

Communication

Proof-of-the-Concept of Spent Mushrooms Compost Torrefaction - Preliminary Studies of Process Kinetics and the Influence of Temperature and Duration on Calorific Value of the Biochar

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Abstract: Poland is the 3rd producer of mushrooms in the world. Mushroom production in Poland accounts for nearly 25% of the total production in the EU, and it is still growing. One type of waste generated during mushroom production is mushroom spent compost (MSC), with a 5:1 (MSC:mushrooms) production rate. We investigated valorizing the MSC to produce fuel via torrefaction ('roasting', a.k.a. low-temperature pyrolysis). Specifically, we developed models for the MSC torrefaction kinetics using thermogravimetric analyses (TGA) and the effects of torrefaction temperature (200~300 °C) and process duration time (20~60 min) on the resulting biochar (fuel) properties. The estimated activation energy value of MSC torrefaction was 22.3 kJ·mol⁻¹. The highest higher heating value (HHV) = 17.9 MJ·kg⁻¹ d.m. was found for 280 °C (60 min torrefaction time). The temperature of torrefaction significantly ($p<0.05$) increased the HHV for constant process duration. The torrefaction duration time significantly ($p<0.05$) increased the HHV for 220 °C and decreased HHV for 300 °C. The highest mass yield 98.5% was found for 220 °C (60 min), while the highest energy yield was found for 280 °C (60 min). In addition, estimations of the value (€132.3·Mg⁻¹ d.m. or 27.7 €·Mg⁻¹ w.m) and quantity of resulting biochar (from torrefied MSC with 65.3% moisture content) were made based on the 280 °C (60 min) torrefaction variant, assuming the price of commercially available coal fuel. We have shown a concept for an alternative utilization of abundant biowaste (MSC). The initial economic evaluation showed that MSC torrefaction might be profitable. This research provides a basis for alternative use of an abundant biowaste and can help charting improved, sustainable mushroom production.

Keywords: waste to energy; mushroom spent compost, renewable energy; biochar; biomass valorization; torrefaction; activation energy; fuel properties; proximate analysis; carbon sequestration

1. Introduction

The production of mushrooms in Poland is growing rapidly. During 2006-2018, the production of mushrooms increased from 196 thousand Mg·year⁻¹ to 325 thousand Mg·year⁻¹, which currently accounts for 24.15% of the total production in the European Union (EU) [1,2]. Poland is the largest grower of mushrooms in Europe and the third in the world. One of the abundant wastes arising during the cultivation of mushrooms is a worn-out substrate – mushroom spent compost (MSC) which accounts to ~5 kg of MSC per 1 kg of produced mushrooms [3]. This amounts to 5.6 and 1.6 million Mg·year⁻¹ of MSC, in the EU and Poland, respectively [1,4].

The sustainable management of MSC is an important issue for the industry. The MSC is currently considered as an 'industrial waste' (02 01 99 code, according to European Waste Classification) which belongs to the group of wastes from agriculture, horticulture, hydroponics, fisheries, forestry, hunting, and food processing [5]. Potential waste treatment methods depend on MSC properties. For example, a white mushroom (*Agaricus bisporus*) is grown on a soil consisting mainly of straw and poultry manure. The manure also contains gypsum, urea, peat, coconut, soy proteins [6]. The mushroom production cycle takes about 6 to 8 weeks on this bedding with three harvestings of mushrooms. After this period, the MSC cannot be regenerated and used again for production. It is a waste which requires to be treated [7]. The MSC is a source of biogenic elements, such as C, N, P, K, S (Table 1). The low level of heavy metals content allows the MSC to be considered as an organic fertilizer [8]. In addition, the MSC also contains a residual fraction of organic compounds, humic and fulvic acids, fraction decalcification, and bitumen [7]. An overview of the properties of the MSC is shown in Table 1.

Table 1. The properties of MSC [1,6,9-12]

Parameter	Unit	Values
Bulk density	kg·m ³	196.5
pH	-	6.23-7.15
Moisture	%	68.7-56.24
Volatile solids	% d.m.	53.97-65.18
Ash	% d.m.	22.43-38.3
Higher Heating Value, <i>HHV</i>	MJ·kg ⁻¹ d.m.	4.06-12.98
Lower Heating Value, <i>LHV</i>	MJ·kg ⁻¹ d.m.	2.03-10.17
C	% d.m.	27.8-40.73
H	% d.m.	3.40-4.86
N	% d.m.	1.80-6.00
S	% d.m.	2.12-2.99
Cl	% d.m.	0.1
O	% d.m.	18.94-26.99
P	g·kg ⁻¹ d.m.	9.06-18.00
K	g·kg ⁻¹ d.m.	15.2-20.00
C/N	-	12.3-18.0:1
Ca	g·kg ⁻¹ d.m.	28-109
Mg	g·kg ⁻¹ d.m.	3.6-18.0
Na	g·kg ⁻¹ d.m.	1.60-1.68
Lignin	% d.m.	25
Cellulose	% d.m.	38
Hemicellulose	% d.m.	19
Cu	mg·kg ⁻¹ d.m.	18.3-54.0
Zn	mg·kg ⁻¹ d.m.	143.0-168.1
Mn	mg·kg ⁻¹ d.m.	164.0-336.8
Fe	mg·kg ⁻¹ d.m.	4.7-4494.5
Mo	mg·kg ⁻¹ d.m.	1.51-2.13
Al	mg·kg ⁻¹ d.m.	987
B	mg·kg ⁻¹ d.m.	12.5-47.7
Se	mg·kg ⁻¹ d.m.	2.25

Li	mg·kg ⁻¹ d.m.	3.27
Ti	mg·kg ⁻¹ d.m.	18.0
Pb	mg·kg ⁻¹ d.m.	2.47-10.40
Cd	mg·kg ⁻¹ d.m.	0.089-6.200
Cr	mg·kg ⁻¹ d.m.	0.21-5.80
Ni	mg·kg ⁻¹ d.m.	2.75-13.30

Thus far, several various methods for MSC management have been developed and used. Those methods were aimed to obtain compost, bioethanol, biogas, enzyme lactase, xylooligosaccharides, or hydrogen. The most popular use of MSC is composting due to its organic nature and balanced ratio of C/N 12.3-18:1 (Table 1). The work of Kalembasa et al. [7] showed that compost from MSC could be an excellent fertilizer improving soil structure because it has a high content of organic matter necessary for the proper development of plants. However, research to date shows some concerns as well [13]. For example, compost from MSC can be highly variable and does not always meet the legal criteria for a fertilizer [8]. This is due to the high variability of the compost parameters such as N, P and K, biogenic elements, C/N ratio, pH, electrolytic conductivity, and the Ca, Mg, Na, Cu, Zn, Fe, Mn, Cd, Cr, Ni, Pb content. The share and content of cellulose, hemicellulose, and lignin can also vary [14]. Thus, the variable MSC composition may cause technological problems of the process and heterogeneity of the obtained fertilizer quality.

Bioethanol production from MSC can be facilitated via hydrolysis with acids or bases, physical treatment using steam followed by fermentation. The difficulty comes from high lignin content. Steam explosion is used for delignification (the breakdown of lignin structures) into simpler cellulose. The literature shows that the highest potential of conversion of MSC to bioethanol requires 20 bar steam pressure [15]. Research on MSC hydrolysis with the addition of surfactants was published [16].

The MSC may also be a source of valuable substances. During the hydrothermal conversion of MSC rich in nutrients (e.g., proteins), production of xylooligosaccharides may be possible [17, 18]. Thanks to the high purity of the obtained product, this process has the industrial potential [15]. The MSC may also be an efficient source of lactase enzyme, which is widely used in industry: paper, clothing, or food production [4].

Biogas production is also feasible. However, it has been found that this process is not such effective as fermentation of other biomass. Anaerobic fermentation of MSC generates ~122 dm³·kg⁻¹ d.m. of biomethane while corn silage can produce 320 dm³·kg⁻¹ d.m. [19]. The biogas yield from other available substrates: cattle manure 324±15.5 dm³·kg⁻¹ d.m., corn silage 653±28.8 dm³·kg⁻¹ d.m., waste fruit and vegetables 678±15.8 dm³·kg⁻¹ d.m., sugar beets pulp 634±235 dm³·kg⁻¹ d.m., whey 736±15.5 dm³·kg⁻¹ d.m. [20], shows that biogas production from MSC is not competitive enough. Another interesting use of MSC is the production of hydrogen already tested in lab-scale. Two-step hydrolysis with acid and base resulted in 2.52 moles of H₂·g COD⁻¹ [21].

Law regulations regarding the management of waste from mushroom production allow using MSC for energy purposes [22]. The 2009/28/WE (April 23, 2009) directive of the European Parliament Council [23] indicates the possibility of considering the MSC as biomass, and in consequence, the energy produced from MSC as energy from a renewable source. However, due to the high moisture, MSC is considered as fuel with low calorific value (Table 1) [24]. The MSC, with approximately 70% moisture, has a lower heating value of ~4.6 MJ·kg⁻¹ d.m. [3]. The MSC characteristics (Table 1) do not indicate the high profitability of the incineration process [25].

We propose to convert the MSC into more efficient solid fuel, according to the 'Waste to Carbon' approach [26] (Figure 1). One of the ways of MSC conversion is the process of torrefaction, otherwise known as high-temperature drying, low-temperature pyrolysis or biomass 'roasting'. It consists of roasting the organic compounds of plant origin out of a substance [27]. Torrefaction may be characterized by the range of temperatures 200~300 °C [28], while according to the act on renewable sources energy [29], the temperature range is 200~320 °C. The residence (process) time of torrefaction

depends on many factors, such as the moisture or volatile content, as well as the type of reactor or substrate type [30]. The residence time usually does not exceed 60 min. The products of torrefaction are solid biochar and gas ('torgas'). Torgas consists of non-flammable substances such as water or CO_2 and flammable: CO , CH_4 , or H_2 [31]. Depending on process parameters and properties of the substrate, a different ratio of flammable to non-combustible parts may be found [28]. The torgas is not an attractive product of torrefaction as biochar due to the high content of non-flammable substances [32,33].

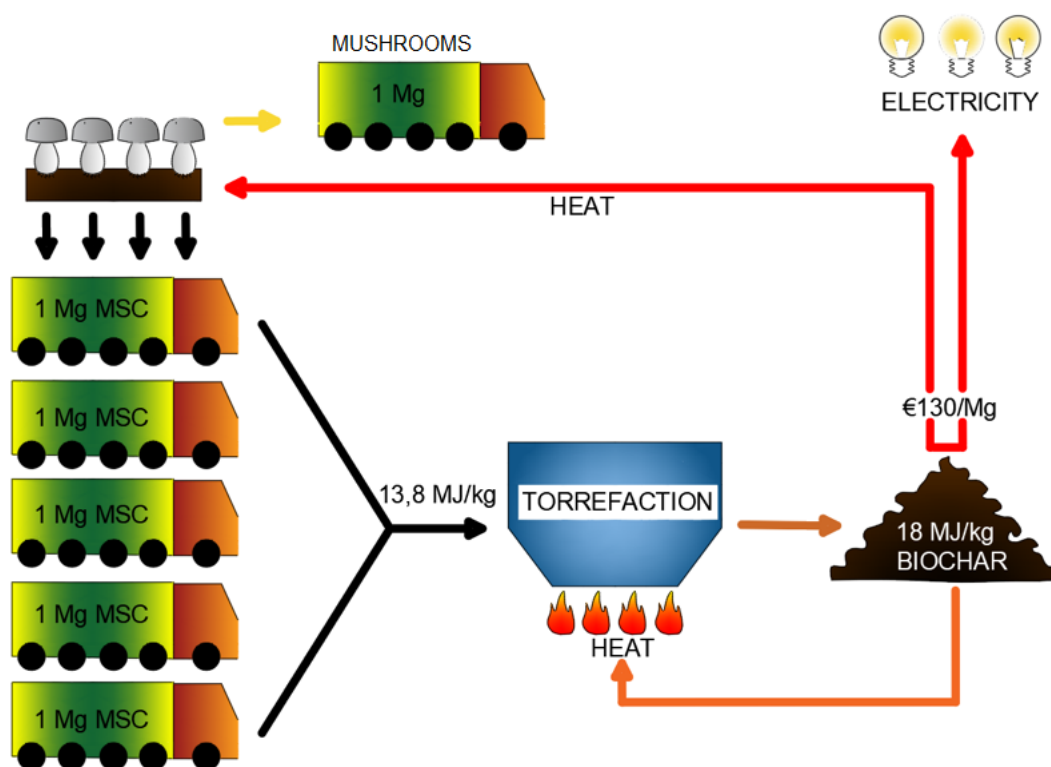


Figure 1. The proposed concept of valorizing mushroom spent compost (MSC) via torrefaction. Resulting biochar can be a valuable source of recovered energy.

The main product of the torrefaction - biochar, according to Polish regulations, should have calorific value not less than $21 \text{ MJ} \cdot \text{kg}^{-1} \text{ d.m.}$ and the feedstock should come from solid substances of origin vegetable, animal or biodegradable to be considered as a 'renewable source of energy' [29].

During the torrefaction process, the loss of mass, as well as the loss of chemical energy from raw material, is observed. However, the degree of mass loss is higher (30~40%) than the energy loss (10%). Due to this difference, energy densification in solid fuels occurs [28]. Despite it, the bulk density of the product is increasing, which positively affects the logistics of fuel [25] transport. Torrefaction increases the C content in the biochar, which improves its calorific value. The product also becomes more homogenous. This affects the further thermal transformation of biochar as a fuel. Because the abrasiveness is reduced, the mechanical grinding requires less energy compared to the raw substrate. There is also a possibility of pelletization of biochar from torrefaction [34]. In addition, the H/C and O/C ratios are reduced, which improves the fuel properties of the biochar in relation to the used substrate [35,36].

Torrefaction of waste is a growing research area. Examples include fractions of industrial and municipal wastes [37,27], sewage sludge [38], brewers' spent grain [39], Oxytree biomass [40] prunings, woodchips, olives waste, Virginia mallow (considered as a potential energy crop) [22]. The high-quality fuels can be obtained due to the torrefaction process. Therefore, it is necessary to carry out research on new substrates, aimed to optimize the torrefaction process to obtain (e.g.) the highest calorific value. For torrefaction optimization, it is necessary to determine the appropriate temperature and residence time for given substrates to achieve the most beneficial fuel parameters [25,41].

The MSC is a new substrate which has not been tested for its conversion to solid fuel during the torrefaction process yet. Therefore, the aim of this study was the determination of the MSC torrefaction process kinetics parameters and the preliminary selection of technological parameters, under which biochar with the highest calorific value may be obtained. This article presents pioneering, novel research being a proof-of-the-concept of a new technology of MSC reuse, by conversion to high-quality solid fuel (Figure 1).

2. Materials and Methods

2.1. The properties of MSC

The samples of MSC originated from a mushroom farm in Gogołowo, Poland. MSC samples were first dried for 24 h in a WAMED laboratory dryer, model KBC-65W (Warsaw, Poland) under the temperature of 105 °C. Then, dry MSC sample was ground through a 0.1 mm screen. For grinding, the laboratory knife mill TESTCHEM, model LMN-100 (Pszów, Poland), was used. The raw biomass of MSC was characterized by the determination of moisture content, volatile solids (VS) content, ash content, higher heating value (HHV) (Table 2).

Table 2. The properties of raw MSC.

Parameter	Unit	Mean ± Standard Deviation
Moisture	%	65.32 ± 0.05
VS	% d.m.	71.60 ± 2.31
Ash	% d.m.	28.40 ± 2.31
HHV	MJ·kg ⁻¹ d.m.	13.79 ± 0.50

2.2. MSC torrefaction kinetics measurements

The thermogravimetric analysis (TGA) of the MSC torrefaction process was conducted according to the protocol described elsewhere [38]. To ensure that the inert atmosphere was maintained, the CO₂ gas was introduced from the bottom of the reactor at a rate of 0.6 mL·min⁻¹. The investigated MSC sample was placed in the cuvette and introduced inside the reactor. The cuvette was integrated with the electronic balance with 0.01 g resolution to enable the measurement of the mass loss during the torrefaction process. The parameters of the torrefaction process were registered by a PC and exported to the file. Approximately 2.25 g of dried MSC samples were placed in the reactor and heated at different constant temperatures of 200, 220, 240, 260, 280, and 300 °C for up to 1 h. Temperature range and intervals were typical for torrefaction temperatures and based on the methodology described by Bialowiec et al. [37]. The torrefaction rate constant was evaluated using the first-order reaction rate model [42]:

$$M_s = M_s^0 \times \exp^{-k \times t} \quad (1)$$

$$\ln M_s^0 / M_s = k \times t \quad (2)$$

where: M_s^0 = initial MSC mass, g, M_s = unit mass, g, k = torrefaction rate constant, s⁻¹, t = time, s.

The Arrhenius equation describes the dependence of torrefaction rate constant (k) and temperature (T):

$$k(T) = A \exp - E_a / RT \quad (3)$$

and in logarithmic form:

$$\ln k(T) = \ln A - E_a / RT \quad (4)$$

where: R = gas constant, 8.314, J·(mol·K)⁻¹; T = temperature, K; A = frequency factor; E_a = activation energy; J·mol⁻¹, k = torrefaction rate constant, s⁻¹.

The activation energy can be calculated using the torrefaction rate constant and the Arrhenius equation. $\ln(k)$ is a linear function of $1/T$:

$$y = ax + b \quad (5)$$

where: $y = \ln(k)$, $b = \ln A$, $a = E_a/R$.

2.3. The MSC torrefaction and biochar generation

The MSC torrefaction was carried out according to the procedure described by Sygula et al. [43] in a muffle furnace (Snol 8.1/1100, Utena, Lithuania). CO₂ was used as an inert gas with a flow of 10 dm³·h⁻¹. The process was carried out under the setpoint temperatures of 200 °C to 300 °C with intervals of 20 °C. For each temperature, torrefaction was carried out in 20, 40, and 60 min retention time. The samples were heated from 20 °C to the torrefaction setpoint temperature with a heating rate of 50 °C·min⁻¹. The dry mass of the sample used for the tests was 10 g (± 0.5 g). The biochars were removed from the muffle furnace when the interior temperature was lower than 200 °C. The approximate times of cooling from 300 °C, 280 °C, 260 °C, 240 °C, and 220 °C to 200 °C were 38, 33, 29, 23, and 13.5 min, respectively. The approximate cooling time from 300 °C to room temperature (~20 °C) was around 6 h. Analyses of three replicates were carried out.

Mass yield, energy densification ratio, and energy yield were calculated based on Equations (6)–(8) [44].

$$\text{Mass yield} = \frac{\text{Mass of dry biochar}}{\text{Mass of dried raw MSC}} \cdot 100 \quad (6)$$

$$\text{Energy densification ratio} = \frac{\text{HHV of biochar}}{\text{HHV of raw MSC}} \quad (7)$$

$$\text{Energy yield} = \text{mass yield} \cdot \text{energy densification ratio} \quad (8)$$

where:

Mass of dry biochar—mass of (dry) biochar after the process of torrefaction, g;

Mass of dried raw MSC—dried mass of MSC used in the process of torrefaction, g;

100—conversion to percent;

HHV of biochar—high heating value of biochar after the process of torrefaction, J·g⁻¹;

HHV of raw MSC—high heating value of dried MSC (raw material) used for torrefaction, J·g⁻¹.

2.4. Proximate Analysis

The samples were tested in three replicates for:

- Moisture content, determined in accordance with [45], by means of the laboratory dryer (WAMED, model KBC-65W, Warsaw, Poland) (Raw MSC and biochars).
- Volatile solids, determined in accordance with [46], by means of the SNOL 8.1/1100 muffle furnace (Utena, Lithuania) (Raw MSC).
- The ash content, determined in accordance with [47], by means of the SNOL 8.1/1100 muffle furnace (Utena, Lithuania) (Raw MSC).
- High heating value (HHV), determined in accordance with [48], by means of the IKA C2000 basic calorimeter (Raw MSC and biochars).

The obtained data are presented in our previous article [43] and detailed in the Supplementary Material file “MSC torrefaction data.xlsx”. The data article contains the results of the raw MSC and obtained biochars fuel properties, TGA analysis results.

3.1. Torrefaction Process Models

Polynomial models of the influence of torrefaction temperature and MSC residence time in the torrefaction reactor on mass and energy efficiency of the torrefaction process, energy densification ratio, organic matter, ash, the higher heating value of torrefied biomass were built using the raw data [43]. The model parameters were estimated due to the non-linear regression analysis. Regression

analysis used a 2-degree polynomial with a general form, with intercept (a_1) and five regression coefficients (a_{2-6}) (Equation 9).

$$f(T, t) = a_1 + a_2 \cdot T + a_3 \cdot T^2 + a_4 \cdot t + a_5 \cdot t^2 + a_6 \cdot T \cdot t \quad (9)$$

where:

$f(T, t)$ - the biochar property obtained under T - temperature, and t - residence time conditions,

a_1 - intercept (-),

a_{2-6} - regression coefficient (-),

T - temperature, $T = 200-300$ °C,

t - residence time, $t = 0-60$ min.

The regression analysis was performed using the Statistica 13 software (StatSoft, Inc., TIBCO Software Inc. Palo Alto, CA, USA). For the determination of model parameters, the degree of matching to raw data, the determination coefficient (R^2) was calculated.

3. Results

The k values significantly ($p < 0.05$) increased with the temperature of the torrefaction process. The lowest k value was recorded at 200 °C ($k = 1.7 \cdot 10^{-5} \text{ s}^{-1}$) and the highest ($k = 4.6 \cdot 10^{-5} \text{ s}^{-1}$) at 300 °C (Table 3). Similar dependence was confirmed by Dhanavath et al. [49]. However, the increase in k in relation to torrefaction temperature was not linear. The significant ($p < 0.05$) differences in k values were observed for 300 °C, and the values obtained in temperatures between 200 and 260 °C, however no significant increase between 200 °C and 260 °C was observed (Table A1). Torrefaction at 280 °C caused the significant increase of k value in comparison to 200 °C. The results indicate that the temperature must be > 280 °C to achieve the significant acceleration of the torrefaction process.

Similarly, to [50, 51] we estimated the activation energy for the whole torrefaction process. On the base of estimated k values, the activation energy of MSC torrefaction, reaching about $22.3 \text{ kJ} \cdot \text{mol}^{-1}$ was determined (Table 3). The obtained E_a value is low in comparison with typical woody biomass, where, for example, for beech and spruce, these values were $150 \text{ kJ} \cdot \text{mol}^{-1}$ and $155 \text{ kJ} \cdot \text{mol}^{-1}$, respectively [52], for willow from 46 to $152 \text{ kJ} \cdot \text{mol}^{-1}$, [53] pine $131 \text{ kJ} \cdot \text{mol}^{-1}$, and fir $128 \text{ kJ} \cdot \text{mol}^{-1}$ [54]. However, these values have been determined by different methods and models. The kinetic model used in this work was a global first-order kinetics model, as it was part of the preliminary study. This model allows estimating solid mass yield at a specific temperature and time of the process. Due to high ash content in MSC, and low range of used temperatures, we recommend additional experiments on the kinetics of the process, using more complex models based on first-order kinetics with distributed activation energy models (DAEMs), pseudo-kinetics or multi-component first-order kinetic models.

Table 3. The kinetic parameters of MSC torrefaction: torrefaction constant rate (k) for given temperatures (with values of determination coefficients (R^2) for k estimation), Equation (5) parameters, determination coefficient of equation 5 parameters estimation, and activation energy of MSC torrefaction.

Constant rate	Temperature, °C					
	200	220	240	260	280	300
k_1, s^{-1}	0.000008 (0.902)	0.000020 (0.847)	0.000024 (0.821)	0.000028 (0.914)	0.000030 (0.930)	0.000047 (0.845)
k_2, s^{-1}	0.000020 (0.891)	0.000018 (0.823)	0.000023 (0.901)	0.000023 (0.953)	0.000032 (0.957)	0.000039 (0.942)
k_3, s^{-1}	0.000022 (0.812)	0.000017 (0.802)	0.000012 (0.883)	0.000024 (0.925)	0.000034 (0.947)	0.000052 (0.870)
Mean± standard deviation, s^{-1}	0.000017 $\pm 7.5 \cdot 10^{-6}$	0.000018 $\pm 1.5 \cdot 10^{-6}$	0.000020 $\pm 6.5 \cdot 10^{-6}$	0.000025 $\pm 2.7 \cdot 10^{-6}$	0.000032 $\pm 1.7 \cdot 10^{-6}$	0.000046 $\pm 6.3 \cdot 10^{-6}$
Equation (5) parameters	$y = -2678.7x - 5.5$					
Determination coefficient (R^2) of equation 5 parameters estimation	0.893					
Activation energy, $J \cdot mol^{-1}$,	22271.4					

The experiment showed that the HHV increased due to torrefaction in all studied variants in comparison to raw MSC biomass $13.7 \text{ MJ} \cdot \text{kg}^{-1} \text{ d.m.}$ (Figure 2). The significantly ($p < 0.05$) lowest values were noted for temperature 200°C (all duration times) from 14.1 to $14.4 \text{ MJ} \cdot \text{kg}^{-1} \text{ d.m.}$ The best ($p < 0.05$) fuel properties were noted for biochars obtained from MSC under 280°C from 16.9 to $17.9 \text{ MJ} \cdot \text{kg}^{-1} \text{ d.m.}$ In the case of 220°C , the significant ($p < 0.05$) influence of torrefaction duration time on the increase of HHV was noted (Table A2). On the other hand, the increase of torrefaction duration time decreased ($p < 0.05$) the HHV under the temperature of 300°C , which could be related to organic matter volatilization and mineralization. Additionally, the increase of the torrefaction temperature from 200 to 280°C , for the same duration times) increased ($p < 0.05$) the HHV (Figure 2, Table A2). The experiment showed, that to achieve the highest HHV of the biochar, MSC should be torrefied under the temperature of 280°C , and the duration time of 60 min.

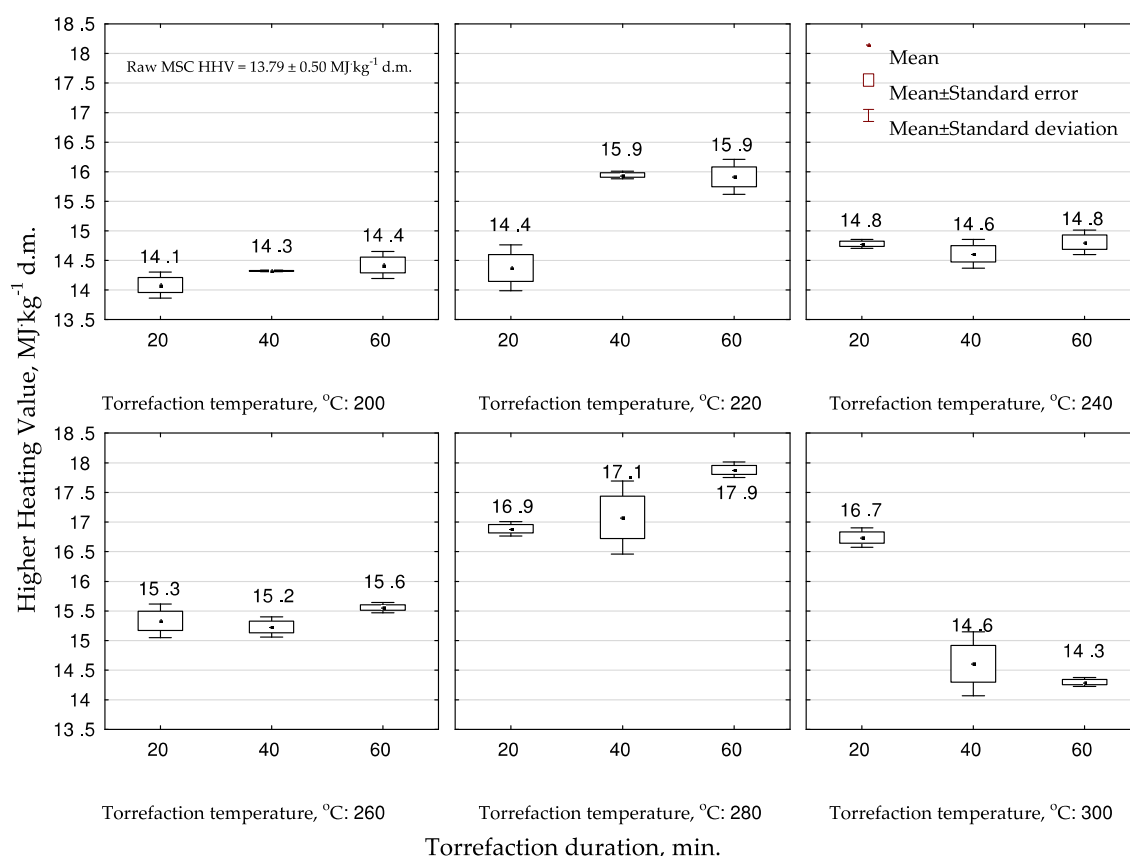


Figure 2. The mean values higher heating value of raw MSC and biochars produced from MSC in relation to torrefaction temperature and torrefaction duration.

The second-degree polynomial model of torrefaction temperature and duration influence on HHV was proposed (Figure 3) using raw data presented previously [43]. The statistical evaluation showed, that determination coefficient was relatively low (0.357) (Figure 3), and only two model regression coefficients (a_3 , and a_6) were statistically significant ($p < 0.05$) (Table A3). Such low fitting degree of the model parameters to existing data could be due to a relatively low number of repetitions ($n=3$ for each variant) or/and to a low degree of the polynomial. To achieve better results suitable for MSC torrefaction optimization, more sophisticated research with a higher number of repetition (to decrease the degree of heterogeneity of the results) with the application of better-fitting models are required.

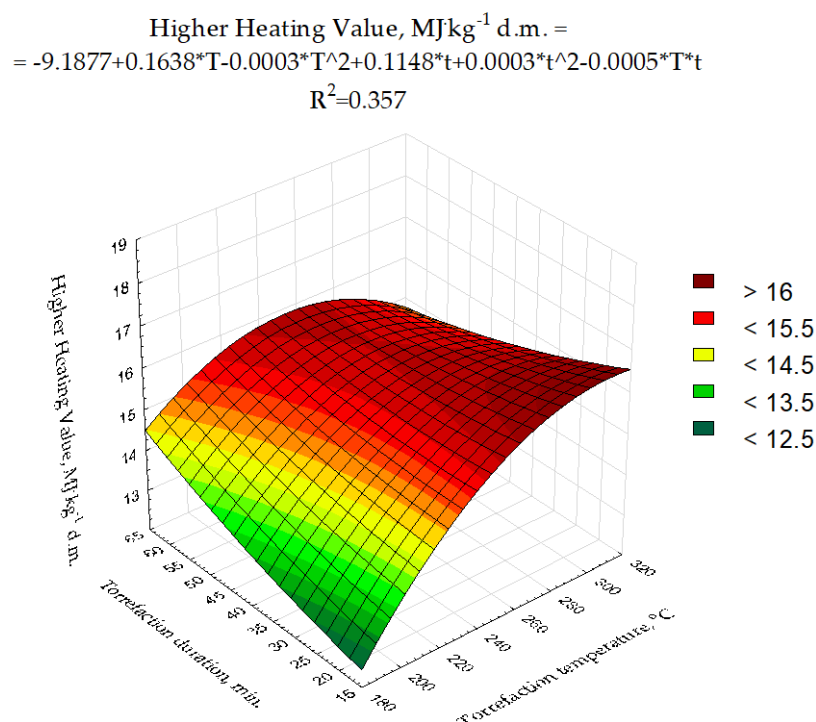


Figure 3. The influence of torrefaction temperature and torrefaction duration on *HHV* of biochars produced from MSC. Mathematical model (Equation 9) includes parameters and determination coefficient of model fitting to experimental data (R^2).

We determined the mass and energy yields to analyze the process efficiency. Mass and energy yields were calculated according to Equations (6)-(8) on the base of the mean values of *HHV* and masses from the TGA [43] for a given torrefaction temperature and duration times. The highest mass yield of biochar was achieved for temperatures 200 and 220 °C and ranged between 96.9 and 98.5%, respectively (Figure 4). Mass yield under higher temperatures decreased and also depended on torrefaction duration time. The increase of duration time decreased the mass yield. The lowest achieved value, 87.9% was in the case of 300 °C, and 60 min (Figure 4). From a practical point of view, the high mass yield is important, when biomass or waste is converted to biochar for agricultural purposes. Therefore, for the optimization of that goal, the second-degree polynomial model of torrefaction temperature and duration influence on biochar's mass yield was proposed (Figure 5). The statistical evaluation showed, that determination coefficient was high (0.953) (Figure 5), but only model regression coefficients related to torrefaction temperature (a_2 , a_3 , and a_6) and intercept (a_1) were statistically significant ($p < 0.05$) (Table A4).

Energy yield in biochar indicates the efficiency of the chemical energy densification due to thermochemical process, concerning the mass loss of the treated MSC. The highest energy yield values exceeding 116.5-120.3% were noted for 280 °C which was also correlated with process duration. The increase of the temperature to 300 °C decreased the energy yield to 91%. Thus, for fuel production, the temperature 280 °C and the process duration of 60 min should be applied. Additionally, for optimization of MSC conversion to biochar for energy purposes, the second-degree polynomial model of torrefaction temperature and duration influence on biochar's energy yield was proposed (Figure 7). The statistical evaluation showed that determination coefficient was not high (0.314) (Figure 7), yet all the regression coefficients were statistically significant ($p < 0.05$) (Table A5). Low degree of model fitting to obtained data could be related to a similarly low degree of fitting of

the model proposed for the *HHV*. *HHV* values are used for energy yield calculations. Similarly, to achieve better results suitable for MSC torrefaction optimization more complex research with a higher number of repetition (to decrease the degree of heterogeneity of the results of *HHV*) with the application of better-fitting models are required.

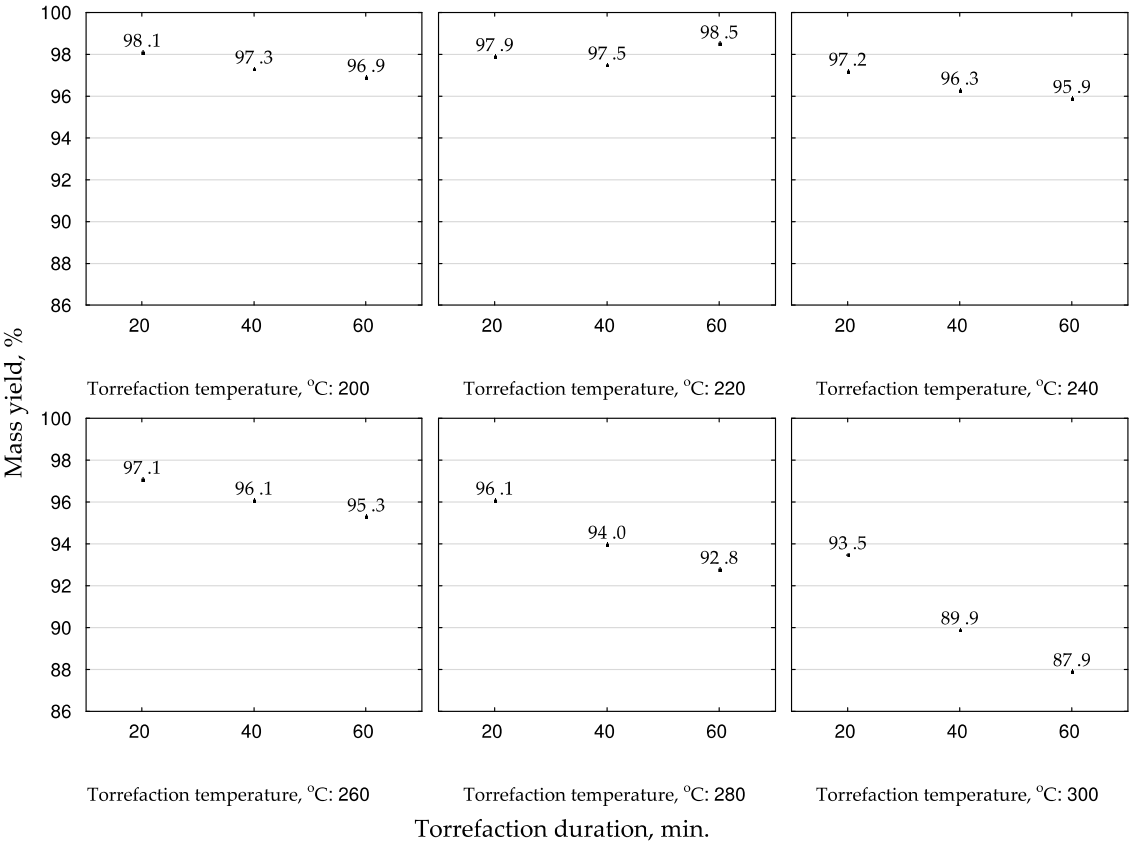


Figure 4. The mass yield values of biochars produced from MSC in relation to torrefaction temperature and torrefaction duration.

Mass yield, % = 39.0175+0.5065*T-0.001*T^2+0.1695*t+0.001*t^2-0.0012*T*t

R²=0.953

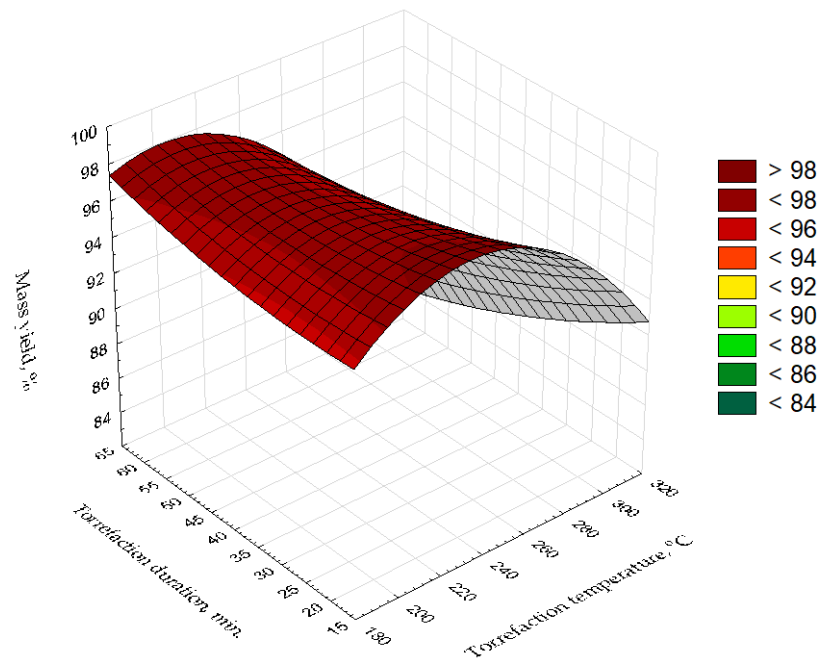


Figure 5. The influence of torrefaction temperature and torrefaction duration on the mass yield of biochars produced from MSC. Mathematical model (Equation 9) includes parameters and determination coefficient of model fitting to experimental data (R²).

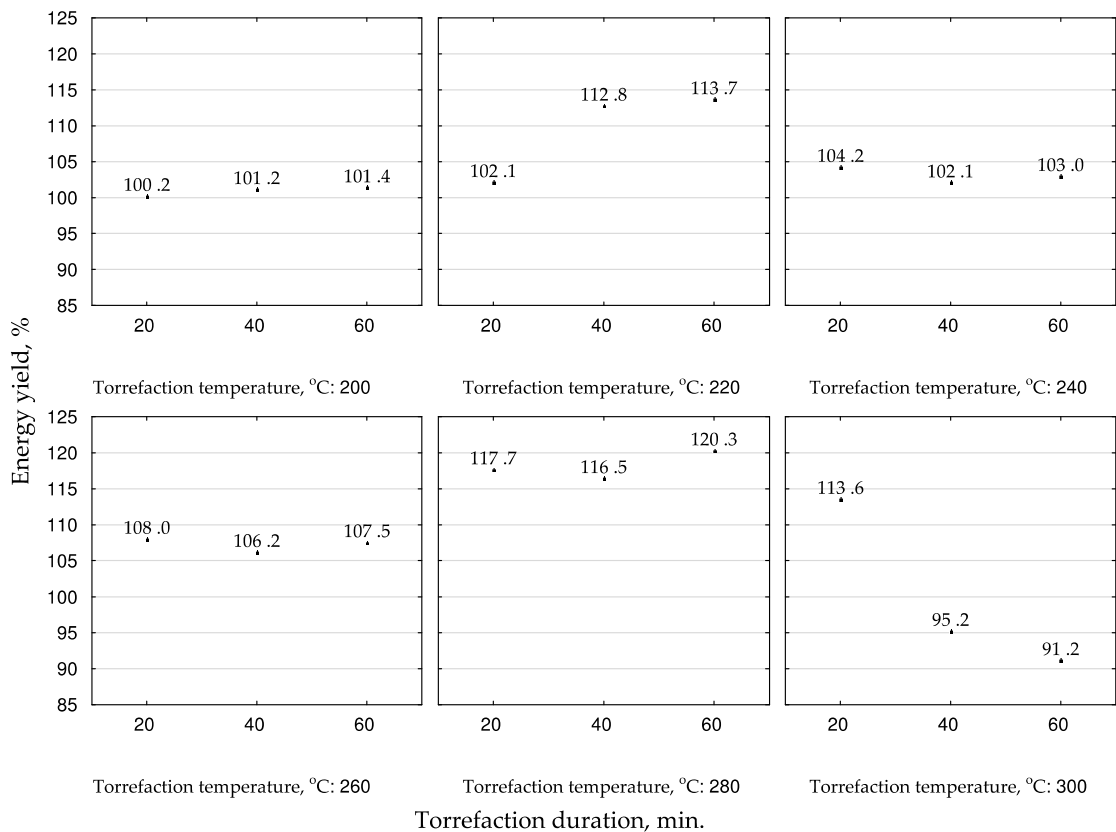


Figure 6. The energy yield values of biochars produced from MSC in relation to torrefaction temperature and torrefaction duration.

$$\text{Energy yield, \%} = -124.8729 + 1.6815 \cdot T - 0.0029 \cdot T^2 + 0.9949 \cdot t + 0.0032 \cdot t^2 - 0.0051 \cdot T \cdot t$$

$$R^2 = 0.314$$

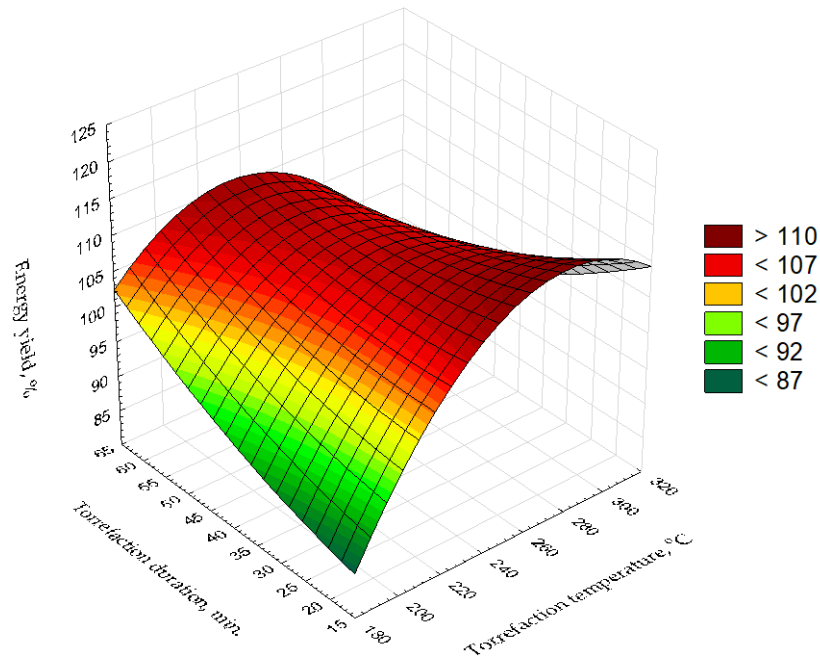


Figure 7. The influence of torrefaction temperature and torrefaction duration on energy yield in biochars produced from MSC. Mathematical model (Equation 9) includes parameters and determination coefficient of model fitting to experimental data (R^2).

4. Discussion

We have shown a concept for an alternative utilization of abundant biowaste (MSC). The MSC has the potential for improved management that is both sustainable and economical [1-25]. We have proposed to treat MSC via torrefaction to produce biochar with improved fuel properties. This research showed that using torrefaction under 280 °C for 60 min, it is possible to increase the *HHV* of raw MSC from $\sim 13.7 \text{ MJ} \cdot \text{kg}^{-1}$ to $\sim 18 \text{ MJ} \cdot \text{kg}^{-1}$. This *HHV* is comparable with energy content in non-agglomerating highly volatile coals ($17.4 < HHV < 23.9 \text{ MJ} \cdot \text{kg}^{-1}$) or lignite ($HHV < 17.4 \text{ MJ} \cdot \text{kg}^{-1}$) [55]. Our research also showed that the highest efficiency (i.e., the energy yield) was achieved under temperature 280 °C and during 60 min of the process.

Based on these results and using the best variant (T and t), a simple model [56] was proposed (after some modifications) for estimating the value of biochar produced in relation to commercial coal fuel available on the market. The model also calculates the theoretical maximum profit from the MSC torrefaction. The calculations assume that part of the torrefied biomass is used to maintain the torrefaction process itself. Calculations do not include labor costs, harvesting, transport, processing, and other costs related to the torrefaction process as well as the distribution of produced fuel.

Data for calculations:

- mass of MSC, Mg, assumed 1 Mg,
- moisture content of MSC, %, assumed 65.32% (Table 2),
- torrefaction parameters of temperature and time assumed 280 °C and 60 min, respectively.

Initial calculations:

The dry mass of MSC:

$$mr_d = mr_w - mr_w \cdot MC \quad (10)$$

where:

mr_d – dry mass of MSC, Mg

mr_w – wet mass of MSC, Mg

MC – moisture content of MSC, %.

Amount of water in MSC:

$$m_w = mr_w - mr_d \quad (11)$$

where:

m_w – mass of water in MSC, Mg.

Main properties of torrefied biomass calculations:

Mass yield (MY) of torrefaction was based on Figure 4. Mass of torrefied biomass after torrefaction:

$$mtb = mr_d \cdot MY \quad (12)$$

where:

mtb – mass of torrefied MSC after torrefaction process at T , and t conditions.

HHV of torrefied MSC was based on Figure 2. The total energy in torrefied MSC:

$$E_{tb} = mtb \cdot HHV \cdot 1000 \quad (13)$$

where:

E_{tb} – energy in torrefied biomass, kJ

1000 – conversion of Mg to kg.

Energy need to torrefaction process:

Data for calculations [56]:

- T_a – ambient temperature, °C, assumed 15 °C,
- T_b – boiling point of water, 100 °C,
- latent heat of water vaporization, 2500 kJ·kg⁻¹ [58],
- specific heat of water, 4.18 kJ·kg⁻¹ [59],
- specific heat of wood (assumed for these calculations), kJ·kg⁻¹, assumed 1.6 kJ·kg⁻¹ [59].

The energy needed to heat water contained in MSC:

$$E_w = m_w \cdot Cp_{water} \cdot (T_b - T_a) \quad (14)$$

where:

E_w – energy needed to heat water contained in MSC, MJ

Cp_{water} – specific heat of water, 4.18 kJ·kg⁻¹.

The energy needed to water vaporization:

$$E_{ev} = m_w \cdot L_h \quad (15)$$

where:

E_{ev} – energy needed to vaporization of water contained in MSC, MJ

L_h – latent heat of water vaporization, kJ·kg⁻¹.

The energy needed to heat MSC during torrefaction:

$$E_{hw} = mr_d \cdot Cp_{wood} \cdot (T - T_a) \quad (16)$$

where:

E_{hw} – energy needed to heat MSC from ambient to torrefaction temperature, MJ

Cp_{wood} – specific heat of wood (assumed for these calculations), kJ·kg⁻¹.

Total energy needed to torrefied MSC:

$$E = E_w + E_{ev} + E_{hw} \quad (17)$$

where:

E – energy needed to torrefied MSC

Estimation of the value of torrefied biomass

Estimations were based on the price of commercial coal fuel available in the Poland market in 2019 and its heating value. The pricing in PLN was converted to € at the current exchange rate. Data for calculations:

- Price of commercial coal fuel, €·Mg⁻¹, assumed 170 €·Mg⁻¹ [60],
- HHV of commercial coal fuel, MJ·kg⁻¹, assumed 23 MJ·kg⁻¹ [60],

The estimated value of torrefied biomass:

$$V_{tb} = \frac{V_{ccf} \cdot HHV_{tb}}{HHV_{ccf}} \quad (18)$$

where:

V_{tb} – estimated value of torrefied MSC, €·Mg⁻¹

V_{ccf} – value (price) of commercial coal fuel, €·Mg⁻¹

HHV_{ccf} – higher heating value of commercial coal fuel, MJ·kg⁻¹.

Profit from torrefied MSC

Mass of torrefied MSC net (when assumed that part of it is used as fuel to the process of torrefaction):

$$mtb_n = \frac{E_{tb} - E}{HHV_{tb}} \quad (19)$$

where:

mtb_n – mass of torrefied MSC net, Mg.

The estimated value of torrefied MSC was obtained for 1 Mg of wet MSC (65.32% moisture content). For MSC torrefaction (280 °C, 60 min) mass yield of MSC biochar was 92.8%, and HHV of torrefied MSC was 17.9 MJ·kg⁻¹. For these conditions, the estimated value of produced biochar was 132.3 €·Mg⁻¹ d.m.. The net mass obtained after torrefaction was 0.209 Mg d.m. Thus, the estimated value of biochar from MSC obtained from 1 Mg of wet MSC was 27.7 €·Mg⁻¹ w.m.

The presented simplified calculation of the value (as a fuel) of the biochar is the first step for the evaluation of the profitability of utilization of torrefaction technology to MSC. The model was based on simple assumptions. Thus, it is affected by varying market conditions. Therefore, more advanced and precise models with a comprehensive analysis of costs are warranted as a separate work.

5. Conclusions

Presented research revealed that it is possible to produce biochar from MSC. The obtained biochar has HHV similar to a good quality lignite coal. Reaction kinetics analyses of MSC torrefaction showed that the intensive organic matter decomposition started above 280 °C. Considering the application of produced biochar from MSC for agriculture, the highest mass yield was obtained under 220 °C. If the MSC biochar production is dedicated to solid fuel production, the torrefaction temperature 280 °C, and 60 min of the process should be applied to maximize the energy yield. For MSC torrefaction (280 °C, 60 min) mass yield of MSC biochar was 92.8%, and HHV of torrefied MSC was 17.9 MJ·kg⁻¹. For these conditions, the estimated value of produced biochar was 132.3 €·Mg⁻¹ d.m.. The net mass obtained after torrefaction was 0.209 Mg d.m. Thus, the estimated value of biochar from MSC obtained from 1 Mg of wet MSC was 27.7 €·Mg⁻¹ w.m. Second-degree polynomial models for the torrefaction process optimization were proposed. However, more complex research is required for model calibration and scaling up. The initial economic evaluation showed that MSC torrefaction may be profitable. This research provides a basis for alternative use of an abundant biowaste and can help charting improved, sustainable mushroom production.

Supplementary Materials: The following are available online at Sygula, E.; A. Koziel, J.; Białowiec, A. Waste to Carbon: Preliminary Research on Mushroom Spent Compost Torrefaction. Preprints 2019, 2019060189 (doi: 10.20944/preprints201906.0189.v1). File “MSC torrefaction data.xlsx”.

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Appendix A

Table A1. Calculated values of probability ‘p’ of ANOVA analysis with Tukey's Test RSD of variable: torrefaction constant rate (*k*). Highlighted (in bold) differences are significant at $p < 0.05000$.

Torrefaction temperature, °C	Calculated values of probability ‘p’				
	200	220	240	260	280
200					
220	0.998400				
240	0.976232	0.999461			
260	0.401048	0.618619	0.793686		
280	0.030215	0.058894	0.099319	0.572968	
300	0.000291	0.000407	0.000562	0.003267	0.051587

Table A2. Calculated values of probability '*p*' of ANOVA analysis with Tukey's Test RSD of variable: Higher Heating Value of biochar. Highlighted differences are significant at $p < 0.05000$.

Torrefaction temperature, °C	Torrefaction duration, min	Calculated values of probability ' <i>p</i> '																
		200	200	200	220	220	220	240	240	240	260	260	260	280	280	280	300	300
		20	40	60	20	40	60	20	40	60	20	40	60	20	40	60	20	40
200	20																	
200	40	0.9996																
200	60	0.9806	1.0000															
220	20	0.9960	1.0000	1.0000														
220	40	0.0002	0.0002	0.0002	0.0002													
220	60	0.0002	0.0002	0.0002	0.0002	1.0000												
240	20	0.1815	0.8098	0.9680	0.9109	0.0009	0.0012											
240	40	0.6147	0.9965	1.0000	0.9996	0.0002	0.0003	1.0000										
240	60	0.1425	0.7419	0.9426	0.8636	0.0012	0.0017	1.0000	1.0000									
260	20	0.0004	0.0057	0.0191	0.0105	0.3675	0.4470	0.5434	0.1461	0.6228								
260	40	0.0011	0.0202	0.0621	0.0361	0.1546	0.2009	0.8356	0.3518	0.8887	1.0000							
260	60	0.0002	0.0004	0.0012	0.0007	0.9386	0.9675	0.0865	0.0124	0.1127	0.9998	0.9862						
280	20	0.0002	0.0002	0.0002	0.0002	0.0125	0.0088	0.0002	0.0002	0.0002	0.0002	0.0002	0.0002					
280	40	0.0002	0.0002	0.0002	0.0002	0.0012	0.0009	0.0002	0.0002	0.0002	0.0002	0.0002	0.0002	1.0000				
280	60	0.0002	0.0002	0.0002	0.0002	0.0002	0.0002	0.0002	0.0002	0.0002	0.0002	0.0002	0.0002	0.0067	0.0632			
300	20	0.0002	0.0002	0.0002	0.0002	0.0694	0.0509	0.0002	0.0002	0.0002	0.0002	0.0002	0.0007	1.0000	0.9799	0.0011		
300	40	0.6309	0.9972	1.0000	0.9997	0.0002	0.0003	1.0000	1.0000	1.0000	0.1389	0.3382	0.0116	0.0002	0.0002	0.0002	0.0002	
300	60	0.9999	1.0000	1.0000	1.0000	0.0002	0.0002	0.7392	0.9909	0.6640	0.0041	0.0146	0.0003	0.0002	0.0002	0.0002	0.0002	0.9924

Table A3. Statistical parameters of the polynomial model of the influence of torrefaction temperature and MSC residence time in the torrefaction reactor on the higher heating value of biochar. Regression analysis used a 2-degree polynomial with a general form, with intercept (a_1) and 5 regression coefficients (a_2 -6) (Equation 9). Highlighted values are significant at $p < 0.05000$.

Regression coefficients	Value of regression coefficient	Standard Error	T value, df=156	Determined p value	Lower range of confidence interval	Upper range of confidence interval
a_1 (intercept)	-9.18772	8.404435	-1.09320	0.279763	-26.0860	7.710533
a_2	-0.00025	0.000130	-1.94593	0.057531	-0.0005	0.000008
a_3	0.16382	0.065675	2.49436	0.016114	0.0318	0.295867
a_4	0.00031	0.000687	0.45333	0.652351	-0.0011	0.001692
a_5	0.11483	0.080328	1.42947	0.159347	-0.0467	0.276336
a_6	-0.00055	0.000232	-2.35809	0.022491	-0.0010	-0.000081

Table A4. Statistical parameters of the polynomial model of the influence of torrefaction temperature and MSC residence time in the torrefaction reactor on mass yield value of biochar. Regression analysis used a 2-degree polynomial with a general form, with intercept (a_1) and 5 regression coefficients (a_2 -6) (Equation 9). Highlighted values are significant at $p < 0.05000$.

Regression coefficients	Value of regression coefficient	Standard Error	T value, df=12	Determined p value	Lower range of confidence interval	Upper range of confidence interval
a_1 (intercept)	39.01744	11.29449	3.45455	0.004765	14.40886	63.62603
a_2	0.50652	0.08826	5.73904	0.000093	0.31422	0.69882
a_3	-0.00105	0.00017	-6.00537	0.000062	-0.00143	-0.00067
a_4	0.16952	0.10795	1.57039	0.142306	-0.06568	0.40473
a_5	0.00104	0.00092	1.12846	0.281182	-0.00097	0.00305
a_6	-0.00122	0.00031	-3.91408	0.002057	-0.00190	-0.00054

Table A5. Statistical parameters of the polynomial model of the influence of torrefaction temperature and MSC residence time in the torrefaction reactor on energy yield value of biochar. Regression analysis used a 2-degree polynomial with a general form, with intercept (a_1) and 5 regression coefficients (a_{2-6}) (Equation 9).

Regression coefficients	Value of regression coefficient	Standard Error	T value, df=12	Determined p value	Lower range of confidence interval	Upper range of confidence interval
a_1 (intercept)	-124.873	119.6896	-1.04331	0.317370	-385.654	135.9085
a_2	1.681	0.9353	1.79781	0.097396	-0.356	3.7193
a_3	-0.003	0.0018	-1.55785	0.145239	-0.007	0.0011
a_4	0.995	1.1440	0.86967	0.401540	-1.498	3.4874
a_5	0.003	0.0098	0.32266	0.752508	-0.018	0.0245
a_6	-0.005	0.0033	-1.55290	0.146412	-0.012	0.0021

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