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THERMAL KINETIC ANALYSIS OF THE SPENT MUSHROOM SUBSTRATE AND HYDROCHAR

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Abstract
A carbon-rich product, hydrochar, was synthesized by hydrothermal carbonization (HTC) of spent mushroom substrate (SMS), at temperature of 260 °C. The thermal kinetic analysis has shown that hydrothermally treatment improve the combustion behavior of hydrochar. The kinetic parameters were determined by Kissinger and Ozawa methods. The SMS-260 had a significantly lower activation energy compared to the SMS, which means that this hydrochar needs a smaller amount of energy to start combustion. Generally, the preliminary results show that HTC is an effective way to transform SMS into alternative solid biofuel.

Introduction
The growing world population and industrial development require more energy than can be supplied by conventional means [1]. Excessive use of fossil fuels is accompanied by an increase in emissions of carbon dioxide, nitrogen oxides and other harmful particles, which has negative consequences for the environment [2]. Therefore, in order to reduce the problem of this kind, the increasing focus is on the use of biomass as a renewable energy source. The advantage of biomass is easy transformation into another form of energy, using various thermochemical processes. HTC compared to other thermochemical methods has shown numerous advantages such as lower reaction temperatures, shorter process duration, the possibility of using biomass without prior drying, low ash content in the obtained products, prevention of CO_2 and other harmful gases during biomass processing, etc [3].
The conversion of biomass to a hydrochar using HTC takes place in an aqueous medium, at a moderate temperature (180–260 °C) and autogenous pressure (2–10 MPa) [4]. The properties of the hydrochar are regulated by process parameters (pressure, temperature, reaction time, and biomass and water ratio) [4]. Depending upon the process conditions used, the hydrochars can be formed with significantly improved fuel characteristics.
In addition, the data obtained from the thermal kinetics of hydrochar can be of great importance for the design of combustion equipment on an industrial scale [5,6]. Therefore, in this study, SMS from Agaricus bisporus production was carbonized using HTC technology at 260 ºC and then kinetic anlysis was carried out of SMS and hydrochar using TG data at three heating rates.

Experimental
Material and synthesis of hydrochar
SMS was obtained from the local mushroom production Ekofungi, located in Belgrade. Synthesis of hydrochar were performed in a autoclave reactor (Carl Roth, Model II). About 10 g of SMS was mixed with 150 mL of deionized water and heated at 260 °C for 60 min. After that, the reactor was cooled down to room temperature. The obtained hydrochar denoted as SMS-260.

Thermogravimetric analysis
The thermal properties of the SMS and SMS-260 were investigated by the simultaneous non-isothermal TGA and DTA using a Setaram Setsys Evolution 1750 instrument. The samples were heated from 25 to 1000 °C with a heating rate of β = 5, 10 and 20 °C min^{-1} in the air atmosphere. The average mass of the samples was about 7 mg.
The relevant kinetic parameter, activation energy (E_a), in the combustion process can be obtained by the Kisinger (1) and Ozawa (2) method, which is based on the functional dependence of the heating rate (β) and the exothermic peak temperature shift (T_{max}):

$$\log\left(\frac{\beta}{T_{max}^2}\right) = \log\frac{Z\cdot R}{Ea} - \frac{Ea}{2.303\cdot RT_{max}} \quad (1)$$

$$\log\beta = \log\frac{Z\cdot Ea}{R} - 2.315 - 0.4567\left(\frac{Ea}{R\cdot T_{max}}\right) \quad (2)$$

According to the Eq. (1) and Eq. (2), the plot of $\log\left(\frac{\beta}{T_{max}^2}\right)$ or $\log\beta$ against $1/T_{max}$ will present a straight line at different heating rates. Then kinetic parameters can be derived from the plot. The activation energy E_a can be calculated from the slope while the pre-exponential factor Z is determined by the intercept of regression lines.

Results and discussion
Kinetic parameters of thermal degradation are required for effective prediction of combustion behavior and optimization of the thermal decomposition of the different feedstock. The crucial kinetic parameters, activation energy (E_a), pre-exponential factor (Z) and correlation coefficient (R^2) at various heating rates of SMS and SMS-260 were designated by the Kisinger and Ozawa.

Results from Table 1, showed that SMS-260 has better combustion properties that the SMS, visible through the lower E_a [2]
The Ea values for SMS were 238.8 and 235.7 kJ mol^{-1}, while for SMS-260 were 53.4 and 61.7 kJ mol^{-1} calculated by Kissinger and Ozawa methods, respectively. The R^2 obtained by the Ozawa was higher than that obtained by the Kissinger, indicating that the Ozawa method was more suitable for the evaluation of the combustion process of samples.

The values of the pre-exponential factor (Z) show the existence of the complex nature of the material and the reactions that take place during combustion. The Z value, less than 10^5 s^{-1} is ascribed to porous structures and suggesting easier and faster decomposition of SMS-260 [7]. On the other hand, the values of Z of more than 10^{14} s^{-1} indicate a slower and difficult decomposition of the SMS structure [7].

Table 1
Kinetic parameters of SMS and SMS-260 by Kissinger and Ozawa.

	Kissinger			Ozawa		
Samples	E_a (kJ mol^{-1})	R^2	Z (min^{-1})	E_a (kJ mol^{-1})	R^2	Z (min^{-1})
SMS	238.3	0.9912	$3.84\cdot10^{21}$	235.7	0.9918	$2.38\cdot10^{21}$
SMS-260	53.4	0.8950	$1.71\cdot10^{3}$	61.7	0.9294	$2.59\cdot10^{3}$

Conclusion
Based on the kinetic parameters, it can be concluded that HTC has improved the combustion property of the SMS. A comparative study of the thermal combustion kinetics of SMS and

SMS-260 at different heating rates was conducted using the Kissinger and Ozawa methods. The Ozawa method has proven to be more suitable for assessing the combustion process of samples. The SMS-260 has shown lower activation energy compared to SMS, showing that HTC technology is efficient for converting SMS into solid biofuel with improved combustion performance and reactivity.

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