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Biochar from agricultural biomass: green material as an ecological alternative to solid fossil fuels

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Abstract: The stalks left after harvesting corn, tomatoes, and tobacco have no further use and are usually burned on agricultural land. Samples of this waste were collected and pyrolyzed in this work at 400 °C for 30 min in a nitrogen atmosphere. The solid residue (biochar) obtained by pyrolysis was analyzed, and the results were compared with widely used solid fuels such as wood, coal, coke and charcoal. The heat values of biochar from tomato, tobacco, corn ZP 6263, and corn BC 398 stalks were 24.12, 23.09, 26.24, and 25.78 MJ kg⁻¹, respectively. These values are significantly higher than the heat value of wood, which is about 12.50 MJ kg⁻¹. The ash content of biochar was 12-20 %, which is consistent with the ash content of solid fuels. No heavy metals were found in biochar samples. The results show that biochar obtained from the pyrolysis of agricultural waste, such as tomatoes, tobacco and corn stalks, has good potential for use as a solid fuel.

Keywords: biochar, agricultural waste, solid fuel.

INTRODUCTION

Fossil fuel consumption has increased significantly in the last few decades, leading to environmental problems, including greenhouse gas (GHG) emissions and deterioration of air quality caused by different gaseous pollutants and fine particles. The production of carbon-neutral and low-GHG fuels from renewable sources, such as biomass, is increasingly important in gradually replacing conventional fossil fuels.¹ Although there are other renewable energy sources, such as wind, sun, geothermal and hydrothermal, biomass is still the most abundant and readily available in the world, considering that a large part comes from agriculture, which is one of the most crucial production sectors in the world, responsible for

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food manufacture.² Biomass can be defined as the biodegradable part of products, waste and residues from agriculture, forestry and related industries, as well as the biodegradable part of industrial and municipal waste. Slow pyrolysis, performed at low temperatures and low heating rates, has been practiced for many years to maximize the yield of solid char.³ Biochar is a solid carbon-rich substance produced during the thermochemical processing of various biomass. Biochar has multiple advantages and potentials as a cheap and environmentally friendly material. It can replace more expensive synthetic carbon materials for many applications in nanocomposites, energy storage, sensors, and biosensors.⁴ As a green material, biochar has attracted great interest in promoting carbon sequestration and reducing GHG emissions. It is also an additive to improve soil quality, increase crop production, and control soil and water pollution.⁵

Unfortunately, raw biomass is not an ideal energy source, and its direct use faces significant obstacles arising from its properties, such as poor grindability, high moisture content and low energy density. For example, poor grinding of biomass material caused by its fibrous structure significantly increases energy consumption and is a challenge during fuel preparation. As for the high moisture content, it lowers the maximum combustion temperature and consequently can reduce the thermal efficiency and increase the emission of pollutants. To overcome these disadvantages, a pre-treatment process is necessary to improve the quality of biomass-derived fuel.⁶ Compared to traditional fuels such as coal, natural gas and oil, biomass fuel, biochar, is a neutral, sustainable alternative with controlled pollutant emission.⁷

This paper describes the characterization of a solid product - biochar obtained by pyrolysis of tomato, tobacco and corn stalks. Despite the range of feedstocks and techniques available for biochar production, relatively few works report understanding the correlation between physical and thermochemical properties related to its potential use as a solid fuel for energy production.⁸ Corn, tobacco, and tomatoes are widely grown and used in almost all regions of Serbia and the surrounding countries. Thus, much waste is available after harvesting and fruit picking. Residual stalks are agricultural waste usually broken down by the burning process in the fields. This treatment is known to cause severe environmental pollution and destruction of agricultural land. As is well known, combustion creates problems not only by the emission of pollutants that are harmful to the environment but also those that can enter the food chain through the growth of new plants. Therefore, the goal of this work was to reuse this agricultural waste through the production of biochar in the pyrolysis process, as well as the assessment of the potential exploitation of biochar in the form of biofuel.⁵



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EXPERIMENTAL

Biomass samples

The samples used in this research were collected in the fall of 2022 in Serbia and air-dried for 30 days before use. The corn stalks collected near the town of Šabac originated from two corn hybrids: ZP 6263 and BC 398. For this research, stalks with leaves were cut approximately 5-10 cm from the ground. Tobacco stalks were collected in the area of Semberija, near the town of Bijeljina. Virginia-type tobacco stalks were cut a few centimeters above the ground. Tomato stalks, type Optima F1, were taken after picking fruits in the greenhouse near Pirot. The stems were pulled from the roots, and the roots were cut off the stalks. The stalks and leaves were cut with scissors into smaller pieces, with an average length of 10 cm. All samples were sieved so that particles of 2-5 mm size used in the experiments were obtained.

Pyrolysis process

Dry samples of agricultural waste were used for pyrolysis experiments. Pyrolysis was performed at a temperature of 400 °C for 30 min using an MTF 10/15/130 tube furnace from Carbolite, UK. Pyrolysis occurs under a constant flow of nitrogen (99.999 %) at 150 cm³ min⁻¹. The heating rate was 100 °C per minute. The pyrolysis of each sample was repeated about 20 times under the same conditions to obtain enough solid residues for analysis. Bio-oil was collected in acetone HPLC, while biochar was dispersed in acetone HPLC and then filtered, i.e. washed, before further analyses. The biochar was washed to remove the remaining liquid fraction (bio-oil) that may have remained on it.

Characterization of biomass and biochar samples

Characterization of biomass samples included determination of ash content, cellulose, hemicellulose and lignin content, heat value, elemental composition (the content of C, H, N, S) and thermogravimetric analysis (TGA). The physicochemical characterization of obtained biochar samples included similar analyses: determination of ash content, elemental analysis and heat value, ICP-OES analysis, and FTIR analysis. Ash content was determined by burning 1 g of sample in the oven at 750 °C (ASTM D2584, ASTM D5630). The method used to determine cellulose, hemicellulose, and lignin content was based on the properties of these compounds to dissolve in different solvents.⁹ Extractive substances: 1 g of biomass (B) was mixed with 60 ml of HPLC acetone at 90 °C for 2 h. After that, samples were dried in an oven at 110 °C until constant weight (E). The amount of extractive substances was calculated using Eq. 1.

$$(B - E) =$$
 amount of extractives (g) (1)

Hemicellulose content: 150 ml of sodium hydroxide solution (0.5 mol l^{-1}) was added to extractives-free biomass \in . The temperature (80 °C) was controlled using a hot plate for 3.5 h. Samples were washed with deionized water until they were free from Na⁺. Samples were dried in an oven at 110 °C until constant weight was obtained (H). The amount of hemicellulose was calculated by using Eq. 2.

$$(E - H) =$$
amount of hemicelluloses (2)

Lignin content: 30 ml of 98.99 % sulfuric acid was added to extractives-free biomass (E). Samples were left for 24 h at ambient temperature and boiled at 100 °C using a hot plate for 1 h. Samples were filtered, and the solid residue was washed using deionized water until it was free from sulfate ions. After that, samples were dried in an oven at 110 °C until constant weight was obtained (L). Value L corresponds to the amount of lignin.

Cellulose amount (C) was determined using Eq. 3.





1 g - ((B - E) + (E - H) + L) = amount of cellulose (C)

The heat value of the sample was determined using the IKA C400 instrument by standard method SRPS CEN/TS 16023:2014. Elemental analysis was performed using a CHNS/O Element Analyzer (Elementar Analysensysteme GmbH, Langenselbold, Germany). Inductively Coupled Plasma-Optical Emission spectroscopy (ICP-OES) was performed using Spectroblue TI ICP-OES instrument and method EPA M 200.7, while for sample preparation, method EPA M 3052/ISO 2598-1 was used. The thermal behavior of biomass was investigated by thermogravimetric analysis (TGA) on TA Instruments TGA Q500, Thermogravimetric Analyzer (Delaware, USA). About 10 mg of the biomass was placed into the platinum crucible, loaded into the TG furnace, and heated from 25 to 700 °C at 5 °C min⁻¹. The FTIR spectra of the biochar samples were acquired using an IRAffinity-1 spectrometer (Shimadzu, Japan). Spectra were collected in the 4000–400 cm⁻¹ spectral range, with a resolution of 4 cm⁻¹. Before analysis, the solid biochar sample was crushed, mixed with KBr and pressed into pellets.

RESULTS AND DISCUSION

Characterization of different types of biomass

Before pyrolysis, biomass samples were characterized. The aim was to determine important physico-chemical characteristics of dried samples and choose relevant conditions for the pyrolysis process. The contents of ash, extractives, hemicellulose, cellulose and lignin are shown in Table I. It is essential to note the high cellulose, hemicellulose, and lignin content in all biomass samples. Hemicellulose is the dominant component in each sample, followed by cellulose and lignin. This composition makes biomass suitable for obtaining carbon-rich materials. Regarding literature data, hemicellulose, cellulose, and lignin decompose over different temperature ranges; generally, hemicellulose decomposes at a lower temperature range (220-315 °C) than cellulose (315-400 °C), while lignin decomposes over a broad range of temperatures (150–900 °C). Compared to cellulose and hemicellulose, the breakdown of lignin is a complicated and complex phenomenon.¹⁰ It is known that a higher lignin content leads to a higher biochar yield. In contrast, a higher hemicellulose and cellulose content leads to a higher yield of liquid fraction. Our results showed that tobacco possesses the highest lignin content, while corn BC 398 has the highest hemicellulose and cellulose content. So, the highest biochar yield was expected from tobacco waste. The lowest yield was expected from corn BC 398.



TABLE I. Chemical composition (%) of biomass samples

Sample	Ash	Ext ^a	Hem ^b	Cell ^c	Lig ^d	Hem+Cell
Corn ZP 6263	4.78	6.00	45.72	28.86	19.42	74.58
Corn BC 398	4.25	4.23	48.24	34.28	13.25	82.52
Tobacco	4.66	5.53	40.00	28.90	25.57	68.90
Tomato	7.67	3.33	49.57	29.58	17.52	79.15

^aExtractives; ^bHemicellulose; ^cCellulose; ^dLignin.

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Table II shows the results of elemental analysis and heat values. These results are consistent with cellulose, hemicellulose, and lignin content. All samples showed the highest content of carbon (40.44-45.68 %), followed by hydrogen, nitrogen, and sulfur.

	composi	thon and near		Joinuss sun	ipies
Sample	С, %	Н, %	N, %	S, %	Heat value / MJ kg ⁻¹
Corn ZP 6263	45.68	6.44	0.86	0.38	17.81
Corn BC 398	44.49	6.29	3.21	0.00	18.17
Tobacco	44.41	6.19	1.03	6.60	17.14
Tomato	40.44	6.09	2.01	0.00	18.68

TABLE II. Elemental composition and heat value of biomass samples

TGA of biomass samples

Thermogravimetric analysis is crucial for characterizing biomass as a raw material for fuel production and understanding the pyrolysis process. Biomass is converted into biochar by pyrolysis in an inert atmosphere and at high temperatures. Thermogravimetric analysis of biomass samples was used to determine the optimal decomposition temperature to be used in the pyrolysis process. The TGA and dTGA curves of the biomass samples are shown in Figure 1, while the characteristic temperatures obtained from the curves can be seen in Table III. The TGA curves for the analyzed samples were very similar, which is not surprising considering that the thermal behavior of the sample depends on its chemical structure. According to literature data, lignin decomposes in the temperature range of 311.5-461.3 °C as the most stable component of biomass. Cellulose is less stable and decomposes in the 326.8-369.7 °C temperature range. As the least stable, hemicellulose decomposes in the temperature range of 223.4-332.8 °C.¹¹

TABLE III. Data obtained by thermogravimetric analysis of tobacco, tomato and corn stalks

Sample	Loss at 120 °C, %	tmax / °C	Residue at 400 °C, %	Residue at 700 °C, %
Corn ZP 6263	4.82	330	31.5	21.81
Corn BC 398	4.18	327	32.5	22.57
Tobacco	4.22	309	37.6	19.80
Tomato	2.55	320	41.5	26.72

Three phases are distinguished on each TG curve from Figure 1. The first phase refers to the evaporation of the remaining moisture in the biomass samples.¹¹ It can be noted that the first mass loss occurs at a temperature of about 120 °C and

is about 2.5 % for tomatoes and almost 5 % for corn samples. The second phase corresponds to the highest mass loss, with a peak on the dTG curve from 309 °C (tobacco) to 330 °C (corn samples). Peak maxima are marked with t_{max} and given in Table III. The second phase ends at temperatures above 400 °C, while the third phase and complete degradation ends at about 700 °C. The solid residue, i.e., biochar, is formed during the third degradation phase. The residue at 700 °C was from 9.80 % for tobacco to 26.72 % for tomato (Table III).



Fig 1. TGA curves of tobacco, tomato and corn stalks

Yield of pyrolysis products

Pyrolysis is the thermal destruction of biomass in the absence of air/oxygen, which produces valuable liquid oils, gases, and solid products. Different conditions lead to the creation of products in different proportions. Many techniques have been developed to increase yields or improve the quality of said products. Pyrolysis can be slow, fast, or flash, depending on the heating rate. Also, if necessary, it can be catalyzed. When biomass is pyrolyzed at low heating rates (5–7 K min⁻¹), a smaller proportion of liquid and gaseous products and a more significant proportion of biochar are obtained. Fast pyrolysis occurs at a heating rate of about 300 °C min⁻¹, which can be used to get a higher liquid product yield. Flash pyrolysis occurs when the reaction time is only a few seconds or less. The heating rate is very high, and this type is used to increase the yield of liquid and gaseous products.¹⁰





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In this work, pyrolysis was performed at 400 °C for 30 min. The weight of obtained biochar and bio-oil was measured after the pyrolysis process. Yields were calculated in relation to the initial weight of biomass. The yield of the gaseous fraction was calculated by subtracting the yield of biochar and bio-oil from 100 %. The yields of all products obtained by pyrolysis of corn, tobacco, and tomato stalks are given in Table IV.

The yield of biochar was around 30 %. Values ranged from 29.7 % for biochar from corn stalks BC 398 to 36.5 % from tomato stalks (Table IV). The obtained yields by pyrolysis (Table IV) were slightly lower than the solid residues obtained by thermogravimetric analysis at 400 °C (Table III). According to TGA results, the residue at 400 °C was 31.5 % for corn ZP 6263, 32.5 % for corn BC 398, 37.6 % for tobacco, and 41.5 % for tomato stalks. At 700 °C, the solid residue ranged from 19.80 % for the tobacco sample to 26.82 % for the tomato sample (Table III). The results showed that the pyrolysis temperature was adequately selected and the yield of biochar obtained by the pyrolysis process followed the expected values obtained based on TGA.

TABLE IV. Yield of bio-oil, biochar and gaseous products obtained by pyrolysis of corn, tobacco, and tomato stalks

Product yield, %	Corn ZP 6263	Corn BC 398	Tobacco	Tomato
Bio-oil	33.5	22.8	28.5	20.5
Biochar	30.6	29.7	34.3	36.5
Gas	35.8	47.6	37.2	43.0

Biochar is formed in the last step of thermal degradation of biomass. As can be seen in Figure 1, complete degradation is achieved at temperatures higher than 400 °C. Lignin, as the most stable compound, does not entirely decompose at 400 °C, so it partially remains as a solid residue. Regarding literature data, with increasing pyrolysis temperature, the yield of the solid residue decreases, and the yield of the liquid fraction increases.¹² Therefore, lower temperatures (such as 400 °C at which we conducted experiments) favor biochar production.

Characterization of biochar samples

Biochar has been characterized, and its properties are compared with solid fuels such as wood, coal, coke and charcoal. Some of the most important features are given in Table V.

The main characteristic of fuel is its ash content. The literature states that the ash content of different types of coal is 5-50 %.¹³ The ash content of biochar samples was 12–20 %, which is in accordance with literature data. The nitrogen content was low (1.49–2.61 %), corresponding to the fuel's characteristics. The content of hydrogen, an element that significantly contributes to the combustible characteristics of the fuel, was from 3.51 % in corn biochar BC 398 to 4.96 % in



corn biochar ZP 6263. The content of sulfur was below the detection limit, which can be explained by the fact that sulfur, during pyrolysis, quickly builds gaseous compounds that do not remain in solid or liquid fractions.

TABLE	V. Ash	content ar	nd elemental	composition	of	obtained	bioch	nai

Sample	Ash content, %	С, %	Н, %	N, %	S, %
Corn ZP 6263	12.84	69.62	4.96	1.64	0.00
Corn BC 398	19.12	65.08	3.51	1.76	0.00
Tobacco	16.54	60.84	4.37	1.49	0.00
Tomato	19.19	52.87	4.21	2.61	0.00

As is well known, solid fuels such as wood, coal, coke, and charcoal are widely used. Due to its composition, wood has been used as a solid fuel since the dawn of man. Wood is mainly formed from cellulose. Coal is a light brown to black sedimentary rock of organic origin that can burn. Coals are formed in swamps by the deposition and accumulating dead plant material made of cellulose, lignin, tannin, etc. During the deposition of plant material, a series of complex biochemical (diagenetic) changes occur under the influence of microorganisms. In anoxic conditions, lignite and brown coal are formed by changing organic matter under the influence of microorganisms and elevated pressure. Furthermore, due to temperature, elevated pressure, and mineral catalysts, complex geochemical (catagenetic) changes in organic matter lead to coal formation.¹³ Therefore, coal is described as a hydrocarbon fuel consisting of various substances containing carbon, hydrogen, and oxygen, as well as smaller amounts of sulfur and nitrogen.¹⁴ Coals can differ according to the origin of organic matter, degree of maturity, class, and purpose.¹⁵ The most interesting here are wet coals that contain a large amount of carbonized cellulose, lignin, and hemicellulose residues. Dark coal and hard coal are examples of wet coal.¹³ Coal can be converted into various products by processes similar or the same as pyrolysis. Pyrolysis or dry distillation processes convert dark coal into charcoal with a higher heat value. The exact process is used to obtain coke from hard coal.¹³ Carbon content is one of the main characteristics that describe the fuel properties of a compound or mixture. The carbon content of biochar from corn, tobacco, and tomato stalks was compared with the carbon content of commonly used solid fuels and presented in Figure 2.





Fig. 2. Carbon content in obtained biochars and widely used solid fuels

The carbon content ranges from about 50 % in wood to about 95 % in coke. In the biochar produced in this work, the carbon content was 52.8 % in tomato biochar, 60.84 % in tobacco biochar, 65.08 % in corn BC 398 biochar, and the highest percentage was 69.62 % in biochar from corn ZP 6268. It can be concluded that any biochar is a carbon-rich material. Therefore, its carbon content is similar to solid fuels (wood, coal, coke, and charcoal). The main characteristic we wanted to monitor and compare is the heat value of the obtained biochar samples.

There are many different types of coal with different heat values. Here, for comparing heat values, high-grade anthracite of the coal type, which has the highest carbon content and heat value of 34.9 MJ kg⁻¹, was used. The heat value of coke is 32.6 MJ kg⁻¹, and that of charcoal is 25.7 MJ kg⁻¹. Figure 3 compares the heat values of standard solid fuels¹⁶⁻¹⁸ with the biochar samples' values from this work.

Considering the results, it can be concluded that biochar produced from corn, tobacco, and tomato stalks possess a high heat value, which is between the heat value of wood and coke. The heat value of tobacco and tomato biochar is lower than coal, but biochar from both corn has a higher heat value. Therefore, these types of biochar have the potential to be used as another type of solid fuel.

ICP-OES analysis showed that each biochar contains different elements that could be interesting from other perspectives and for other uses of these materials. Table VI presents some major elements (metals, sulfur, and phosphorus) that occur in high concentrations.





TABLE VI. Most abundant elements obtained by ICP-OES analysis

		-	
⁻¹ Corn ZP 6263	Corn BC 398	Tobacco	Tomato
<100.00	<100.00	260.93	10285.00
18930.00	16654.00	74037.00	42518.00
4385.00	5440.00	3030.00	11451.00
9474.00	12949.00	25399.00	49513.00
17.65	17.48	25.00	16.85
250.80	391.46	234.88	676.01
31705.00	37198.00	5349.00	3350.00
2148.00	3250.00	3353.00	3001.00
594.42	974.03	3753.00	4336.00
	- ¹ Corn ZP 6263 <100.00 18930.00 4385.00 9474.00 17.65 250.80 31705.00 2148.00 594.42	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	$\begin{array}{c c c c c c c c c c c c c c c c c c c $



All biochar samples contain high Na, K, Ca, Mg, and S concentrations. However, biochar produced from tomatoes has the highest concentration of these elements, contributing to its promising potential for use as a fertilizer. The concentration of Cu is highest in biochar obtained from tobacco, which contributes to the basic properties of biochar. The highest concentration of Al was in biochar obtained from tomatoes. This element comes from the soil. The Si concentration is highest in BC 398 maize biochar and very similar to ZP 6263 maize biochar. In contrast, the silicon concentration is much lower in tobacco and tomato biochar. Phosphorus is the most abundant in tobacco biochar, followed by BC 398 and tomato corn biochar, and the least abundant in ZP 6263 corn biochar. Data from the literature show which elements can be found in materials obtained from agricultural biomass. The main components of wood fuel ash are Ca, K, Mg, and



Si. The amounts of other elements, such as P, S, Na, and Al, are significantly lower. Si, K, and Ca dominate in fuel from agricultural biomass, followed by elements such as Mg, S, P, Na, Al, and Fe, which occur in lower concentrations.¹⁹

It is important to emphasize that the concentrations of heavy metals were below the detection limit, which is significant for the quality of ash after combustion. The results of ICP-OES analysis showed that biochars have good potential for use as solid fuels. It is known that certain elements appear in agricultural biomass as a result of fertilization or post-harvest processing.¹⁹

The results obtained by FTIR analysis (Figure 4) showed the presence of several different functional groups.



Fig.4. FTIR spectra of biochar from corn BC 398 (a), corn ZP 6263 (b), tobacco (c), and tomato (d) stalks



The peak obtained in the region between $(3000-3700 \text{ cm}^{-1})$ corresponds to the OH stretch of water molecules of hydroxyl groups (OH) and phenols. Peaks in the 2900–3000 cm⁻¹ region correspond to aliphatic C-H stretching vibrations. These peaks can be attributed to structures formed by the thermal degradation of cellulose and hemicellulose.²⁰ At about 1600 cm⁻¹, peaks originating from vibrations of double C=C bonds were determined. Peaks at 1300–1450 cm⁻¹ are attributed to the in-plane bending of C-H bonds.²¹ In tobacco and both corn biochars, peaks at 1000–1100 cm⁻¹ are observed, corresponding to the C-O group, which may be

present in various compounds produced in degradation processes. Finally, the peaks in the 400–900 cm⁻¹ region belong to aromatic C-H stretch, -Si-O-Si-, Al-O, Al-O-Si or stretching Si-O groups.^{21,22} This is consistent with literature data and ICP-OES analysis results, which showed the presence of Al and Si.

CONCLUSION

In this work, agricultural biomass, i.e., corn, tobacco, and tomato stalks, widely available in many locations in Serbia, were used for the pyrolysis process. Biomass samples were characterized after air drying, and the results showed its promising potential for high-quality pyrolysis products. Pyrolysis was performed at a lower temperature of 400 °C, where the solid residue is the dominant product. The biochar samples' ash content and heat value indicate good fuel characteristics. The heat values of biochar, which are 23.09–26.24 MJ kg⁻¹, correspond to the heat value of charcoal. Still, it is lower than the corresponding values for coke and anthracite and much higher than the heat value of wood. The results also showed that the heat value of biochar produced from corn stalks is slightly higher than the corresponding value for coal. In comparison, the heat value of biochar from tobacco and tomato stalks is lower. The ash content of each analyzed biochar is relatively low, corresponding to good fuel characteristics. ICP-OES analysis showed high concentrations of elements such as Ca, K, Mg, Na, S, and P, while toxic elements and heavy metals were below the detection limit. This leads to the conclusion that no heavy metals will remain in the ash after combustion. The general conclusion is that biochar obtained by pyrolysis of corn, tobacco, and tomato stalks can be considered green material with a good potential for use as a solid fuel. Pyrolysis of agricultural biomass to obtain biochar is a convenient, environmentally friendly way to reduce this type of waste and get new valuable products.

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ИЗВОД

БИОУГАЉ ИЗ ПОЉОПРИВРЕДНЕ БИОМАСЕ: ЗЕЛЕНИ МАТЕРИЈАЛ КАО ЕКОЛОШКА АЛТЕРНАТИВА ЧВРСТИМ ФОСИЛНИМ ГОРИВИМА

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Стабљике које остају након жетве кукуруза и дувана, као и брања парадајза, немају даљу употребу и обично се спаљују на пољопривредном земљишту. Узорци овог отпада су прикупљени и пиролизовани у овом раду на 400 °C у атмосфери азота током 30 минута. Анализиран је чврсти остатак (биоугаљ) добијен пиролизом, а резултати су упоређени са широко коришћеним конвенционалним чврстим горивима као што су дрво, угаљ, кокс и дрвени угаљ. Калоријске вредности биоугља из стабљика парадајза, дувана, кукуруза 3П 6263 и кукуруза БЦ 398 биле су 24,12, 23,09, 26,24 и 25,78 MJ kg⁻¹. Ове вредности су знатно веће од калоријске вредности дрвета која износи око 12,50 MJ kg⁻¹. Садржај пепела у биоугљу је био 12-20 %, што је у складу са садржајем пепела код чврстих горива. У узорцима биоугља нису пронађени тешки метали. Резултати показују да биоугаљ добијен пиролизом пољопривредног отпада, као што су стабљике парадајза, дувана и кукуруза, има добар потенцијал за употребу као чврсто гориво.

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REFERENCES

- 1. S. Wang, G. Dai, H. Yang, Z. Luo, *Progress in Energy and Combustion Science* 62 (2017) 33 (https://doi.org/10.1016/j.pecs.2017.05.004)
- D. Fetjah, L. Ainlhout, B. Ihssane, A. Houari, Z. Idardare, L. Bouqbis, J. Ecol. Eng. 22 (2021) 36 (<u>https://doi.org/10.12911/22998993/133964</u>)
- S. N. Đurić, S. D. Brankov, T. R. Kosanić, M. B. Ćeranić, B. B. Nakomčić-Smaragdakis, *THERM SCI* 18 (2014) 533 (https://doi.org/10.2298/TSCI120711021D)
- 4. Z. Hu, L. Wei, J. Compos. Sci. 7 (2023) 354 (https://doi.org/10.3390/jcs7090354)
- R. Font, J. Moltó, A. Gálvez, M. D. Rey, J. Anal. App. Pyrol. 85 (2009) 268 (<u>https://doi.org/10.1016/j.jaap.2008.11.026</u>)
- 6. Z. Liu, G. Han, Fuel 158 (2015) 159 (https://doi.org/10.1016/j.fuel.2015.05.032)
- 7. B. Song, P. Hall, *Front. Energy Res.* 8 (2020) (https://doi.org/10.3389/fenrg.2020.00058
- W. A. Wan Ab Karim Ghani, P. S. Fernandez, M. Q. Halele, S. Sobri, J. Jasni, MATEC Web of Conf. 62 (2016) 04003 (https://doi.org/10.1051/matecconf/20166204003)
- M. A. Maisyarah, L. J. Shiun, A. F. Nasir, H. Haslenda, H. W. Shin, *Chem. Eng. Trans.* 72 (2019) 79 (<u>https://doi.org/10.3303/CET1972014</u>)
- 10. H. B. Goyal, D. Seal, R. C. Saxena, *Ren. Sust. Energy Rev.* **12** (2008) 504 (https://doi.org/10.1016/j.rser.2006.07.014)
- D. Chen, K. Cen, X. Zhuang, Z. Gan, J. Zhou, Y. Zhang, H. Zhang, *Comb. Flame* 242 (2022) 112142 (<u>https://doi.org/10.1016/j.combustflame.2022.112142</u>)
- 12. X. He, Z. Liu, W. Niu, L. Yang, T. Zhou, D. Qin, Z. Niu, Q. Yuan, *Energy* **143** (2018) 746 (<u>https://doi.org/10.1016/j.energy.2017.11.062</u>)
- 13. I. Kojic, Study of synergetic effect of co-pyrolysis of lignite and high density polyethylene in an open system petrographic and geochemical approach, *PhD thesis* (in Serbian), 2022 (<u>https://phaidrabg.bg.ac.rs/view/o:25866</u>)
- 14. R. Arisanti, STI 3 (2018) 100 (https://doi.org/10.26554/sti.2018.3.2.100-106)
- P. I. Premović, R. S. Nikolić, M. P. Premović, *Geological Society, London, Special Publications* 125 (1997) 201 (<u>https://doi.org/10.1144/GSL.SP.1997.125.01.16</u>)





- 17. I. V. Miroshnichenko, D. V. Miroshnichenko, I. V. Shulga, Y. S. Balaeva, V. V. Pereima, *Coke Chem.* 62 (2019) 143 (<u>https://doi.org/10.3103/S1068364X19040057</u>)
- A. O. Otieno, P. G. Home, J. M. Raude, S. I. Murunga, A. Gachanja, *Heliyon* 8 (2022) e10272 (<u>https://doi.org/10.1016/j.heliyon.2022.e10272</u>)
- 19. M. Praspaliauskas, N. Pedišius, D. Čepauskienė, M. Valantinavičius, *Biomass Conv. Bioref.* **10** (2019) 937 (https://doi.org/10.1007/s13399-019-00457-7)
- C. Hadey, M. Allouch, M. Alami, F. Boukhlifi, I. Loulidi, *The Sci. World J.* 2022 (2022) 2554475 (<u>https://doi.org/10.1155/2022/2554475</u>)
- A. Supriya, R. Samantray, S. C. Mishra, *IOP Conf. Ser.: Mater. Sci. Eng.* 178 (2017) 012022 (<u>https://doi.org/10.1088/1757-899X/178/1/012022</u>)
- H. Huang, N. G. Reddy, X. Huang, P. Chen, P. Wang, Y. Zhang, Y. Huang, P. Lin, A. Garg, Sci Rep. 11 (2021) 7419 (<u>https://doi.org/10.1038/s41598-021-86701-5</u>).