Serbia, and it has a significant role in Serbian economy, with a share of more than 10% in gross domestic product (GDP). The production of primary energy in Serbia mostly relies on the use of conventional fossil fuels: coal, oil, and natural gas. Oil shales represent unconventional fuels and their share in energy production is still modest as is the case with renewable energy sources. Since domestic production of energy meets only part of the primary energy needs (64.1%), Serbia belongs to countries that are dependent on energy imports (35.9%). According to the data from the Energy Balance for 2021, fossil fuels account for 85% of the total primary energy consumption, in which coal accounts for 45%, oil for 27.4%, and natural gas for 12.6%. 80% of oil needs and even 84% of natural gas needs are provided from imports. In the structure of primary energy production, coal participates with 68.5%, oil with 8%, natural gas with 3.1%, hydro potential with 7.2%, and biomass with 11.8%, while geothermal energy, solar energy, wind energy, and biogas participate with 1.4%. Crude oil and oil derivatives have the largest share in energy imports, which amount to 60%, followed by natural gas with 25%, coal with 8%, electricity with 6.6%, and biomass with less than 1% (RSGov, 2022). It can be concluded that coal is the main source of primary energy produced and consumed in the Republic of Serbia, while oil and gas are the main energy sources that are imported. Therefore, the energy sector of Serbia primarily depends on the production and import of non-renewable energy sources. Since climate change, caused by the increase in emissions from the energy sector, as well as the reduction of fossil fuel reserves, has initiated numerous measures at the global level to mitigate them, one of those measures is the increase in utilization of renewable energy sources, which is defined in the European Union's directives on Renewable Energy (2009/28/EC, 2018/2001/EC) (EU, 2018). Serbia, as a candidate for joining the EU, has obliged to implement EU principles and specific measures to support the production and use of "green"

energy. In this regard, in 2015, the National Assembly of the Republic of Serbia adopted the Energy Development Strategy until 2025, with projections until 2030 (MMERS, 2016). According to this Strategy, the development of the economy in Serbia should be based on the more efficient use of relatively clean energy. In the future, the Serbian energy system should rely more on renewable energy sources. However, the extent of substitution of imported oil and gas with domestic renewable energy sources will depend on the costs and benefits of such a transition. Namely, reorientation to renewable energy sources is possible only with extensive investments in infrastructure facilities. Based on the results in the present study, the potential of using BC samples from Serbia in the energy sector can be assessed by analyzing their graphitization and aromatization degree according to the obtained H/C and O/C ratios. All samples display remarkably low H/C ratios and relatively low O/C ratios. However, BC samples obtained by pyrolyzing beech biomass at 700°C and 800°C have the lowest H/C and O/C ratios and can be designated as the best candidates for further application as an energy source compared to other synthesized samples. Furthermore, considering the beneficial environmental aspects of BC utilization for the mentioned purpose (reduced air pollution), it can be suggested that the implementation of BC in energy technologies in Serbia should be considered extensively in the near future. However, in order to create adequate conditions for this, systematic research in this area will be crucial.

4. Conclusion

As a transition country, the Republic of Serbia is obliged to enhance the production of its energy from renewable sources to speed up the development and implementation of the circular economy model on the domestic market. In this sense, the potential applications of biochar (BC) in many sectors of Serbia's economy can boost the aforementioned process. In order to make a comprehensive analysis of BC's sustainable future application in Serbia, various biomass residues originating in Serbia were collected and the corresponding BC samples were produced by lab/industrial scale pyrolysis. After the systematic examination of physicochemical properties of the obtained chars, it can be suggested that BCs exhibited a wide range of elemental and mineralogical composition, morphology, porosity, surface functionality, aromatization degree, and polarity. Since different thermochemical treatment conditions and feedstock sources were applied to design certain BC features, it can be expected that this material will be a highly promising option for addressing various environmental concerns in Serbia in the future. Based on the current situation regarding the development of the Serbia's industrial and agricultural sector, the utilization of BC has the highest perspectives in the field of soil amendment and carbon sequestration, animal feed, anaerobic digestion processes, water and wastewater treatment, and energy production. However, prior to its implementation in real practice, economic advantages and environmental impacts must be evaluated

by the performed techno-economic and life-cycle analysis of BC. The prospective long-term exploitation of BC in Serbia will imply the mutual collaboration between material scientists, environmental scientists, chemists, technologists, economists, and social scientists. Thus, it is needed to facilitate the finding of new opportunities in the field of BC research in Serbia and to motivate the official representatives of the economy sector to consider its practical applications, consequently increasing future sustainability and embracing a zero-waste philosophy.

Disclosure statement

The authors report there are no competing interests to declare.

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All authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Highlights

- Pyrolytic biochar (BC) was produced from different biomass sources from Serbia
- Composition, structure and texture of BCs were examined by standard techniques
- Current state regarding renewable energy sources in Serbia was surveyed
- BC structure-potential sustainable application relationship was proposed for directions to sustainable future BC utilization in Serbia