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## Combustion characteristics of biochar from food processing waste

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### Abstract

This work examines biochar from carbonization of grape waste, and oat and buckwheat husks at 450°C. The main aspects of the work concern the analysis of the fixed carbon and ash content in accordance with the European Standard. Obtained results showed that biochar from oat and buckwheat husk can be used for barbecue charcoal and barbecue charcoal briquettes production, whereas biochar derived from grape waste can be used for the charcoal briquettes production. Thermogravimetric analysis showed that biochar from grape stalk is characterized by the highest ignition and burnout performance, but in relation to the remaining samples, combustion process occurs in a narrow range of time and temperature. Obtained results showed that biochar from oat and buckwheat husks has properties, as well as combustion stability and reactivity, similar to commercial charcoal.

**Keywords:** Oat; Buckwheat; Grape; Biochar, Barbecue

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### 1. Introduction

The use of charcoal has increased significantly in the 21st century. This is related to the habits of society and the aspect of spending free time or organizing events, and to the fact that it is a source of heat in African countries [1]. According to the literature, the top charcoal-producing countries are Brazil, Nigeria, Ethiopia, Ghana, Tanzania, India and China, while the world production of charcoal already exceeds 50 million tons

[2]. However, an important issue is the impact of charcoal production on the natural environment. Only in Kenya, from 1988, the reduction of land use and grasslands reached over 30%, whereas over 12% of Nigeria's forest has been lost since 1990 [3]. This situation, as well as legal regulations on environmental protection in individual countries, and an increase in the price of wood, led to finding alternative sources of charcoal production. This aspect has been presented by Kluska et al. [4], who indicated the possibility of producing charcoal from corn cobs. In these terms, Lu et al. [5] examined carbonization of palm

## Nomenclature

$D_f$  – burnout index, wt.%/min<sup>4</sup>  
 $D_i$  – ignition index, wt.%/min<sup>3</sup>  
 $(dw/dt)_{max}$  – maximum combustion rate, wt.%/min  
 $(dw/dt)_{mean}$  – mean combustion rate, wt.%/min  
 $H_f$  – combustion index, °C  
 HHV – higher heating value, MJ/kg  
 $S$  – combustion index, wt.%<sup>2</sup>/min<sup>2</sup> °C<sup>3</sup>  
 $t$  – time, s

$T$  – temperature, °C  
 $T_f$  – burnout temperature, °C  
 $t_f$  – burnout time, min  
 $T_i$  – ignition temperature, °C  
 $t_i$  – ignition time, min  
 $T_p$  – maximum peak temperature, °C  
 $t_p$  – maximum peak time, min  
 $\Delta t_{1/2}$  – time range of  $(dw/dt)/(dw/dt)_{max} = 0.5$ , min  
 $Y_i$  – mass fraction, kg/kg

fiber and eucalyptus. An interesting and promising material for biochar production is also sunflower waste [6], as well as rice straw and eggshells [7]. In addition, Hu et al. [7] indicated that biochar from rice straw is characterized by high NH<sub>4</sub><sup>+</sup> adsorption capacity.

This work presents the possibility of using food processing waste in the carbonization process, for the production of barbecue charcoal or briquettes. In recent years, due to increased consumption of wine and grape products, grape production reached over 79 million tons [8]. For this reason, grape processing waste is becoming an increasing problem in terms of waste management. In turn, buckwheat production reached almost 3 million tons [9], and due to the continuous increase in its consumption, the waste management problem becomes significant. In addition, world oat production reached over 20 million tons [10]. Characteristics of biochar from oat husk have been presented by Ferraz and Yuan [11] and Fan et al. [12] in terms of activated carbon preparation. In turn, buckwheat husk carbonization has been investigated by Yu et al. [13] in terms of the possibility of carbon materials production. Deiana et al. [14] showed the possibility of carbonization of grape stalks for activated carbon production, whereas del Pozo et al. [15] presented the characteristics of grape pomace pyrolysis and biochar.

The main aspects of the present work concern characteristics of combustion of obtained biochar samples, and comparatively, the commercial charcoal, using thermogravimetric analysis (TGA) and the determination of combustion, ignition and burnout indexes for comparing the quality of the analyzed samples as well as energy balance of the process. While the literature acknowledges the existence of biomass pyrolysis, there is a dearth of comprehensive findings pertaining to the carbonization process. Specifically, there is a lack of studies considering the energy balance and providing a detailed analysis of the energy derived from both liquid and gaseous products. Addressing this aspect is crucial, as per the European Biochar Certificate standards [4], where a significant portion (at least 70%) of the waste energy released during the combustion of pyrolysis gases is required to be utilized as a heating source or for drying biomass. The combustion characteristics of obtained biochars are interesting and show the potential for their use as an additive in the production of barbecue briquettes. This consideration is particularly significant in light of environmental protection laws and legislative measures in various countries aimed at preserving forest resources. This situation contributes to an escalation in the cost of wood waste and simultaneous deterioration in the quality of wood charcoal.

## 2. Materials and methods

### 2.1. Proximate analysis of raw materials

The proximate and ultimate analyses (Table 1) of the oat and buckwheat husks, grape pomace and stalk (waste from grain processing and the oil products industry), were conducted using an X-ray fluorescence spectrometer (S1 Titan, Bruker Scientific Instruments), a CHNS/O Flash 2000 Analyzer (Thermo Scientific) and EkotechLAB calorimeter. The technical analysis of the samples was determined in accordance with the EN 1860-2 Standard (*Appliances, solid fuels and firelighters for barbecuing – Part 2: Barbecue biochar and barbecue biochar briquettes – Requirements and test methods*).

Table 1. Proximate and ultimate analysis of oat and buckwheat husks, and grape waste.

	Grape stalks	Grape pomace	Oat husks	Buckwheat husks
HHV [MJ/kg]	18.12	17.11	17.7	18.54
Moisture [wt%, as delivered]	20.21	41.14	12.19	11.30
<b>Proximate [wt.%<sub>db</sub>]<sup>a</sup></b>				
Volatiles	64.63	52.80	81.5	78.7
Fixed carbon	28.41	40.17	17	20
Ash	6.95	7.03	1.5	1.3
<b>Ultimate [wt.%<sub>db</sub>]<sup>a</sup></b>				
C	46.21	53.61	48.73	51.25
H	5.77	5.21	7.33	7.01
O	47.65	40.89	40.08	38.05
N	0.37	0.29	3.86	3.69

<sup>a</sup>db – dry basis

### 2.2. Preparation of biochar

Experimental investigations were carried out in the laboratory scale reactor (Fig. 1) with a capacity of 3 l (400 mm in length and an internal diameter of 145 mm). During every experiment, the reactor chamber was firstly heated to 450°C (and maintained with a PID controller) and then a crucible with a sample (1000 g for oat and buckwheat husk, 1000 g for grape stalk, and 1500 g for grape pomace) was loaded into the chamber. The final temperature was set at 450°C and measured by two thermocouples placed 20 mm from the crucible wall and in the bed core, respectively. Once the desired temperature was reached, the process was stopped and the reactor was removed from the heating

chamber. The temperature of 450°C was set to maximize the yield of the solid fraction, with a fixed carbon content above 65%.

As for the liquid phase, the obtained products were collected using a steel cylinder (1 l) filled with isopropanol and kept at 0°C, and three isopropanol-filled scrubbers were kept in cryostat at the temperature of -20°C. Before, and after each experiment, the cylinder and all washers were weighed in order to perform mass balance.

The water content in the liquid products was analyzed by Karl-Fisher titrator, whereas the calorific value was determined using a calorimeter (EkotechLAB, Poland). The gaseous products were collected using tedlar bags and then analyzed by a gas chromatograph with a thermal conductivity detector (SRI Instruments 310).

The calorific value of a gaseous product was calculated according to the formula:

$$\text{HHV} = Y_{\text{CO}} \cdot \text{HHV}_{\text{CO}} + Y_{\text{CH}_4} \cdot \text{HHV}_{\text{CH}_4} + Y_{\text{H}_2} \cdot \text{HHV}_{\text{H}_2} + Y_{\text{N}_2} \cdot \text{HHV}_{\text{N}_2} + Y_{\text{CO}_2} \cdot \text{HHV}_{\text{CO}_2}, \quad (1)$$

where  $\text{HHV}_i$  [MJ/kg] denotes the calorific value of the  $i$ -th gas component ( $i = \text{CO}, \text{CH}_4, \text{H}_2, \text{N}_2, \text{CO}_2$ ), and  $Y_i$  represents its mass fraction [17].

### 2.3. Thermogravimetric analyses

In order to determine the combustion characteristics of biochar samples and commercial charcoal, TA Instruments SDT Q600 Thermogravimetric Analyzer was used. All samples were heated from 30 to 850°C at the rate of 10 °C/min. The mass of each sample was 6–8 mg, and the airflow rate was set, based on the research findings [17–19], at 100 ml/min.

Combustion characteristics of different fuels can be characterized using TGA analysis, by the intensity and rate of combustion, combustion reactivity or intensity of devolatilization [16,19]. A group of parameters, taking into account the ignition temperature ( $T_i$ ), burnout temperature ( $T_b$ ) and, respectively, the time of ignition ( $t_i$ ) and burnout ( $t_b$ ), maximum combustion rate  $(dw/dt)_{\text{max}}$  and, respectively, temperature ( $T_{\text{max}}$ ) and time ( $t_{\text{max}}$ ), can be determined to compare the combustion reactivity of biochar samples [21,22]. Taking into account differential thermogravimetric (DTG) analysis,  $T_{\text{max}}$  and  $(dw/dt)_{\text{max}}$  most often indicate reactivity, for which a high value of  $(dw/dt)_{\text{max}}$  at low temperature  $T_{\text{max}}$  characterizes the high reactivity of the sample [20]. The  $S$  index determines the combustion reactivity of the sample according to the equation:

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

where the ignition temperature ( $T_i$ ) refers to the combustion reaction rate which reaches 1 wt.%/min, and the burnout temperature ( $T_b$ ) pertains to the combustion rate decreasing to 1 wt.%/min [16,17]. The second index of combustion is  $H_f$ , which characterizes intensity and combustion rate [19]:

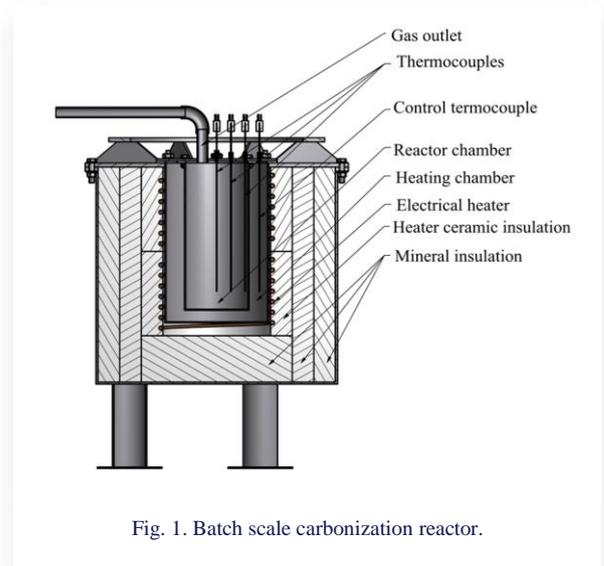


Fig. 1. Batch scale carbonization reactor.

$$H_f = T_{\text{max}} \ln \left( \frac{\Delta T_{1/2}}{(dw/dt)_{\text{max}}} \right), \quad (3)$$

where  $T_{\text{max}}$  represents the temperature for which the mass loss rate reaches maximum value,  $\Delta T_{1/2}$  is the range of temperature, in which  $(dw/dt)/(dw/dt)_{\text{max}} = 0.5$  [19]. A low value of  $H_f$  indicates better combustion characteristics [23]. In order to determine the intensity of volatiles release, the ignition index  $D_i$  is defined as:

$$D_i = \frac{(dw/dt)_{\text{max}}}{t_{i \text{max}}}, \quad (4)$$

where  $t_{\text{max}}$  represents the time for which the mass loss rate reaches a maximum value. The ignition index indicates ignition performance and allows us to compare the ease of ignition of different samples. A higher  $D_i$  value indicates a faster start of a combustion process [24]. The burnout index  $D_f$ , which indicates whether the combustion process ends slowly or rapidly [20], is defined as:

$$D_f = \frac{(dw/dt)_{\text{max}}}{\Delta t_{1/2} t_p t_b}, \quad (5)$$

where  $\Delta t_{1/2}$  is the time range in which  $(dw/dt)/(dw/dt)_{\text{max}} = 0.5$ . A high value of  $D_f$  means that the combustion process ends rapidly [25]. Furthermore, to characterize the stability of combustion, the process stability index ( $D_w$ ) can be defined according to the equation:

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

The stability index  $D_w$  characterizes combustion stability between the ignition point and burnout point. A high value of this index indicates good stability of the combustion process [26].

### 3. Results and discussion

#### 3.1. Characterization of heating rate during the carbonization process

Figure 2 presents the characteristics of oat and buckwheat husks, grape pomace and grape stalk samples. The experimental investigation showed that for the carbonization of corn stalk, the heating rate reached 10 °C/min at 20 mm from the wall and 9.2 °C/min in the core of the bed (Table 2). In the case of oat and buckwheat husks and grape pomace, the heating rate at the core of the reactor reached a similar value.

In the case of carbonization of oat and buckwheat husks a significant plateau can be observed. For the buckwheat husk sample, the slowdown in the heating rate attributed to the evaporation of moisture lasted approximately 100 minutes.

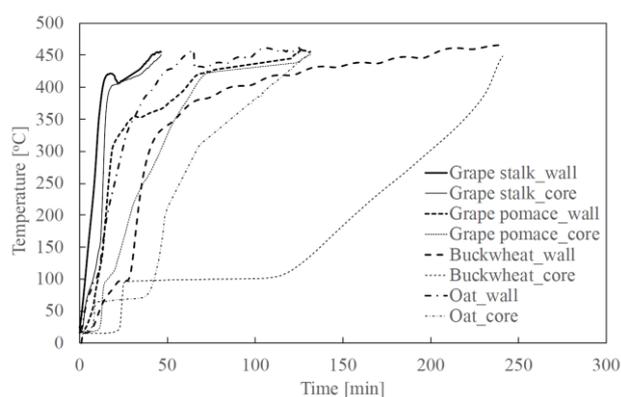


Fig. 2. Characteristics of the heating rate of the fixed bed.

Table 2. Characterization of fixed bed heating rate during carbonization process

		Grape stalk	Grape pomace	Oat husks	Buckwheat husks
Wall	[°C/min]	10.0	3.5	7.0	4.2
Core		9.2	3.4	3.3	5.2

The carbonization of grape pomace is characterized by two heating rate ranges. To reach 300°C near the wall, the average heating rate was 22 °C/min, and when it was reached the rate dropped to 1.5 °C/min. In the case of the core temperature, the heating rate reached 6.7 °C/min; however, after reaching 400°C, it dropped to 0.8 °C/min. A similar situation was observed for the buckwheat husk sample. Below the temperature of 300°C near the wall, the average heating rate was 22.1 °C/min, and above it, the rate dropped to 1.8 °C/min.

#### 3.2. Proximate and ultimate analysis of biochar samples

Table 3 presents the proximate and ultimate analysis of obtained biochar from carbonization at 450°C and from commercial charcoal. In accordance with the European Standard EN 1860-2:2005, biochar for barbecue charcoal production requires an ash content below 8% and fixed carbon above 75%. In the case of barbecue charcoal briquettes, ash content must be below 18% and fixed carbon content above 60% [16,27]. The obtained results showed that biochar from oat and buckwheat husk carbonization can be used to produce barbecue charcoal as well as barbecue charcoal briquettes. Biochar from the grape stalk and pomace can be used only to produce barbecue charcoal briquettes due to the low content of fixed carbon and high ash content in the case of the grape stalk, and fixed carbon content lower than 75% in the case of grape pomace. In addition, biochar from the grape stalk, due to high ash and low fixed carbon content, is characterized by the lowest higher heating value of 22.80 MJ/kg.

#### 3.3. Energy balance of carbonization products

Table 4 presents the mass and energy balance of the liquid and gas products, which is significant in terms of energy management, including water content in the mixture of gases and tars. Due to International Biochar Initiative (IBI) and European Biochar Certificate (EBC) guidelines, which determine the parameters of biochars and their certification, at least 70% of excess heat from the carbonization process must be used (for drying biomass, generating electricity) to obtain certificates for biochar [27]. The present study results showed that carbonization at 450°C of oat and buckwheat husks leads to the production of a significant amount of water (~35% and 29%, respectively) and

Table 3. Proximate and ultimate analysis of biochar samples from carbonization of oat and buckwheat husks, and grape waste, at 450°C.

	Grape stalk	Grape pomace	Oat husks	Buckwheat husks	Commercial charcoal
HHV [MJ/kg]	22.80	29.95	28.92	28.76	29.71
Moisture	3.23	4.81	4.02	5.04	5.58
Proximate [wt.% <sub>db</sub> ] <sup>a</sup>					
Volatiles	34.24	22.55	22.70	22.90	25.00
Fixed carbon	60.12	69.85	71.00	73.00	74.00
Ash	15.64	7.60	6.3	4.10	1.00
Ultimate [wt.% <sub>db</sub> ] <sup>a</sup>					
C	62.75	64.38	55.13	63.57	71.34
H	2.99	2.99	3.34	3.34	3.36
O	33.76	32.34	41.19	32.70	24.82
N	0.50	0.29	0.34	0.39	0.48

<sup>a</sup>db – dry basis

Table 4. Characteristics of pyrolysis products – a mixture of liquid and gas fractions.

	Grape stalk	Grape pomace	Oat husks	Buckwheat husks
Biochar	43.51	34.32	32.16	36.25
Liquid+gas	56.49	65.68	67.84	63.75
<b>Composition<sub>liquid+gas</sub></b>				
Water content [%]	4.25	14.27	35.37	28.77
Bio-oil [%]	28.10	72.82	26.87	28.74
HHV [MJ/kg]				
Gases [%]	42.73	12.91	15.48	15.86
CO [%]	22.42	29.36	29.39	29.20
CO <sub>2</sub> [%]	65.66	58.39	54.65	57.83
H <sub>2</sub> [%]	1.31	1.26	1.27	1.16
CH <sub>4</sub> [%]	5.61	5.99	4.56	6.82
HHV [MJ/kg]	3.36	4.16	3.78	4.37
HHV <sub>liquid+gas</sub> [MJ/kg]	2.63	19.60	10.39	9.31
HHV <sub>liquid+gas</sub> [MJ/kg <sub>feedstock</sub> ]	1.43	12.14	6.82	5.58

gas mixture (~15%), whereas carbonization of grape stalk and pomace is characterized by lower water content (~4% and ~14%, respectively). In the case of grape stalk, the carbonization process led to high yields of gas (42%). Carbonization of grape pomace resulted in the production of high amount of bio-oils (~73%), which affected the calorific value of the derived liquid and gaseous products (19.6 MJ/kg), and the amount of energy in pyrolysis gases obtained from one kilogram of feedstock reached 12.14 MJ. Carbonization of oat and buckwheat husks was characterized by lower and similar calorific values of the derived liquid and gaseous products (10.39 and 9.31 MJ/kg, respectively), which translated to the energy amount of 6.82 and 5.58 MJ/kg<sub>feedstock</sub>, respectively. Due to low bio-oils content, liquid and gaseous products of grape stalk carbonization were characterized by significantly lower calorific values (2.63 MJ/kg and 1.43 MJ/kg<sub>feedstock</sub>).

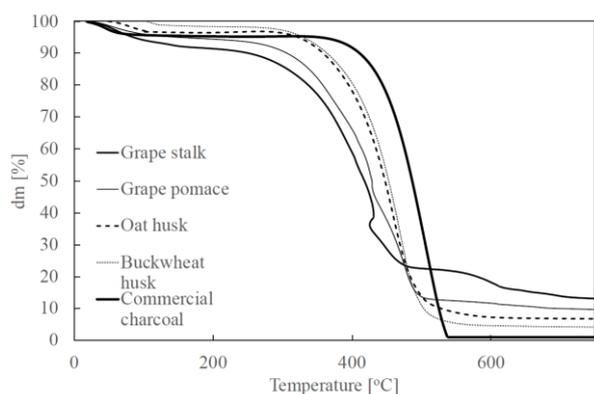


Fig. 3. TG curves for biochar from oat and buckwheat husks, grape waste and commercial charcoal.

### 3.4. Thermogravimetric investigation of oat and buckwheat husks

Figures 3 and 4 present characteristics of biochar combustion using thermogravimetric analysis. The TG analysis showed that the overall mass loss reached the maximum value for commercial charcoal, which is caused by the lowest ash content (1%), whereas the lowest overall mass loss has been observed for biochar from grape stalk with an ash content of 15%. Obtained results revealed that biochars from oat husks and buckwheat husks are characterized by a curve with a similar slope and overall mass loss.

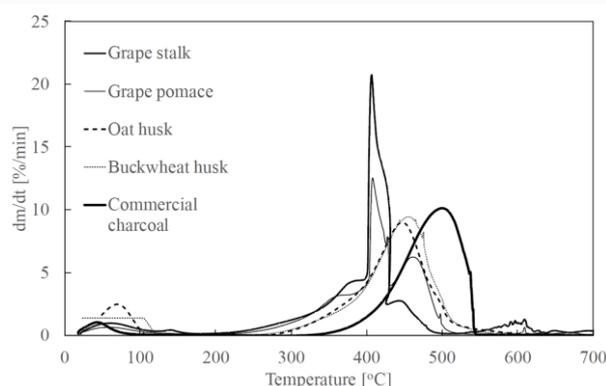


Fig. 4. DTG curves for biochar from oat and buckwheat husks, grape waste and commercial charcoal.

It was also found that ignition temperature ( $T_i$ ), which refers to ignition performance, reached the highest value for the commercial charcoal (388°C), while the lowest value was obtained for biochar from the grape stalk and pomace (286°C and 299°C, respectively), as given in Table 5. This aspect was also reflected in ignition time ( $t_i$ ). The burnout process started the fastest for biochar from buckwheat husks and grape stalks (22 and 26 min, respectively), and the latest in the case of commercial charcoal (37 min). Proximate analysis of obtained samples (Table 3) indicates that biochar from grape stalks has the highest volatile content.

According to the literature, an increase in volatile matter leads to faster devolatilization and accelerates the ignition process at lower temperatures [18]. This is also reflected in the ignition index ( $D_i$ ), which reached a higher value for biochar from the pomace stalk and indicates a faster start of the combustion process. In this case,  $(dw/dt)_{max}$  and  $t_{max}$  were also significant (Table 5). Biochar from grape stalk reached the highest maximum mass loss rate (20.76 wt.%/min), but in relation to the remaining samples, in a narrow range of time and temperature ( $\Delta t_{1/2} = 1.1$  min). In this case, the biochar closest to commercial charcoal is biochar from oat husks, for which the ignition index  $D_i$  reached 8.23 wt.%/(min<sup>3</sup>×10<sup>-3</sup>), while for the commercial charcoal only 5.74 wt.%/(min<sup>3</sup>×10<sup>-3</sup>). Considering the burnout temperature ( $T_b$ ), biochar from the grape stalk is characterized by the lowest value (473°C), while the remaining samples have a burnout temperature above 500°C. The maximum temperature was reached for the commercial charcoal (542°C), for which this process was completed at the latest (52 min). High burnout temperature may be reflected in the difficulty of burning the sample,

Table 5. Characteristic combustion parameters.

		Grape stalk	Grape pomace	Oat husks	Buckwheat husks	Commercial charcoal
$T_i$	[°C]	286	299	327	327	388
$T_b$	[°C]	473	499	514	517	542
$T_{max}$	[°C]	407	408	447	455	500
$\Delta T_{1/2}$	[°C]	27	57	77	54	92
$t_i$	[min]	26	28	28	22	37
$t_{max}$	[min]	37	38	39	34	47
$\Delta t_{1/2}$	[min]	1.1	5.4	7.8	7.9	9.4
$t_b$	[min]	45	48	47	42	52
$(dw/dt)_{max}$	[%/min]	20.76	12.60	8.99	9.45	10.13
$(dw/dt)_{mean}$	[%/min]	3.32	3.80	4.34	4.53	6.29
$S$	[wt. %/(min <sup>2</sup> °C <sup>3</sup> )]	17.84	10.70	7.08	7.73	7.81
$D_i$	[wt. %/(min <sup>3</sup> × 10 <sup>-3</sup> )]	20.71	11.67	8.23	12.21	5.74
$D_f$	[wt. %/(min <sup>4</sup> × 10 <sup>-5</sup> )]	1115.4	125.7	62.8	82.8	43.3
$H_f$	[°C × 10 <sup>3</sup> ]	106.96	616.12	959.19	795.67	1102.87

which leads to a longer time for completing the process of conversion. On the other hand, longer fuel combustion on the grill grate has its economic, positive aspects.

Burnout properties can also be correlated with the burnout index ( $D_f$ ). The carried out study showed that biochar from grape waste is characterized by the highest values of  $D_f$ , which indicates that the combustion process ends faster than for other biochars [28]. However, the characteristics obtained indicate that despite the maximum value  $(dw/dt)_{max}$  reached 20.76 %/min, the average value of mass loss reached only 3.32 %/min. This is caused by high ash content and extended time related to the heating of a sample and its afterburning after passing through the maximum combustion peak. In the case of commercial charcoal,  $(dw/dt)_{max}$  reached 10.13 %/min, but the combustion process takes place less rapidly with an average value of mass loss of 6.29 %/min. Taking into account the combustion reactivity, biochar from grape stalks is characterized by the highest  $S$  index of 17.8 %<sup>2</sup>/(min<sup>2</sup> °C<sup>3</sup>), whereas biochars from oat and buckwheat husks reached similar values (7.08 and 7.73 %<sup>2</sup>/(min<sup>2</sup> °C<sup>3</sup>), respectively) to commercial charcoal (7.81 %<sup>2</sup>/(min<sup>2</sup> °C<sup>3</sup>)) which means similar combustion reactivity characteristics. In addition, the combustion index  $H_f$  reached the lowest value for biochar from the grape stalk, whereas for the commercial charcoal and biochar from oat husks, it reached the highest value. As regards the combustion stability index ( $D_f$ ), biochars from oat and buckwheat husks showed values similar to commercial charcoal.

#### 4. Conclusions

This work presents characteristics of biochar in terms of barbecue charcoal and briquette application. The experimental investigation was focused on the biochar from the carbonization of grape waste, and oat and buckwheat husks at 450°C. The main aspects concern the analysis of the fixed carbon and ash contents in accordance with the European Standard. The study revealed that biochar from oat and buckwheat husks can be used for barbecue charcoal and barbecue charcoal briquettes production, whereas biochar from grape waste can be used for charcoal briquettes production. Combustion characteristics using thermogravimetric analysis showed that biochar from the grape stalk is characterized by the highest ignition and burnout performance, but compared to other samples, the combustion process occurs

in a narrow range of time and temperature. It was found that biochar from oat and buckwheat husks has properties (the course of DTG curve), average and maximum value of mass loss, and combustion reactivity and stability, similar to commercial charcoal. Due to an increase in world production of oat and buckwheat as well as grape-derived food products, adding biochars from the carbonization of the food industry waste, may be an interesting alternative for wood resources and affect the economic and environmental aspects of the production of barbecue charcoal and briquette.

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