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Characterization of Sunflower Waste Carbonization: Energy Balance and Water Holding Properties

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Abstract: This paper characterizes the carbonization process of biomass wastes, including sunflower husk pellets and sunflower sponge stalk pellets, at carbonization temperatures of 450 and 550 °C. These studies are important because of the reductions in wood resources for the preparation of barbecue charcoal, as well as agricultural benefits in terms of soil additives. In terms of energy balance, the obtained pyrolysis ensures the autothermal process. The heating characteristics of fixed bed showed that, due to the difference in bulk density, the bed temperature of the sunflower husk pellets reached 450 °C in 110 min, whereas the bed temperature of the sunflower stalk sponge reached the same temperature in 200 min. Additionally, the energy used for the sunflower husk carbonization increased from 2.9 kWh at 450 °C to 3.3 kWh at 550 °C, while the sunflower stalk sponge increased from 3.5 to 3.9 kWh. The combustion characteristics assessed using TGA showed that the carbonization of sunflower husk leads to obtained biochar with a higher combustion activity than biochar derived from sunflower stalk sponge. According to the experimental results, biochar from sunflower husk pellets has a higher water content capacity and water absorption rate than biochar from sunflower stalk sponge pellets.

Keywords: sunflower husk; sunflower sponge stalks; biochar; carbonization; water holding capacity; water absorption rate

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1. Introduction

Biochar, as a product of the carbonization process, is a valuable source of renewable biomass. Moreover, the demand for biochar is increasing not only due to the higher level of consumption of grill charcoal as a domestic application, but also due to its potential for application in fields such as chemical products, agriculture, and industry [1]. However, due to environmental protection, wood resources are decreasing, resulting in the need to find other substrates for the production of biochar. For this reason, a great deal of research is focused on the search for other biomass wastes. Moreover, biochar can also be used as a soil amendment to improve the soil's nutrient bioavailability, increase its pH, and reduce heavy metals in contaminated soil [2,3]. Kavitha et al. [4] showed that biochar doping with chemicals such as limestone reduces cadmium uptake by up to 80% in straw from rice and wheat plants.

Many studies have been conducted on sunflower husks for a variety of purposes. The production of sunflowers, due to the demand for sunflower oil, has increased and reached over 47 million tons and more than 10 million tons of sunflower seeds [5]. Only in Ukraine, the production of pellets from sunflower husks has reached over 240,000 tons per year [6]. As a result, sunflower waste, mainly sunflower husks or sunflower husk pellets, has emerged as a promising raw resource in a variety of sectors. The presented paper, in accordance with the need to search for other sources for the production of biochar for various applications, reports on investigations of the carbonization processes of sunflower stalk sponge and sunflower husk pellets.

Marx et al. [7] described the characterization of biochar from thermochemical liquefaction under different atmospheres (N_2, CO_2). In turn, Hubetska et al. [8] characterized active carbons prepared from sunflower husks. An experimental investigation of the sorption properties of biochars from sunflower husk carbonization at 600 °C was presented by Tomczyk et al. [9]. Nguyen et al. [10] showed the possibility of the activation of biochars from sunflower husks with H_3PO_4 in terms of adsorption of pharmaceuticals, such as ibuprofen or tetracycline.

Based on a novel experimental stand, this work demonstrates the effect of temperature on a comprehensive analysis of mass and energy balance, taking into account the quantity of energy contained in gasses and tars as well as the process's energy requirement. Energy balance is a critical aspect of research that should be considered in all carbonization processes. According to the European Biochar Certificate [11], at least 70% of the energy obtained in pyrolysis must be utilized as a heating source or for drying biomass.

This experimental work also encompassed the properties of biochar. The first aspect presents the possibilities of using biochars in terms of charcoal production [12]. This is relevant because of the ongoing increase in demand for barbecue charcoal as a heat source, particularly in African regions [13]. Ethiopian consumption alone reached 4 million tons per year. In addition, in Mozambique, more than 70% of the population uses charcoal for household needs [14].

In fact, world production of barbecue charcoal reached over 50 million tons, and the largest producers include Brazil, India, China, and African countries [15]. Worldwide, over 2.4 billion people depend on wood fuel, such as charcoal, for cooking, while small businesses also rely on wood fuel and charcoal as key energy sources [16]. Alternative biomass sources may lead to a reduction in deforestation and result in reduced habitat loss for wildlife and biodiversity. In nearly all countries involved in charcoal production, deforestation and forest degradation are identified as significant outcomes of the production process. Also notable is the deforestation rate, which has reached 390 km^2 and 2400 km^2 in Central and South America, over 5000 km^2 in Asia, and about 39,000 km^2 in Africa [17]. Such statistics suggest that it is critical to identify alternate waste sources for barbecue charcoal and briquette production.

The second important characteristic is water holding capacity (WHC). In the literature, there are many studies that have highlighted the usefulness of utilizing biochar in agriculture to improve soil water retention [18–21]. Liu et al. [22] found that biochar resulting from mesquite carbonization at 400 °C led to an increase in the WHC of sandy soil. Li and Tan [23] showed that biochar characterized by high porosity and functional group content led to an increase in soil water retention. Sun et al. [24] showed that biochar with high acid functional group content led to a decrease in N leaching in clay soil.

According to the literature, the addition of biochar is an essential strategy for future agriculture application [25]. In turn, Shoudho et al. [26] indicated that biochar contributes to climate change mitigation by carbon sequestration in the soil for long durations, thereby lowering greenhouse gas emissions. According to estimates, biochar effectively captures 1–35 gigatons ($GtCO_2$) of CO_2 each year. Additionally, it improves soil fertility, boosts water retention, and enhances nutrient cycling, all of which support increased crop productivity [27].

Moreover, the present paper presents characteristics of combustion reactivity using TGA analysis and, based on the work presented by Xiong et al. [28], provides a comparison of the quality of the biochar obtained through specific process temperatures and times, as well as parameters like combustion, ignition, and burnout indexes. The obtained data indicate whether biochar from sunflower husk and stalk sponge is an attractive material to produce charcoal products but also present its properties in terms of combustion quality.

2. Materials and Methods

2.1. Materials

The characteristics of biomass samples are presented in Table 1. Characteristics include sunflower husk pellets and sunflower stalk sponge pellets, collected from plantations in northern Poland. Elemental analyses were carried out by using a CHNS/O Analyzer (Thermo Scientific, Waltham, MA, USA) and an X-ray fluorescence spectrometer (Bruker Scientific Instruments, Billerica, MA, USA). Ash, volatiles, and fixed carbon content were determined using the EN 1860-2 Standard [29]. All samples for elemental analyses were previously ground to 0.2 mm using a rotary mill (Millmix 20, Domel, Železniki, Slovenia).

Table 1. Proximate and ultimate analysis of sunflower husk and stalk sponge pellets.

Parameter	Sunflower Husk Pellets	Sunflower Stalk Sponge Pellets
HHV [MJ/kg]	21.18	16.92
Moisture [a]	9.61	13.88
Proximate [wt.%]		
Volatiles	83.89	74.20
Fixed carbon	14.80	21.00
Ash	1.31	4.80
Ultimate [wt.%]		
C	47.89	44.19
H	6.62	6.73
O	36.92	41.69
N	1.19	2.24

[a] as delivered.

2.2. Carbonization Stand

The batch reactor, which is a model of an industrial crucible, is characterized by a heating chamber with a crucible with a length of 400 mm and an internal diameter of 145 mm (Figure 1). The temperature inside the reactor was determined by a control thermocouple ($T_{control}$) located in the reactor heating chamber. In each experiment, the temperature in the heating chamber was set at 450 °C. The measuring system included a PID controller to keep the temperature in the heating chamber at the desired level. When the temperature decreased below 450 °C, due to heat consumption during the carbonization process, the controller activated the heater. The heater was shut off once the temperature reached 450 °C. To achieve a carbonization temperature of 550 °C, the temperature in the heating chamber was first set to 450 °C. After reaching 450 °C in the fixed bed, the temperature in the chamber was raised to 550 °C.

The heating rate of the fixed bed was analyzed by two thermocouples located in the experimental crucible. The first thermocouple was located 20 mm from the crucible wall, while the second in the core of the crucible. Moreover, the experimental stand (PID controller) was equipped with an energy meter to analyze the energy balance of the process and determine the energy needs for the carbonization.

Experimental investigations were carried out for final carbonization temperatures of 450 and 550 °C and kept at temperature for 30 min. Dufourny et al. [30] indicate that it does not significantly affect the mechanical parameters of biochar. However, according to the literature, the final temperature is the most important carbonization parameter [31]. To evaluate the experimental investigation of these fuels, sunflower husk pellets as well as sunflower stalk sponge pellets were prepared as 8 mm in diameter and 10–15 mm in length. Following each experiment, the resulting biochar and scrubbers with tar were weighed in order to perform a mass balance. The results were replicated three times for each experimental series.

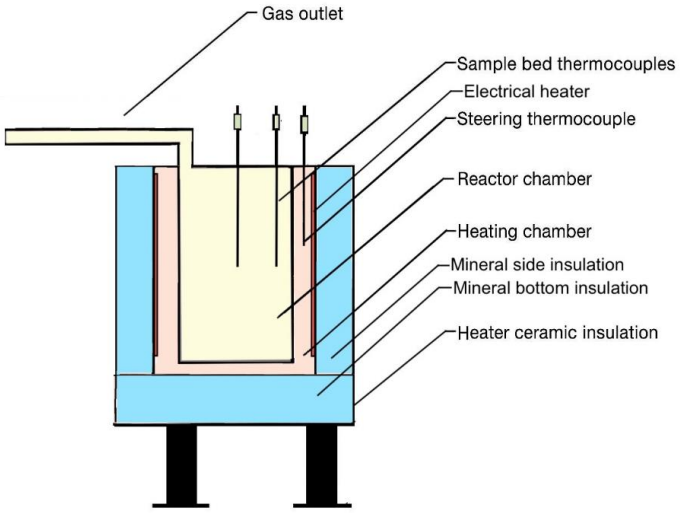


Figure 1. The experimental setup presenting the batch reactor.

2.3. Liquid and Gaseous Product Collection

The liquid product collection from the carbonization process was carried out using a 1 L cylinder filled with isopropanol and kept at 0 °C combined with 3 isopropanol washers, which were kept in a cryostat at −20 °C. Before and after each experiment, the cylinder and all washers were weighed, and the mass of the liquid phase was determined. The water content in the liquid products was analyzed by a Karl Fisher titrator (Metler Toledo, V20 Volumetric KF Titrator, Warsaw, Poland). The tars were also dried in a crucible at 105 °C for 60 min and then analyzed using a calorimeter (EkotechLAB, Gdańsk, Poland) to determine the higher heating value. The gaseous product compositions were collected using Tedlar bags, with a volume of 1 L, and determined by a Gas Chromatograph with a thermal conductivity detector (SRI Instruments, 310 GC, Torrance, CA, USA). In the case of gas composition, the higher heating value was determined in accordance with [18]:

$$HHV = Y_{CO} \cdot HHV_{CO} + Y_{CH_4} \cdot HHV_{CH_4} + Y_{H_2} \cdot HHV_{H_2} + Y_{N_2} \cdot HHV_{N_2} + Y_{CO_2} \cdot HHV_{CO_2} \quad (1)$$

where HHVi [MJ/Nm^3] represents the higher heating value of the Yi gas component.

In each experiment, samples were collected every 20 L, with a simultaneous online measurement of the amount of produced gas.

2.4. Water Holding Capacity

The water holding capacity (WHC) was measured according to the methodology presented by Zhang and You [32]. A 2 mm thick biochar sample was soaked with water for a period of 24 h and next placed on the dry sand for 2 h to remove any free water. After the biochar sample was weighed, it was dried at 105 °C. The dry sample was weighed again. Analyses were performed for three biochar samples from each experiment.

2.5. Water Absorption Rate

According to the literature, the water absorption rate (WAR) was determined using a container with an accuracy of 0.2 mL [32]. In each analysis, the apparent densities of the biochars were determined using a mercury porosimeter, and the mass of the samples as well as apparent volume were determined before the experimental investigation. In the next step, a sample of biochar was mixed with water, and the change in the mixture volume was recorded at time intervals. Analyses were performed for three biochar samples from each experiment.

2.6. TGA and DTG Analysis

Thermogravimetric analyses (TG and DTG) of husks and stalk pellets were carried out using a SDT Q600 Thermogravimetric Analyzer (TA Instruments, New Castle, DE, USA). The biochar samples were heated from 30 to 850 °C at a rate of 10 °C/min. The mass of each sample was 6–8 mg; the air flow rate was 100 mL/min.

The DTG analysis of char behavior during the combustion process was carried out using a TA Instruments SDT Q600 Thermogravimetric Analyzer. The sample, with a mass set as 6 mg, was heated from 30 to 800 °C at a rate of 10 °C/min. In order to define the reactivity of char during combustion, the S index was defined according to the equation [28,33–35]:

$$S = \frac{(dw/dt)_{max}(dw/dt)_{mean}}{T_i^2 T_b} \quad (2)$$

where T_i represents the ignition temperature at which the combustion reaction rate exceeds 1 wt.%/min and T_b represents burnout temperature at which the combustion rate decreases to 1 wt.%/min [36]. Moreover, the combustion process can be characterized by the ignition index (D_i) defined as [37]:

$$D_i = \frac{(dw/dt)_{max}}{t_i t_p} \quad (3)$$

where t_i represents the ignition time [min] and t_p represents time, at which the combustion rate reached the maximum value [min].

In addition, the D_f index was defined according to equation:

$$D_f = \frac{(dw/dt)_{max}}{\Delta t_{1/2} t_p t_b} \quad (4)$$

where $\Delta t_{1/2}$ represents the range of time, in which $(dw/dt)/(dw/dt)_{max} = 0.5$, and t_b represents the time of burnout temperature [min]. This index indicates if the combustion process of the sample ends rapidly or slowly [38,39].

The combustion characteristic can also be described by the H_f combustion index, which provides information about the intensity and rate of the combustion process [40,41]:

$$H_f = T_{MAX} \ln\left(\frac{\Delta T_{1/2}}{(dw/dt)_{max}}\right) \quad (5)$$

where $\Delta T_{1/2}$ represents the range of temperature, in which $(dw/dt)/(dw/dt)_{max} = 0.5$, and T_{max} represents the temperature for $(dw/dt)_{max}$. Sieradzka et al. [42] indicate that a low value of H_f means a better combustion performance. The stability of the combustion process can be defined as

$$D_w = \frac{(dw/dt)_{max}}{T_i T_{max}} \quad (6)$$

The combustion stability index (D_w) indicates the stability of the combustion process between ignition and burnout point [43].

3. Results and Discussion

3.1. Thernogravimetrics Analysis of Sunflower Husk and Stalk Pellets

Figure 2 presents the TGA curve for sunflower husk and stalk pellets. The obtained results indicate that in the first stage (100–120 °C), a mass loss occurs due to moisture evaporation. The main phase, associated with the release of volatile compounds, takes place in the range of 242–378 °C for sunflower husk pellets and 218–413 °C for sunflower stalk pellets. The obtained results indicate that in the case of sunflower stalk pellets, the thermal degradation process starts earlier; however, the maximum degassing intensity reached 5.49%/min (at 308 °C), whereas for sunflower husk pellets, it reached 6.61%/min (at 342 °C). However, these are not significant differences.

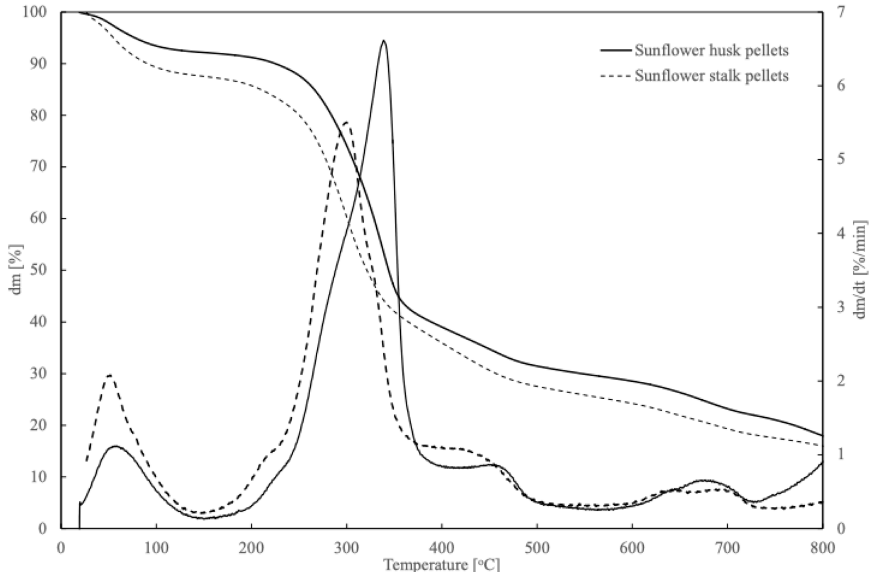


Figure 2. TGA and DTG analysis of sunflower husk pellets and sunflower stalk pellets.

3.2. Heating Rate of Fixed Bed During Carbonization Process

Figure 3 presents the characteristics of the carbonization process at 450 °C. The carbonization process, due an increase in fuel particle energy, is mainly a chemical phenomenon. The heat transfer to the surface and subsequently to the interior of a fuel particle is primarily physical and proceeds by means of a different way, radiation, convection, and conduction and depends on the bulk density, particle size, and free space between particles, which are important.

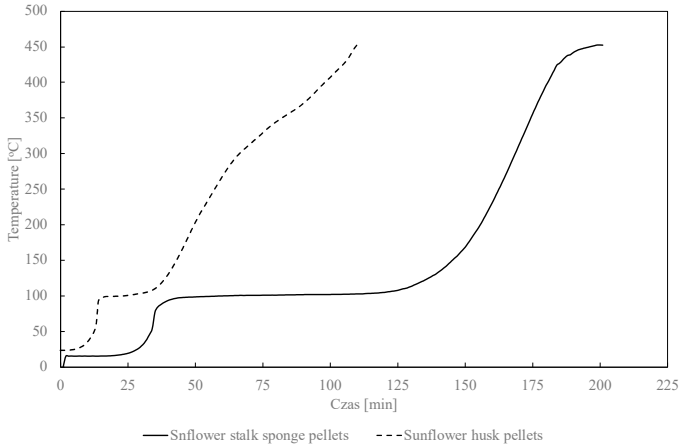


Figure 3. Characteristics of the heating rate of the fixed bed.

The results of the temperature in the fixed bed showed differences in heating rates of pellets for both. Due to a difference in bulk density, the bed temperature of the sunflower husk pellets reached 450 °C in 110 min, whereas the bed temperature of the sunflower stalk sponge pellets reached the same temperature in 200 min.

A shortened time of fixed bed heating to the set temperature also had an impact on power input, recorded with an energy meter. The energy used for the sunflower husk carbonization increased from 2.9 kWh for a final carbonization temperature of 450 °C to 3.3 kWh for 550 °C, while the sunflower stalk sponge increased from 3.5 to 3.9 kWh.

3.3. The Effects of Carbonization Temperature

The experimental results showed that carbonization temperature affected the yields of biochar as well as liquid and gas. The yield of the obtained char decreased with the

temperature, from 32% at 450 °C to 29.98% at 550 °C for sunflower husk pellets, and from 30.52% at 450 °C to 26.48% at 550 °C for sunflower stalk sponge pellets.

Considering the individual components of lignocellulosic biomass, the temperatures of thermal decomposition fall within the ranges 220–315 °C for hemicellulose, 315–400 °C for cellulose, and 170–900 °C for lignin [44,45]. In the case of the sunflower husk, the main stage of the carbonization process occurs between 300 and 500 °C, which is related to a high cellulose and hemicellulose content, which reached about 83%. The slowdown of the carbonization process near 500 °C may be caused by the thermal decomposition of lignin, the content of which is approximately 17%, similar to that of sunflower stalk sponge [46]. During the carbonization process of biomass materials, an increase in temperature leads to the breaking of the weaker bonds. As a result, this leads to the reduction in hydrogen and oxygen content and relative increase in carbon content (Table 2). A decrease in hydrogen content is mainly associated with the formation of liquid and gaseous products. In turn, a decrease in oxygen content is mainly caused by the emission of carbon monoxide and carbon dioxide and water [47].

Table 2. The effects of carbonization temperature on product yield and elemental composition of biochar.

Parameter	Sunflower Husk Pellet		Sunflower Stalk Sponge Pellet	
Temperature	450 °C	550 °C	450 °C	550 °C
Biochar	32.16	29.89	30.52	26.48
Liquid	48.35	46.76	50.25	52.16
Gases *	19.49	23.35	19.23	21.36
Elemental analysis of biochar [%]				
C	73.06	78.85	71.23	82.85
H	3.54	3.14	3.12	2.82
O	23.3	17.91	25.55	14.23
N	0.1	0.1	0.1	0.1
H/C	0.05	0.04	0.04	0.03
O/C	0.32	0.23	0.36	0.17
(O+N)/C	0.32	0.29	0.36	0.17

* Obtained by difference.

The obtained results show that with an increase in carbonization temperature, H/C and O/C mass ratio decrease for sunflower stalk sponge and sunflower husk pellets and decrease to similar values. Similar results were obtained by Jabłońska and Gliniak [48] for the carbonization of sunflower husks at 450–550 °C. According to the literature, a decrease in H/C and O/C mass ratio results in hydrophilic char surface [1,49]. Adhikari et al. [20] showed that groups containing nitrogen and oxygen, along with aliphatic hydrogen, enhanced the WHC of the biochars examined and decreased the evaporation of the water bound from the biochar. This aspect has also been presented by Sarkar et al. [50]. Zhang et al. [51] analyzed biochar from straw and pine sawdust and indicated that an increase in oxygen, nitrogen, and hydrogen content leads to an increase in WHC and, additionally, a decrease in water evaporation from biochar. Nitrogen in the biochar was primarily present in pyridinic and pyrrolic forms, while oxygen appeared as C=O and C-O groups; these nitrogen and oxygen structures could act as hydrogen bond acceptors, connecting to H_2O molecules. Aliphatic hydrogen, in turn, could serve as a hydrogen bond donor, attaching to H_2O molecules [52,53]. This aspect makes the nitrogen content in biochar a significant parameter for WHC [20,54]. Biochars produced at lower temperatures typically have higher polarity because they retain more oxygen-containing functional groups, such as hydroxyl (-OH), carboxyl (-COOH), and carbonyl (C=O) groups, which are polar and can bind water [55,56]. Weber and Quicker showed that the O/C ratio is an important aspect in the polarity of biochars and thus has a significant impact on the water retention capacity and the adsorption of pollutants [30].

A low H/C ratio also corresponds to the low content of functional groups [30]. Functional groups play an important role in water purification and the adsorption of nitrogen- and phosphorus-containing compounds [57]. In turn, an O/C ratio between 0.15 and 0.36 indicates biochar stabilization [58]. In addition, Schimmelpfennig and Glaser [59], due to the analysis of different biochars, showed that O/C < 0.4 and H/C < 0.6 indicate the possibility of using biochars for soil amendment and C sequestration. A similar aspect is presented by Dong et al. [60], who showed that for an O/C ratio in the range 0.2–0.6, the half-life of biochar may be characterized by 100–1000 years.

3.4. Proximate Analysis of Char

Table 3 presents the characterization of biochar obtained from the carbonization of biomass waste samples at different process temperatures, and for comparison characterization of commercial charcoal. The experimental results showed that an increase in carbonization temperature caused increases in fixed carbon content in all situations. Fixed carbon content increased from 77% to 84% for sunflower husk pellets and 64% to 72% for sunflower stalk sponge. Notable is the high ash content, which increased from 12% to 19% in sunflower stalk sponge. The obtained results indicate that biochar made from sunflower husk pellets can be used to produce charcoal in accordance with European standards. The biochars from sunflower stalk sponge are characterized by excessively high ash content and excessively low fixed carbon content and cannot be used for a charcoal production.

Table 3. The effects of carbonization temperature on biochar products' proximate analysis.

Temperature	Biochar Sample	Moisture	Volatile	Fixed Carbon	Ash	HHV
[°C]				[wt.%]		[MJ/kg]
450	Sunflower husk pellets	2.01	18.08	77.02	4.90	31.15
	Sunflower stalk sponge pellets	3.01	19.10	64.60	16.30	29.89
550	Sunflower husk pellets	2.21	7.88	84.00	8.12	32.91
	Sunflower stalk sponge pellets	3.83	1.30	72.00	15.80	31.04

3.5. Characteristics of Pyrolysis Gases

Table 4 shows liquid and gas products characteristic of carbonization sunflower husk and sunflower stalk sponge pellets. The obtained results showed that increasing the carbonization temperature caused a decrease in CO and CO_2 content for both carbonized sunflower husk and sunflower stalk sponge. According to the literature, the high amount of CO and CO_2 is caused by the cracking of carbonyl and carboxyl groups [61,62]. An increase in carbonization temperature resulted in an increase in hydrogen and methane content. The hydrogen content increased from 1.42 to 5.66% for sunflower husk and from 1.37 to 5.04% for sunflower stalk sponge, while the methane content increased from 9.61 to 12.51% for sunflower husk and from 6.65 to 11.84% for sunflower sponge stalk.

Taking into account the characteristics of the obtained bio-oils, considering only the tar content, obtained results showed that carbonization at 450 °C and 550 °C leads to a much higher bio-oil yield for sunflower husk than for sunflower stalk sponge. In addition, bio-oils from the carbonization of sunflower husk are characterized by a much higher HHV. Similar HHVs of bio-oils from pyrolysis at 450 °C were obtained by Santos et al. [62] for oat hulls and sugarcane bagasse.

The obtained results showed the HHV of the products obtained from the carbonization of sunflower husk and stalk sponge. Nath et al. [63] showed the characterization of wheat straw pyrolysis. These results indicate a higher content of gas fraction, with a higher hydrogen content and lower methane content. In turn, Sedmihradská et al. [18] presented a detailed analysis of pyrolysis products from wheat straw pellets. The resulting pyrolysis gases from the carbonization process at 400 °C consisted primarily of CO_2 (60%), CO (33%), CH_4, (3%), and H_2 (1.5%), with HHV at 7.60 MJ/m^3, while the liquid fraction, which constituted 49% of the products, had an HHV of 12.8 MJ/kg. Taking into account the HHV

of bio-oils, the obtained results are higher than the results presented by Rout et al. [64] (19.75 MJ/kg) for bio-oils from coconut shell pyrolysis.

Table 4. Characteristics of pyrolysis gases for sunflower pellet carbonization at different temperatures.

	Sunflower Husk Pellets		**Sunflower Stalk Sponge Pellets**	
Composition	450 °C	550 °C	450 °C	550 °C
Water [wt.%]	53.95	59.47	73.59	65.91
Bio-oil [wt.%]	22.21	30.52	20.79	27.16
HHV [MJ/kg]	37.03	34.90	28.98	31.16
Gases [wt.%]	23.84	24.72	21.30	20.32
CO [vol%]	30.38	25.94	24.46	22.64
CO_2 [vol%]	58.39	50.90	62.52	55.48
H_2 [vol%]	1.42	5.66	1.37	5.04
CH_4 [vol%]	9.61	12.51	6.65	11.84
HHV [MJ/kg]	5.34	6.55	3.87	5.81
MJ/kg	10.10	12.27	6.85	9.65
$MJ/kg_{feedstock}$	6.41	6.89	4.37	6.92
Energy needs [MJ/kg]	4.86	5.94	4.06	4.53

Table 4 also shows the energy balance of the carbonization process. The obtained results showed that the HHV of pyrolysis gases, taking into account the content of liquid fractions of water and tars, as well as gas mixtures, increased for sunflower husk from 6.41 to 6.89 MJ/kg per kilogram of feedstock, while it increased from 4.37 to 6.92 MJ/kg for the sunflower stalk sponge. The obtained results showed that for sunflower husk and sunflower husk pellets, the produced pyrolytic gases may ensure the autothermal process.

3.6. Water Content Properties of Biochar

Experimental results showed an increase in water content capacity of biochar from sunflower husk pellets from 0.49 g/g at 450 °C to 0.71 g/g at 550 °C, which is higher than the results obtained for sunflower stalk sponge pellets at −0.41 g/g and 0.50 g/g, respectively. According to the literature, increasing the carbonization temperature leads to an increase in the surface area of biochar and an increase in the hydrophobic properties of biochar [30]. During carbonization, polar surface functional groups likely to increase in heating temperatures are removed, which results in a decrease in the O/C ratio (Table 2). The obtained results showed that the water absorption rate (WAR) also reached a higher value for biochar from sunflower husk pellets. According to the literature, except for the surface area and hydrophobic properties of biochar, total pore volume and pore structure and distribution are significant factors affecting WAR [32]. In the case of sunflower husk, water content reached 0.2 g/g for 550 °C and 0.15 g/g for 450 °C after 400 min, while for the biochar from the sunflower stalk sponge, water content reached 0.07 g/g and 0.05 g/g after 400 min (Figure 4). The obtained results are lower than the values obtained for biochar from pine and poplar carbonization and presented by Zhang and You [32]. In this work, after 800 min, water content reached 2 g/g and 0.6 g/g for poplar char produced at 450 and 550 °C, respectively, while in the case of pine char, it reached 3 g/g at 450 °C and 0.8 g/g at 550 °C.

In the case of WHC, Zhang and You [32] obtained 3.44 g/g and 1.19 g/g for poplar char produced at 450 and 550 °C, respectively, and 3.98 g/g and 1.37g/g for pine char. These results indicate that an increase in carbonization temperature leads to a decrease in WHC. In turn, Zhang et al. [51] received around 7 g/g for the wheat straw biochar from 450 °C and 3 g/g for the pine wood biochar. Comparing these two studies, in the case of sunflower residues, a higher carbon content and a lower H/C ratio indicate greater aromaticity, lower polarity, and a higher hydrophobicity of the sunflower biochar, which contributes to a lower WHC value of the biochar [51]. In turn, Jeong et al. [65] presented the characteristic of the water holding capacity for biochar from sugarcane and rice biochar from the carbonization

process at 450–750 °C. Rice husk biochar is characterized by similar WHC (0.4–0.6 g/g), while biochars from sugarcane bagasse and leaves reached a significantly higher value (1.26–2.0 g/g). Ali et al. [66] showed that biochar from sewage sludge carbonization at 550 °C reached 1.01 g/g, and biochar from rubberwood carbonization at 550 °C reached 3 g/g.

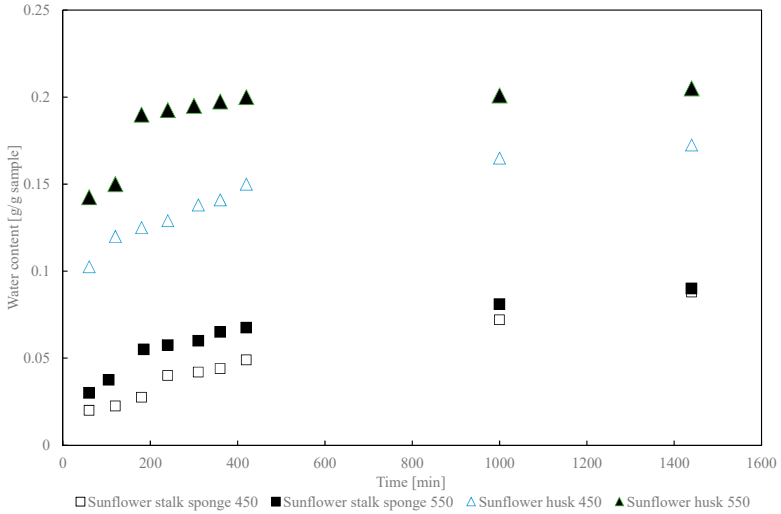


Figure 4. WAR of biochar from sunflower husk and sunflower stalk sponge pellets.

3.7. Combustion Characteristics of Obtained Biochar

Figure 5 presents the DTG characteristics of biochar from sunflower waste carbonization at 450 and 550 °C. According to the literature, parameters like ignition temperature (T_i) and ignition time (t_i), burnout temperature (T_b) and burnout time (t_b), and $(dw/dt)_{max}$, T_{max} and t_{max} can compare to the individual combustion parameters of biochar samples [67–69]. These results show that sunflower husk pellets reached ignition temperature (T_i) from 300 °C for carbonization at 450 °C to 325 °C for carbonization at 550 °C for sunflower husk. The first peak of the sunflower husk at 350 °C may be caused by a high amount of volatile content in the biochar sample (32%) and is related to degassing volatiles under the influence of heating. In the case of sunflower sponge stalk samples from the carbonization process, the ignition temperature reached 358 °C at 450 °C and 331 °C for carbonization at 550 °C. These results indicate that biochars from sunflower husk are characterized by higher fuel reactivity than biochars from sunflower sponge stalk.

In the case of burnout temperature (T_b), biochar from sunflower husk carbonization at 450 °C is characterized by a lower higher temperature than sunflower sponge stalk. This aspect is also reflected in the burnout index (D_f). According to the literature, a high value of D_f means that the combustion process ends faster [70], which is consistent with the results. The difference in DTG curves and maximum values between biochar from sunflower husk and sunflower sponge stalk is caused by volatile matter, bound carbon, and ash content. A higher amount of volatile matter and rapid emission under low temperature lead to acceleration of ignition at a lower temperature [35]. Moreover, Mureddu et al. [37] showed that a high amount of ash content may lead to decreases in oxygen diffusion and slow down heat transfer during the combustion process.

According to the literature, the combustion S index describes the reactivity of char and shows comprehensive characteristics of ignition and burnout [28,70]. Experimental investigation and TGA analysis showed that biochar from sunflower wastes is characterized by a mean value of combustion intensity, which increased with an increase in the carbonization temperature from 4.72%/min to 5.60%/min for the sunflower husk and from 3.50%/min to 5.83%/min for the sunflower stalk sponge.

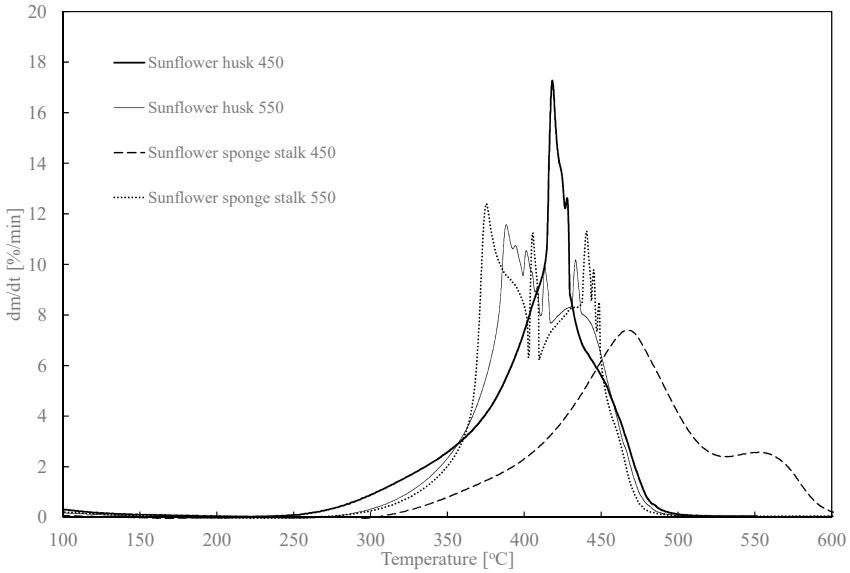


Figure 5. DTG curves of char from the carbonization of sunflower wastes.

Temperature characteristics showed that in the case of biochar from sunflower husk pellets, the maximum reaction rate of biomass occurs at lower temperatures than for biochar from sunflower stalk sponge pellets (Table 5). The characteristic time range ($\Delta t_{1/2}$), in which $(dw/dt)/(dw/dt)_{max} = 0.5$, indicates that biochar from the carbonization of sunflower husk pellets at 450 and 550 °C is characterized by a shorter range than sunflower stalk sponges, which makes biochar from sunflower husk burn faster. In addition, obtained results showed that in the case of biochar from sunflower stalk sponges, an increase in the carbonization temperature leads to a decrease in ($\Delta t_{1/2}$), which shortens the burning time of the sample.

Table 5. Combustion characteristic parameters of biochar (SH—sunflower husk pellets; SS—sunflower sponge stalk).

Parameter [Unit]		SH450	SH550	SS450	SS550
T_i	[°C]	304	325	358	331
T_b	[°C]	478	474	583	471
T_{max}	[°C]	418	408	466	375
$\Delta T_{1/2}$	[°C]	24	81	81	81
t_i	[min]	28	29	33	31
t_{max}	[min]	38	35	44	34
t_b	[min]	45.9	45.0	56.7	45.6
$\Delta t_{1/2}$	[min]	1.9	8.1	9.1	7.7
$(dw/dt)_{max}$	[%/min]	17.27	10.51	7.39	12.39
$(dw/dt)_{mean}$	[%/min]	4.72	5.60	3.50	5.83
$S \times 10^7$	$[\%^2/(min^2\ °C^3)]$	18.44	11.72	3.46	13.98
D_i	$[\%/(min^3 \cdot 10^{-3})]$	15.17	9.97	4.98	11.37
D_f	$[\%/(min^4 \cdot 10^{-5})]$	523.4	81.35	32.64	101.69
H_f	$[°C \cdot 10^3]$	674.6	1089.3	1468.2	1461.2
D_w	$[\%/(min°C^2 \cdot 10^{-5})]$	13.60	7.92	4.43	9.98

The obtained higher values of the S index and Di index indicate that biochars from sunflower husk are characterized by a higher char combustion activity and indicate that combustion is more efficient, stable, and active than for biochar from sunflower sponge stalk. In the case of the H_f index, biochar from carbonization of sunflower is characterized by lower value than biochar from sunflower sponge stalk and commercial charcoal. According to the literature, the H_f index indicates the flame stability after ignition [37]. Overall, the obtained results indicate that sunflower processing waste can be used as an additive

for the production of barbecue charcoal, which may be reflected in the economic and environmental aspects for the barbecue industry.

3.8. The Effects of Carbonization Temperature on Elemental Composition of Biochars

Experimental results showed that concentrations of inorganic elements in the biochars are different for different samples (Table 6). Taking into account common elements in biochar, like Ca, Si, Al, and K, it can be seen that Ca and K content in biochar from sunflower stalk sponge is much higher than for sunflower husk pellets.

Table 6. Elemental analysis of biochar from different carbonization temperatures.

Element		Sunflower Husk Pellets		Sunflower Stalk Sponge	
		450	**550**	**450**	**550**
			[°C]		
Al	[mg/kg]	100	111	120	181
B		21	27	120	199
Ba		7	9	89	100
Cr		<5	<5	78	97
Cu		33	39	39	40
Fe		450	753	990	1211
Mn		21	32	31	42
Na		14	15	225	440
Ni		<5	<5	18	29
Sr		33	40	224	280
Zn		32	51	112	154
As			<5		
Cd			<5		
Pb			<5		
Ca	% (m/m)	1.09	1.21	5.71	7.81
K		4.37	4.31	7.78	7.91
Mg		0.71	0.78	0.93	0.95
Cl		0.15	0.18	1.01	1.18
P		0.47	0.48	1.26	1.29
S		0.17	0.19	0.21	0.26
Si		0.06	0.08	0.26	0.31

Moreover, it is visible that the increase in carbonization temperature leads to an increase in P, Mg, Ca, and K content in all biochar samples. This aspect has also been presented by Zheng et al. [71], who indicated that that increase in P content with carbonization temperature is caused by an increase in the crystallized minerals forms, which represent less-soluble P forms. Moreover, K volatilization from the biomass waste starts in the range of 700 and 800 °C [72], which shows the difference with an increase to 300 to 500 °C and from 500 to 700 °C of carbonization temperature. These results are also compatible with those of Al-Wabel et al. [73] for the carbonization of conocarpus wastes, which also indicated that an increase in alkaline content in biochar may be responsible for the effects of liming caused by carbonization at high temperatures. The obtained results showed, that according to biochar from phytoremediation residue presented by Huang et al. [74] are characterized by lower As, Cd, Pb and Zn content. It should be emphasized that using biochar for agriculture must be free from negative environmental influences and show that biochar from forest residues is characterized by a low risk.

A high concentration of alkali elements, such as Na, Ca, Mg, and K, could be the reason behind the high pH of produced biochar. Experimental results showed that the pH value of biochar from sunflower husk pellets increased from 8.8 to 10.4, while the pH value of biochar from sunflower stalk sponge increased from 7.5 to 10.4, which is consistent with the literature [1,73]. The high concentration of pH is an important parameter due to agricultural application, especially as soil amendment [30]. Adding acidic biochar to soil

can significantly increase its pH and thus improve the nutrient bioavailability. The result will be an improvement in soil quality and a possible increase in crops [75]. The pyrolysis process leads to the release of the functional groups having an acid character (hydroxyl, carboxyl, and formyl groups), which causes the solid fraction to become more basic [30].

4. Conclusions

The research highlights the potential for using sunflower waste to produce biochar. Experimental results revealed that only biochar made from sunflower husk pellets meets the specifications for producing charcoal and barbecue briquettes due to its high fixed carbon concentration and low ash percentage. Biochar from sunflower stalk sponge can be utilized as a soil supplement due to its high ash concentration. However, the results show that biochar from sunflower husk has better water content features, such as water holding capacity and water absorption rate. The obtained results showed that carbonization of sunflower husk and sunflower sponge stalk pellets leads to the production of pyrolysis gas mixtures with an HHV higher than the energy demand of the process (in relation to 1 kg of feedstock). Combustion characteristics using TGA revealed that biochars from sunflower husk have higher combustion activity, indicating that combustion is more efficient, stable, and active than for biochar from sunflower sponge stalk and can be used as an additive for the production of barbecue charcoal.

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