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Estimation of the Biochar Effect on Annual Energy Crops Grown in Post-Mining Lands

Mykola Kharytonov[1], Irina Klimkina[2], Nadiia Martynova[3], Irina Rula[1] Maria Gispert[4], Giovanni Pardini[4]

[1] Dnipro State Agrarian and Economics University, Dnipro, 49600, Ukraine
[2] Dnipro University of Technology, Dnipro, 49005, Ukraine
[3] Oles Honchar Dnipro National University, Dnipro, 49010, Ukraine
[4] Girona University Girona, 17003, Spain
* Corresponding author's email: kharytonov.m.m@dsau.dp.ua

ABSTRACT
The ability of biochar as a soil additive to influence productivity, accumulation of heavy metals and thermal characteristics of energy crops was studied. Maize, Sudan grass and Sweet sorghum were grown in containers with low humus black soil and red-brown clay. It turned out that the addition of biochar improves seed germination from 1.5% to 15% and promotes an increase in the growth of aboveground biomass and roots. For Maize and Sweet sorghum plants, the most pronounced effect is revealed on red-brown clay, and for Sudan grass on black soil. Biochar indirectly affects the intensity of accumulation of heavy metals by reducing their mobility and availability to plants. In both variants of the experiment with Maize, the application of biochar had the greatest effect on the accumulation of zinc. In the experiment with Sudan grass on black soil, the greatest effect was observed for manganese, and on red-brown clay for zinc and lead. In the experiment with sugar sorghum, the most pronounced reaction took place for copper on both substrates, and for zinc only on red-brown clay. The biochar addition led to the more complete combustion of the Sweet sorghum biomass grown on black soil and, conversely, increasing the ash content of the biomass grown on red-brown clay. During the combustion of Sudan grass biomass in the trial with red-brown clay, the addition of biochar contributed to the significant reduction in thermolysis duration and shifting of the extremum point of cellulose decomposition to the area of lower temperatures. In the case of Maize biomass, a similar effect was observed, but only in the trial with black soil.

Keywords: biochar, post-mining lands, energy crops, pollution, thermolisys.

INTRODUCTION

Active human activity contributes to the rapid increase in the number of unproductive lands characterized by low fertility, high degree of erosion, high acidity or alkalinity, salinity, as well as pollution with heavy metals and other toxic elements [Toy and Hadley 1987, Strijker 2005, Navarro et al. 2007, Papadopoulos et al. 2015]. As a rule, such soils are not suitable for growing agricultural plants. Therefore, technologically disturbed lands are increasingly considered as potential areas for growing energy crops [Gopalakrishnan et al. 2011, Nalepa and Bauer 2012, Kang et al. 2013, Blanco-Canqui 2016]. There is ample evidence of successful cultivation of various energy plants on marginal lands [Zhuang et al. 2011, Stoof et al., 2015, Feng et al. 2017, Mehmood et al. 2017]. However, there is a problem of obtaining stable economically profitable yields in these territories. One of the ways to solve this task is to use various soil amendments that increase productivity and reduce soil toxicity. Soil amendments must have a high binding capacity and be safe for the environment and not adversely affect soil structure, soil fertility or ecosystem. Biochar produced from carbonization of organic wastes can be considered as an alternative additive, which may not only affect carbon sequestration of soil, but also change its physicochemical and biological properties [Chan et al. 2007, Lehmann and Joseph 2009, Ibrahim et al. 2013, Masek et al. 2013]. Effects of biochar on soil chemical properties and soil biota are being actively studied. Soil amendment with biochar is evaluated as a means to improve soil fertility. [Lechman et al. 2011]. Biochar addition helps to reduce soil density, increase water retention capacity, hydraulic conductivity [Verheijen et al. 2009, Laghari et al. 2015]. There are various data on the impact of biochar on productivity. Depending on the growing conditions, application methods and composition of biochar, yields can increase, remain unchanged, or even decrease [Spokas et al. 2012, Schulz et al. 2013, Gang et al. 2016, Wang et al. 2019]. In a review of various publications provided by Ippolito et al. [2012], it is assumed that reactions with negative or neutral yield may result from low doses of nitrogen addition or immobilization due to the use of low-temperature biochar. Biochars, obtained at low pyrolysis temperatures, consists mainly of aliphatic and cellulose structures. They are good substrates for bacteria and fungi, which mineralize them, utilizing waste organic matter in this way. As the pyrolysis temperature increases, the ash content in the biochar usually increases due to its thermal stability, while the ratios of carbon, hydrogen, oxygen and nitrogen become lower [Chaiwong et al. 2013, Jin and Wang 2017]. It is believed that high temperature biochar is preferred for carbon sequestration. So it is characterized by a high surface area and microporosity, while at low temperatures a biochar with a low adsorption capacity is formed [Day et al. 2005, Brown et al. 2006]. The raw materials from which biochar is produced also determine its properties. For example, when producing biochar from organic waste with high potassium content, the product will contain more potassium than biochar made entirely from wood [Chan et al. 2008, Sohi et al. 2010, Ren et al. 2016]. Many technologically disturbed lands, especially after mining, are contaminated with heavy metals. It was found that heavy metals inhibit the growth and development of plants, adversely affect numerous structural and functional changes in the photosynthetic apparatus, disrupt the processes of respiration, transpiration, transport of substances etc [Prasad 2004, Meharg 2005, Clemens 2006, Hassa and Aarts 2011, Shahid et al.2017]. The total content of heavy metals in soils may not reflect their phytotoxicity and plant availability. Phytoavailability is a readily available form of a heavy metal that is absorbed by plants. It is very important to reduce the availability of heavy metals for plants in contaminated soils. The issue of using environmentally friendly natural compounds for detoxification of contaminated soils is becoming more and more significant. According to many studies, biochar can reduce the concentration of heavy metals in plant shoots, depending on the application rate, soil type and kind of metal, from 17% up to 60% [Al-Wabel et al. 2015, Kim et al. 2015, Chen et al. 2018, Wang et al. 2020]. Thus, the raw material for the production of biochar, the manufacturing technology, as well as the application doses determine the nature of the effect of biochar on the soil and plants growing on it. However, despite the large number of publications devoted to biochar, many issues related to its use still need to be studied.

The main objective of this study was to estimate the biochar effect on annual energy crops grown in post-mining lands.

MATERIALS AND METHODS

A model experiment was performed. Three energy annual crops (Maize, Sudan grass and Sweet sorghum) were grown in the vegetation containers with two types of post-mining soils: low humus black soil (BS) and red-brown clay (RBC). The soil samples were collected in two sites from the Western Donbass coal mining region in the southeastern part of Ukraine. The basis of the reclamation sites was formed by a mining rocks (MR) as 10 m layer covered with various capacities of black soil or rock substrate (red brown clay).Mining rocks consist of three main components as argillite, aleurolite and piryte. Main source of harmful chemical influence is pyrite turn into iron sulfate and sulfuric acid after oxidation [Kharytonov and Kroik 2011]. First site is famous now as the Pavlograd land reclamation station located in Western Donbass (eastern Ukraine) nearly mine “Pavlogradska” (coordinates 48°33’24” N, 35°58’46” E). The station was founded in 1976 in the floodplain of the Samara River in order to examine the several artificial profiles i.e. MR + 50 cm BS [Klimkina et al 2018]. Second site made in 2005 at the distance 1 km from first one follow one soil artificial profile: mining rock +50 cm red brown clay.

Soil and rock samples were collected from the topsoil layer (0-20 cm), mixed thoroughly, air-dried and sieved through a 2-mm diameter stainless steel screen. Soil pH and electrical conductivity (EC) were measured using a soil-to-water ratio of 1:1. pH and EC distribution in two land reclamation profiles are shown in Figures 1 and 2. The differences in pH and EC profile distribution between two profiles cause with mining rocks negative impact in space and time.

The soil samples were treated with 0.0 and 3.0% (w/w) biochar. The biochar applied in this study was produced by pyrolysis of nutshell. The substrata samples (0.5 kg) of untreated and treated black soil and red-brown clay with nutshell biochar were placed in pots. Five seeds of Maize, Sudan grass and Sweet sorghum were planted in the each pot and then thinned to 3 plants after germination. All pots were adjusted daily to water content of 75% field capacity (FC) by weight.

Germinating ability and growth parameters were studied by biometric methods. The content of heavy metals in above-ground biomass was determined. After 45 days from planting, shoots of Maize, Sudan grass and Sweet sorghum plants were cut at the soil surface and washed with distilled water.

Shoots and roots were oven-dried and weighed for dry matter yield. Shoots biomass was weighing 2 g each, combusted in a muffle furnace at 450°C by means of drying method and then dissolved in 5 ml of 6N spectral purity hydrochloric acid. The ash digestives were analyzed for Fe, Mn, Zn, Cu and Pb by Varian Cary-50. The received data represented the arithmetic means of three replicates of each sample, their ranges and standard deviations values. The thermal characteristics of crops biomass were studied by thermogravimetric analysis. The analysis was performed using the derivatograph Q-1500D of the "F. Paulik-J. Paulik-L. Erdey" system. Differential mass loss and heating effects were recorded. The results of the measurements were processed with the software package supplied with the device.

Samples of biomass were analyzed dynamically at a heating rate of 10 °C/min in an air atmosphere. The mass of samples was 100 mg. The reference substance was aluminum oxide.

RESULTS AND DISCUSSION

The effect of biochar application on morphometric indicators

The addition of biochar into substrates had a positive impact on seed germination. The best

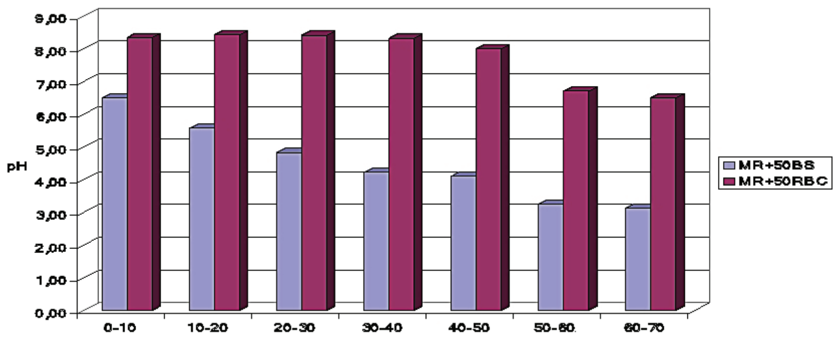

Figure 1. pH distribution in two artificial profiles

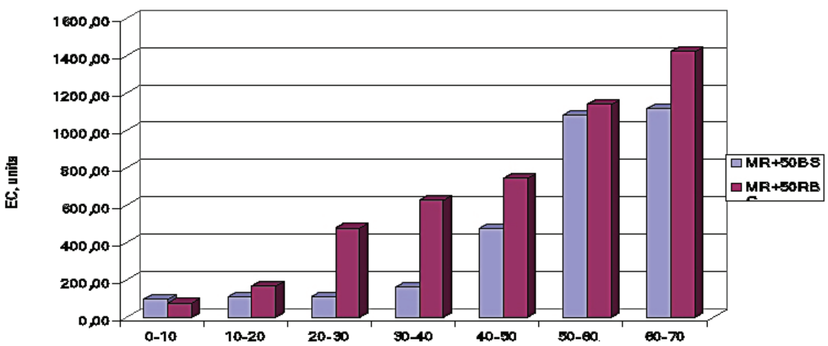

Figure 2. Electrical conductivity distribution in two artificial profiles

result was observed on red-brown clay. Among the studied plants, the greatest effect was noted for Maize and Sweet sorghum. Germination improved by 8–15% (Fig. 3). At the same time, differences in germination of Sudan grass were insignificant.

An increase in growth occurred when biochar was added to substrates with Maize. Height of Sudan grass seedlings was 13% higher in variant BS+biochar and 30% lower in variant RBC+biochar. Sweet sorghum seedlings, on the contrary, were lower in option BS+biochar and slightly higher in option RBS+biochar (Fig. 4).

Despite some effect that inhibits the vertical growth of the studied plants, the addition of a biochar contributed to an increase in the aboveground and root biomass (Fig. 5). The most pronounced effect was observed on red-brown clay for Sweet sorghum plants. For Sudan grass, a significant increase in biomass was noted only on black soil – 36–48%, while on red-brown clay it amounted to only 4–9%. The increase in Maize biomass did not exceed 10% on black soil and 30% on red-brown clay.

It was revealed that under the influence of a biochar, the ratio of aboveground and underground biomass decreases (Fig. 6). This suggests that the adding of biochar in substrates affects to a greater extent the growth of root biomass than aboveground.

The effect of biochar application on heavy metal accumulation

Among the studied energy crops, maize has the lowest ability to accumulate heavy metals (Table 1). The only exception was manganese, whose content in the biomass of the Sudan grass was slightly lower. Sweet sorghum was an active accumulator of manganese and copper on both substrates and lead on black soil. At the same time, Sudan grass intensively accumulated iron on both substrates, zinc on black soil and lead on red-brown clay (Table 2).

During experiment, it was realized that biochar contributes to reduce the heavy metal content in plant biomass. However, the plants reacted differently to the introduction of biochar. In Maize grown on black soil, the accumulation of heavy metals decreased by an average of 13-24.5% (Fig. 7). The greatest effect was observed for zinc (42.7%). No effect on iron uptake was noted. In biomass grown

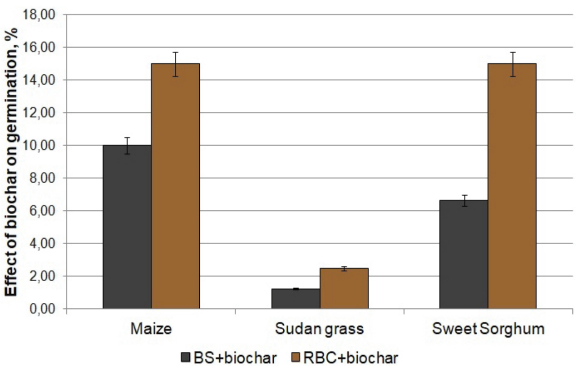

Figure 3. The effect of biochar on seed germination

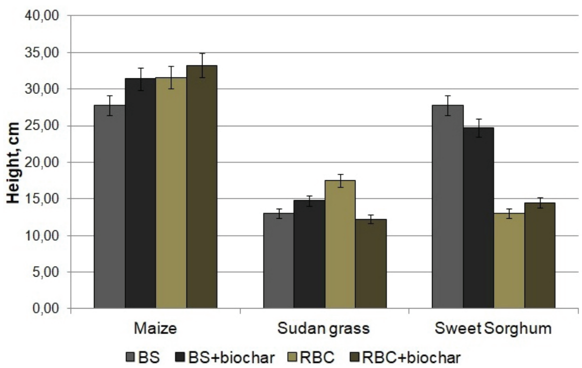

Figure 4. Height of studied plants

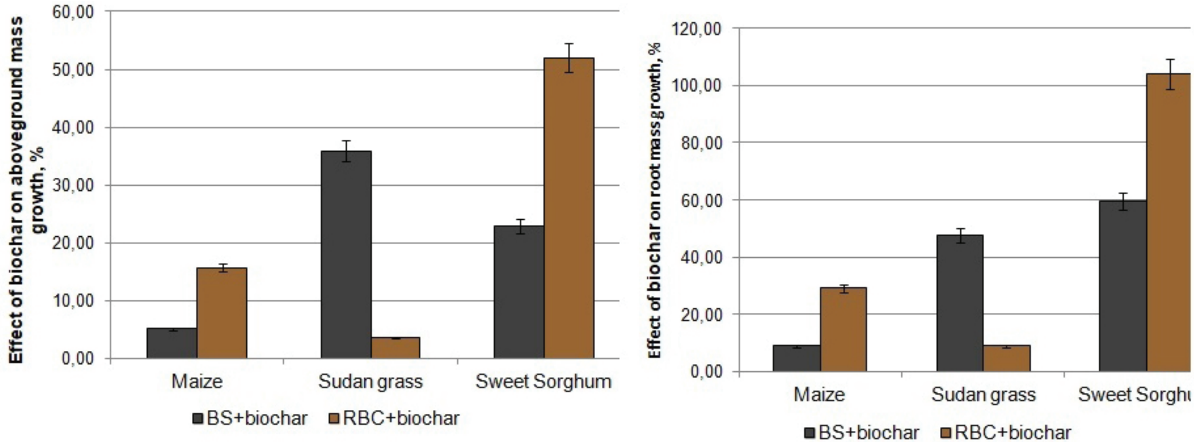

Figure 5. The effect of biochar on aboveground and root biomass growth, %

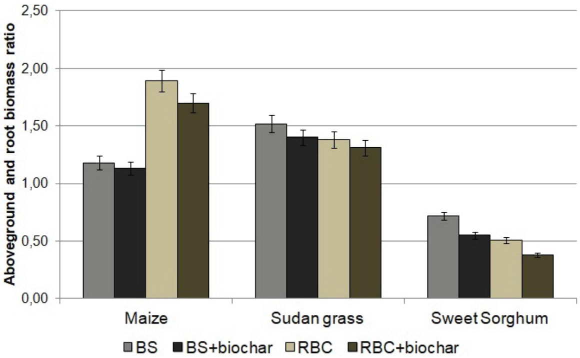

Figure 6. Aboveground biomass/root biomass ratio

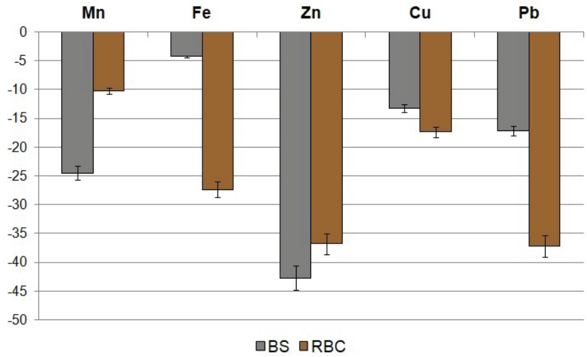

Figure 7. The effect of biochar on the heavy metal accumulation by Maize biomass, %

Table 1. Heavy metal accumulation by energy crops

Crops	Experiment options	Heavy metal content, mg/g				
		Mn	Fe	Zn	Cu	Pb
Maize	BS	152.3±0.48	431.2±1.07	37.5±0.24	7.5±0.10	15.1±0.11
	BS+biochar	115.0±0.90	412.5±0.75	21.5±0.15	6.5±0.07	12.5±0.10
	RBC	166.7±0.72	460.5±1.27	37.8±0.30	11.5±0.14	32.5±0.15
	RBC+biochar	149.7±0.54	334.4±0.84	23.9±0.12	9.5±0.12	20.4±0.16
Sudan grass	BS	143.3±0.44	750.0±1.19	51.3±0.26	7.7±0.10	22.7±0.16
	BS+biochar	98.3±0.32	560.0±0.93	37.7±0.23	6.7±0.08	18.3±0.14
	RBC	89.3±0.44	1032.0±1.49	61.4±0.35	20.2±0.16	42.0±0.22
	RBC+biochar	82.1±0.49	889.3±1.61	38.2±0.14	16.7±0.12	29.0±0.15
Sweet sorghum	BS	212.5±0.40	708.3±1.16	49.6±0.39	25.4±0.18	32.1±0.17
	BS+biochar	189.6±0.64	615.4±1.34	45.0±0.18	14.2±0.15	29.2±0.15
	RBC	182.1±0.47	991.7±0.88	62.5±0.26	30.4±0.21	35.0±0.18
	RBC+biochar	164.2±0.36	766.7±0.69	41.7±0.18	17.5±0.15	33.3±0.17

Table 2. Distribution of energy crops according to the level of heavy metals accumulation (from smallest to largest)

Element	BS	RBC
Mn	Sudan grass →Maize →Sweet sorghum	Sudan grass →Maize →Sweet sorghum
Fe	Maize → Sweet sorghum →Sudan grass	Maize →Sweet sorghum →Sudan grass
Zn	Maize →Sweet sorghum →Sudan grass	Maize →Sudan grass →Sweet sorghum
Cu	Maize →Sudan grass →Sweet sorghum	Maize →Sudan grass →Sweet sorghum
Pb	Maize →Sudan grass →Sweet sorghum	Maize →Sweet sorghum →Sudan grass

on red-brown clay, the addition of biochar had the greatest effect on the accumulation of zinc and lead, decreasing their content by 36.8% and 37.2%, respectively. The iron content decreased by 27.4%, copper by 17.4%, manganese by 10.2%.

In Sudan grass grown on black soil, the intensity of manganese accumulation has decreased more than other metals (by 31.4%). At the same time, this effect was not observed on red-brown clay (Fig. 8). The content of iron and copper also decreased slightly, by 13.8% and 17.3%, respectively. The greatest effect was noted for lead (30.9%) and zinc (37.8%).

In the experiment with Sweet sorghum, the greatest effect from the biochar addition was observed for copper (Fig. 9). The accumulation of this metal on black soil decreased by 44.1% and on red-brown clay by 42.4%. Also, on this substrate, a significant decrease in the zinc content (33.3%) was noted, while on black soil, the data obtained on the site without the addition of biochar and with the addition of biochar did not practically differ. Also, the addition of biochar had a very insignificant effect (from 5% to 11%) on the accumulation of manganese and lead on both substrates.

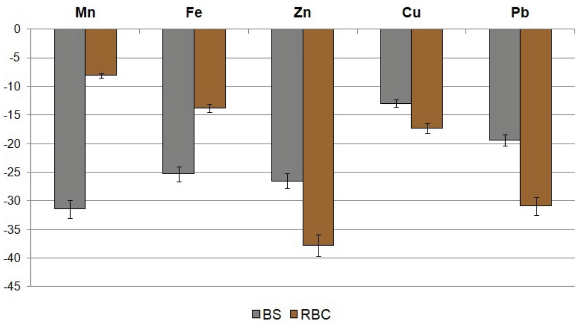

Figure 8. The effect of biochar on the heavy metal accumulation by Sudan grass biomass, %

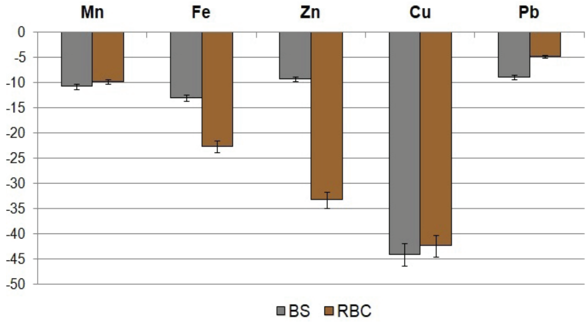

Figure 9. The effect of biochar on the heavy metal accumulation by Sweet sorghum biomass, %

Effect of biochar application on the thermal characteristics of biomass

Thermal destruction of the biomass of three studied species has been occurred in two stages: the evaporation of water and volatile compounds (stage 1) and the decomposition of the main components: hemicellulose, cellulose and lignin (stage 2).

The first stage has taken place in a temperature range of 50-180°C. The process was slow, the maximum speed was not exceeded 5-8%/min, the extreme point was observed at a temperature of 100-110°C. The weight loss has been insignificant, namely 4.5–7.5%.

The second stage has been divided into two phases: decomposition of holocellulose with beginning of lignin decomposition (phase 1), and termination of lignin decomposition and formation of an incombustible residue (phase 2).

The destruction of holocellulose was occurred in the temperature range of 190-390 °C. Due to the large amount of hemicellulose in the biomass of studied plants, its decomposition was shifted into the region of higher temperatures. Therefore, the ranges of destruction of hemicellulose and cellulose were overlapped, and only one extreme point was observed on the DTG curves. The process proceeded at high speeds with the peak of destruction in the temperature range of 280-310 °C. The weight loss was also the most significant and ranged from 50 to 55%.

Lignin decomposition proceeded rather slowly, with one minor peak in the temperature range of 420-440°C. The weight loss was established as 26-30%. At the first stage, the process proceeded predominantly with heat absorption; the reactions of the second stage were exothermic with noticeable thermal effects in the areas of cellulose and lignin decomposition (Fig. 10).

There were observed the differences in the thermal characteristics of biomass grown on different substrates and with biochar addition. The destruction of holocellulose was slower in Sweet sorghum biomass taken from the site with red-brown clay in contrast to lignin, which degraded faster than in trial with black soil. In addition, the proportion of incombustible residue was almost 2 times less (Table 3). The duration of thermolysis decreased in the trial with black soil after biochar adding. There were observed the slight increase in the reaction rate for cellulose decomposition (by 1.2 times) and significant increase for lignin destruction (by 5 times). Besides, the extremum point of lignin destruction was shifted to the area of higher temperatures. Moreover, in the trial with biochar, more complete biomass combustion was observed (Fig. 11 on the left).

On the plot with red-brown clay, the biochar addition contributed to the increase in thermal stability of biomass, especially at the initial stages of destruction. The cellulose degradation rate became slightly higher, although the lignin degradation proceeded at slower rate (Fig. 11 on the right). In addition, the part of incombustible residue increased 1.8 times. Combustion of Sudan grass biomass on both substrates proceeded in a similar manner. However, in the variant with red-brown clay, the extremum point of cellulose decomposition was shifted to the region with higher temperatures, the lignin decomposition proceeded slightly faster, and the proportion of incombustible residue was 1.3 times less (Table 4).

The biochar addition did not reveal any significant deviations in the thermal behavior of the biomass grown on black soil (Fig. 12 on the left). In the trial with red-brown clay, the biochar addition contributed to the significant

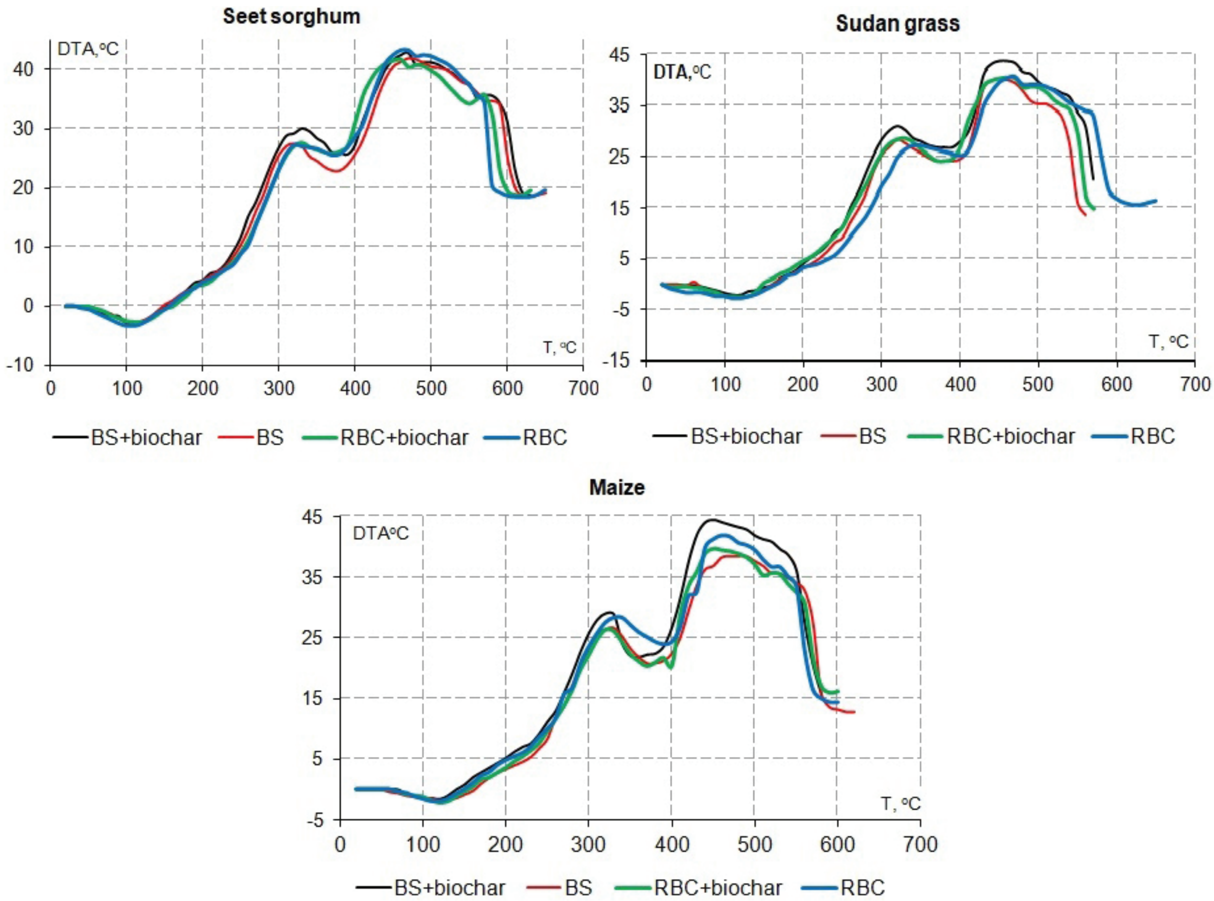

Figure 10. DTA curves of Sweet sorghum, Sudan grass and Maize thermolysis

Table 3. Thermal characteristics of Sweet sorghum biomass decomposition

Stage	Black soil				Black soil + biochar			
	Interval, °C	Extremum point, °C	Maximum rate, %/min	Weight loss, %	Interval, °C	Extremum point, °C	Maximum rate, %/min	Weight loss, %
I	50–160	100	7.4	5.8	40–150	100	8.0	5.71
II	160–400	290	24.4	52.92	150–400	290	27.6	54.27
III	400–630	420	1.2	25.78	400–600	440	6.4	28.96
Part of residual mass, %				15.64	Part of residual mass, %			11.06
Activation energy, kJ/mol		Initial		68.29	Activation energy, kJ/mol	Initial		63.33
		Main components		49.58		Main components		47.56
Stage	Red-brown clay				Red-brown clay + biochar			
	Interval, °C	Extremum point, °C	Maximum rate, %/min	Weight loss, %	Interval, °C	Extremum point, °C	Maximum rate, %/min	Weight loss, %
I	60–170	100	6.4	7.42	60–160	100	6.4	5.66
II	170–400	290	21.4	53.97	160–400	290	24.4	52.92
III	400–580	430	2.0	30.07	400–580	420	1.2	25.78
Part of residual mass, %				8.54	Part of residual mass, %			15.64
Activation energy, kJ/mol		Initial		36.77	Activation energy, kJ/mol	Initial		65.07
		Main components		49.43		Main components		51.55

reduction in the thermolysis duration, as well as, shifting in the extremum point of cellulose decomposition to the area with lower temperatures (Fig. 12 on the right).

The first stage of Maize biomass thermolysis was slightly shorter in the trial with black soil in comparison with red-brawn clay and was accompanied by less weight loss (Table 5).

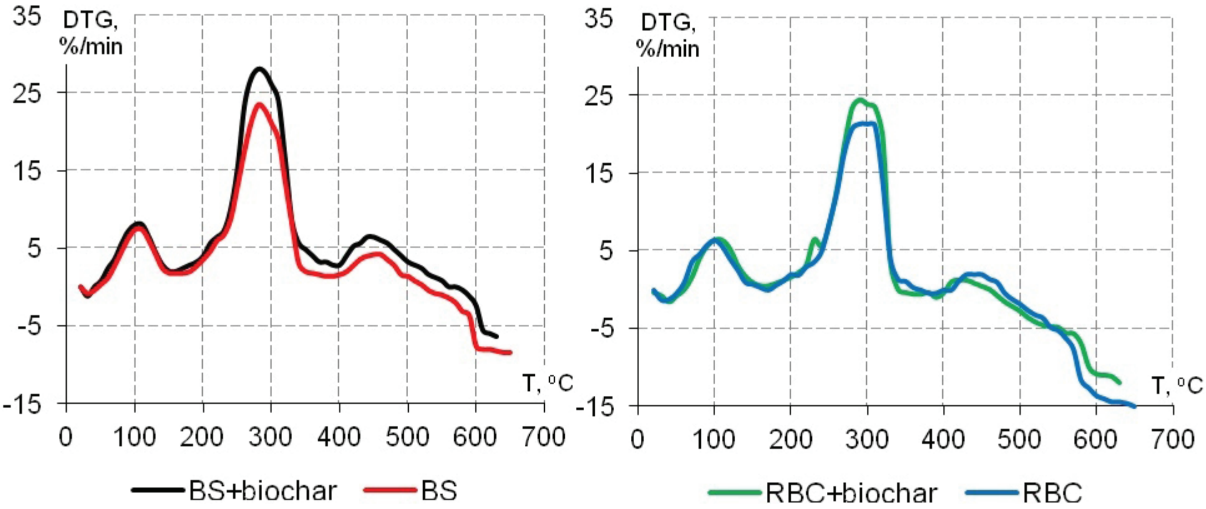

Figure 11. DTG curves of Sweet sorghum thermolysis

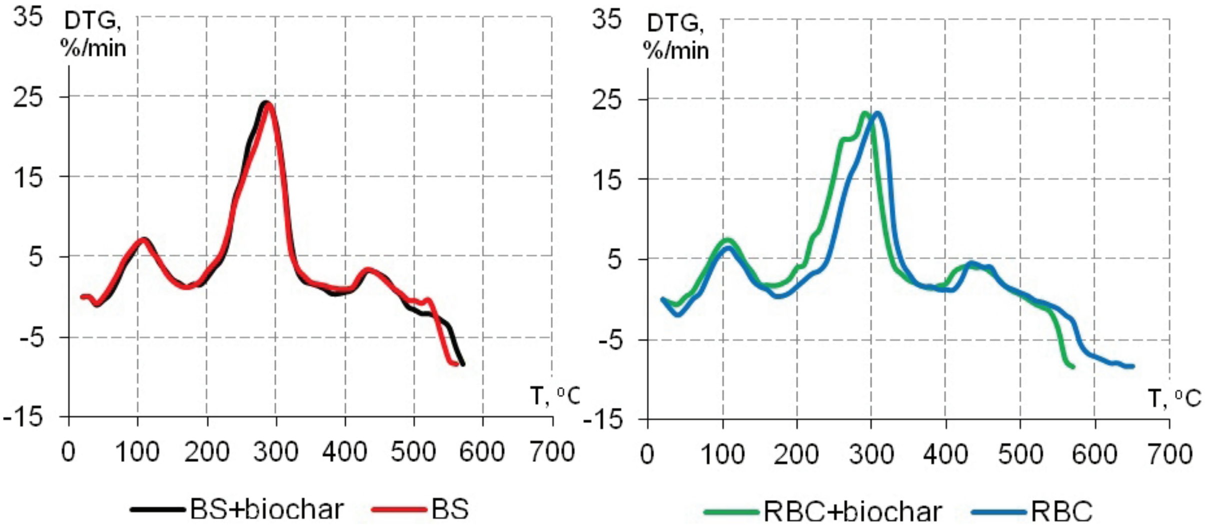

Figure 12. DTG curves of Sudan grass thermolysis

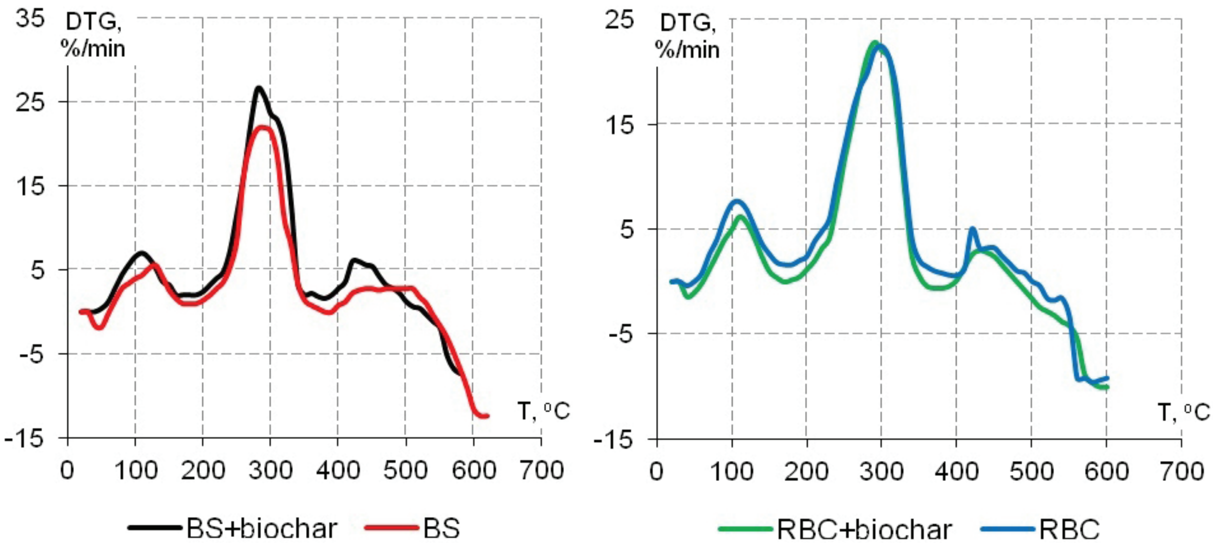

Figure 13. DTG curves of maize thermolysis

Table 4. Thermal characteristics of Sudan grass biomass decomposition

Stage	Black soil				Black soil + biochar			
	Interval, °C	Extremum point, °C	Maximum rate, %/min	Weight loss, %	Interval, °C	Extremum point, °C	Maximum rate, %/min	Weight loss, %
I	60–170	110	7.0	5.86	60–170	110	7.2	5.0
II	170–390	290	24.0	51.91	170–390	280	24.0	54.0
III	390–550	430	3.4	26.26	390–570	430	3.2	26.2
Part of residual mass, %				15.97	Part of residual mass, %			14.8
Activation energy, kJ/mol		Initial		68.74	Activation energy, kJ/mol	Initial		68.61
		Main components		46.88		Main components		49.76
Stage	Red-brown clay				Red-brown clay + biochar			
	Interval, °C	Extremum point, °C	Maximum rate, %/min	Weight loss, %	Interval, °C	Extremum point, °C	Maximum rate, %/min	Weight loss, %
I	60–180	110	6.4	6.87	50–170	110	7.4	6.53
II	180–400	310	23.2	52.11	170–380	290	23.28	53.24
III	400–640	430	4.4	28.69	380–570	430	4.2	27.54
Part of residual mass, %				12.33	Part of residual mass, %			12.69
Activation energy, kJ/mol		Initial		51.02	Activation energy, kJ/mol	Initial		63.50
		Main components		46.95		Main components		45.23

Table 5. Thermal decomposition of Maize biomass

Stage	Black soil				Black soil + biochar			
	Interval, °C	Extremum point, °C	Maximum rate, %/min	Weight loss, %	Interval, °C	Extremum point, °C	Maximum rate, %/min	Weight loss, %
I	70–180	130	5.6	4.4	50–180	110	7.0	5.2
II	180–390	290	22.0	50.0	180–380	280	26.6	51.6
III	390–600	440	2.8	26.0	380–560	420	6.0	28.6
Part of residual mass, %				19.6	Part of residual mass, %			14.6
Activation energy, kJ/mol		Initial		40.79	Activation energy, kJ/mol	Initial		87.48
		Main components		55.81		Main components		52.39
Stage	Red-brown clay				Red-brown clay + biochar			
	Interval, °C	Extremum point, °C	Maximum rate, %/min	Weight loss, %	Interval, °C	Extremum point, °C	Maximum rate, %/min	Weight loss, %
I	60–180	110	7.6	6.8	70–170	110	6.2	6.2
II	180–400	300	22.4	55.0	170–380	290	22.8	50.0
III	400–590	420	5.0	27.0	380–590	430	3.0	29.6
Part of residual mass, %				11.2	Part of residual mass, %			14.2
Activation energy, kJ/mol		Initial		61.67	Activation energy, kJ/mol	Initial		100.0
		Main components		43.45		Main components		49.68

The same tendency was observed during the decomposition of holocellulose. At the same time, the lignin destruction in variant with black soil lasted longer, the extremum point was shifted to the region of higher temperatures, the process rate was almost two times lower than in variant with clay, and the proportion of incombustible residue was 1.7 times higher.

It was revealed that application of biochar as addition to black soil promoted an increase in the rate of holocellulose and lignin decomposition and a shifting of the extremum points towards the area with lower temperatures (Fig. 13 on the left). A more complete combustion of biomass was also observed in the variant with biochar. In the variant with red-brown clay, the application of biochar had a less noticeable effect compared to black soil (Fig. 13 on the right). The nature of the thermolysis stages changed insignificantly.

An increase in the thermal stability of biomass was observed at the initial stages of decomposition by 2.1 times (black soil) and 1.6 times (red-brawn clay) on both substrates with biochar.

CONCLUSIONS

The addition of biochar slightly improves the seed germination of Sudan grass – from 1.5% to 2.5%. For Maize and Sweet sorghum, this index is higher, from 7% to 15%. Under the influence of the biochar, the growth of both aboveground and root biomass also increases. For Maize and Sweet sorghum plants, the most pronounced effect is revealed on red-brown clay, and for Sudan grass on black soil.

The studied plants are not hyperaccumulators of heavy metals. However, among the researched species, Maize has the lowest absorption capacity. Biochar indirectly affects the intensity of accumulation of heavy metals by reducing their mobility and availability to plants. The type of substrate and the species of plant also matter. In both variants of the experiment with Maize, the application of biochar had the greatest effect on the accumulation of zinc. In the experiment with Sudan grass on black soil, the greatest effect was observed for manganese, and on red-brown clay for zinc and lead. In the experiment with sugar sorghum, the most pronounced reaction took place for copper on both substrates, and for zinc only on red-brown clay.

The specific characteristics of substrates may affect the thermal characteristics of the biomass of annual energy crops. The biochar addition led to the more complete combustion of the Sweet sorghum biomass grown on black soil and, conversely, increasing the ash content of the fuel grown on red-brown clay. During the combustion of Sudan grass biomass in the trial with red-brown clay, the addition of biochar contributed to the significant reduction in thermolysis duration and shifting of the extremum point of cellulose decomposition to the area of lower temperatures. In the case of Maize biomass, a similar effect was observed, but only in the trial with black soil.

Changes in the thermal behavior of biomass of the studied species may be associated with changes in the composition of extracted substances. The extracted substances are the most sensitive to the environmental influence, and in turn, may have a significant effect on the thermal characteristics of the raw materials.

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