Upgrading fuel potentials of waste biomass via hydrothermal carbonization

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Abstract

In recent decades, massive exploitation of fossil fuels caused a growing demand for the production of energies from renewable sources. Hydrochar obtained from waste biomass via hydrothermal carbonization (HTC) possesses good potentials as a biofuel. Therefore, we performed HTC of corn cob, paulownia leaves, and olive pomace at different temperatures (180, 220, and 260 °C). The main goal of this study was to comparatively evaluate the influence of HTC conditions on the structure and fuel characteristics of the obtained solids. The results showed that the yields of hydrochar decrease significantly with increasing temperature in all samples. The carbon content and higher heating value increased and reached the highest values in hydrochars obtained at 260 °C, while the content of volatile matter decreased. Furthermore, the Van Krevelen diagram reveals that the transformation of feedstock to lignite-like products upon HTC was achieved. In this study, the results showed that processes of dehydration and decarboxylation during HTC provoke intensive biomass transformation and that hydrochars obtained at higher temperatures have significantly enhanced fuel properties and fewer volatiles compared to the feedstock.

Keywords: biomass conversion; hydrochar; biofuel; corn cob; paulownia leaves; olive pomace.

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1. INTRODUCTION

Over the years, the increasing demand for energy caused extensive depletion of fossil fuels, which led to a series of environmental problems. To minimize these damaging effects, many countries have turned to the adoption and implementation of the concept of a bio-based economy, which involves the utilization of waste biomass as new value-added materials, instead of landfilling. Waste biomass is a source that includes different agricultural and forest residues, municipal waste streams, sewage sludge, organic waste, and others. However, the direct application of crude biomass has several disadvantages that include low energetic potential, hygroscopic nature, and release of volatiles during combustion [1,2]. Additionally, high ash content due to the presence of different metals in raw biomass causes corrosion, clogging, and/or clinkers formation in the furnaces. The mentioned problems impair the quality and combustion efficiency of the solid fuel and therefore reduce the motivation for waste biomass utilization. To overcome these disadvantages, development of thermochemical conversion processes of biomass into multi-functional products received considerable attention. These technologies are torrefaction, pyrolysis, gasification, and hydrothermal carbonization (HTC) [3-5]. The last-mentioned technology has been recognized as highly effective for production of carbon-rich material, hydrochar, from wet and waste biomass.

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HTC process is carried out in a sealed autoclave, in which the biomass in water suspension is exposed to moderate temperatures (180-280 °C) and autogenetic pressure (up to 50 bar). Reaction times vary from several minutes to several hours. Unlike traditional conversion methods, the main advantage of HTC is that it proceeds at much milder reaction conditions. Besides, water as a reaction medium enables processing of wet biomass without prior drying. These characteristics significantly reduce the costs and energy consumption during carbonization and enable utilization of a wide range of waste biomass. Moreover, HTC exhibits a high carbon conversion rate, without methane or CO_2 emission [4-7].

Main products of feedstock decomposition under HTC conditions are carbon-rich hydrochar and process water, rich in organic components. Reaction pathways that cause transformation of the raw biomass into hydrochar include hydrolysis, dehydration, decarboxylation, condensation, polymerization, and aromatization [8]. During the HTC process, water acts as a non-polar solvent and catalyzes the degradation of the biomass constituents. As previously established, this degradation begins with hydrolysis, which requires lower reaction temperatures, while higher temperatures promote dehydration, decarboxylation and condensation reactions [3,9]. Furthermore, carbonization in aqueous medium provides a number of oxygenated functional groups at the solid surface [9]. It is known that the structure and characteristics, and thus further application, of the obtained carbonaceous solids, depend on the applied process conditions, as well as the feedstock type [4,5,7,10]. Previous research has shown that reaction temperature has the most significant role in hydrochar formation. At lower reaction temperatures, hydrochars abundant in functional groups on their surface are formed. This feature makes these materials suitable for potential utilization as adsorbents. On the other hand, elevated temperatures provoke the formation of materials with higher carbon contents and better energetic properties, but with lower solid yield due to intense degradation [9,11].

Summarizing previous findings, it can be concluded that the structure and characteristics of the obtained hydrochars are significantly different from the parental feedstock. Hydrochars exhibit superior performance that includes higher carbon content and energy density, better dewaterability and stability, more reactive groups on the surfaces and improved fuel properties [2,11,12]. Moreover, during carbonization inorganic components are leached into the process water, so hydrochar displays a lower ash content as compared to the starting biomass [6]. Current valorization of hydrochar involves its potential utilization for water purification, as an energy source, for carbon sequestration, as bio-fertilizers, energy storage materials, *etc.* [2,4,5,13-15]. With this regard, numerous waste streams (agricultural residues, algae, municipal solid waste, and sewage sludge) have been utilized as precursors to produce hydrochars [2]. Special attention is drawn to the use of waste lignocellulosic biomass, like agricultural and forest residues, since HTC conversion of these materials provides valuable chemicals, energy sources, adsorbents, and more.

This paper focuses on the valorization of three different bio-residues (corn cob, paulownia leaves, and olive pomace) *via* HTC. The main goal was to examine the influence of process temperature on the structure and characteristics of the obtained hydrochars, towards determination of potentials for further utilization as an alternative energy source. With this aim, solids yield, elemental analysis, along with combustion characteristics that include volatile matter contents, higher heating values (*HHV*), and energy densification (*ED*) were determined in all obtained hydrochars and compared to the feedstock. The practical significance of this paper is to determine suitability of selected biomass as a precursor for the production of energy-rich biofuels, with simultaneous reduction of waste generation in the environment.

2. MATERIALS AND METHODS

2. 1. Biomass collection and preparation

The selected waste biomass samples, corn cob (CC), paulownia leaf (PL), and olive pomace (OP) were randomly collected from open landfill sites where they were disposed after processing. The collected feedstock was air-dried, ground, and sieved in order to provide homogeneity of the sample prior to hydrothermal treatment. Hydrothermal experiments were performed with sieved sample fractions of 0.5 mm.

2. 2. Hydrothermal experiments and hydrochar characterization

In order to produce hydrochar from prepared feedstock, a laboratory autoclave (Carl Roth, Model II, 250 cm^3, Germany) equipped with a temperature controller, thermocouple and a manometer, was used. During the treatment, 10 g of waste biomass in 150 cm^3 of ultrapure water (solid to liquid mass ratio 1:15) were hydrothermally carbonized at three different temperatures: 180, 220, and 260 °C, within 1 h. The pressure during the carbonization process was not controlled. It was autogenic and saturated corresponding to the applied carbonization temperature. Upon completion of carbonization, the solid product was separated from the process water by filtration, rinsed several times using ultrapure water, dried in an oven at 105 °C to constant weight, weighted, and stored until further experiments. The obtained hydrochars were labeled according to the biomass type and temperature at which it was produced, as follows: CC-180, CC-220 and CC-260 (for the CC carbonized at 180, 220, and 260 °C, respectively); PL-180, PL-220 and PL-260 (for the PL carbonized at 180, 220, and 260 °C, respectively), and OP-180, OP-220 and OP-260 (for the OP carbonized at 180, 220, and 260 °C, respectively).

Mass yield of the obtained hydrochars was determined as the ratio of dry hydrochar and dry biomass [4]. Volatile matter (VM) and ash was determined by the standard ASTM D1762-84 (2007) procedure. Additionally, elemental analysis (C, H, N, S) of all samples was performed by using a Vario EL III; C, H, N, S/O Elemental Analyzer (Elementar, Germany) equipped with a thermal conductivity detector (TCD), while O contents (%) were calculated by subtracting the sum of the obtained elemental values from 100 %. The *HHV* and *ED* values were calculated from the results of elemental analysis according to equations (1) and (2), respectively [16,17]:

$$HHV = 0.3491C + 1.1783H + 0.1005S - 0.1034O - 0.0151N - 0.0211Ash \qquad (1)$$

where *C, H, S, O, N* and *Ash* are the mass percentages of the elemental carbon, hydrogen, sulfur, oxygen and nitrogen, and ash content, respectively.

$$ED = \frac{HHV_{\text{hydrochar}}}{HHV_{\text{biomass}}} \qquad (2)$$

All experiments were performed in triplicate and average values is shown in the results.

3. RESULTS

Influence of the process temperature on the solid yield of hydrochars obtained at 180, 220, and 260 °C for the three starting biomass types (CC, PL and OP) is demonstrated in Figure 1.

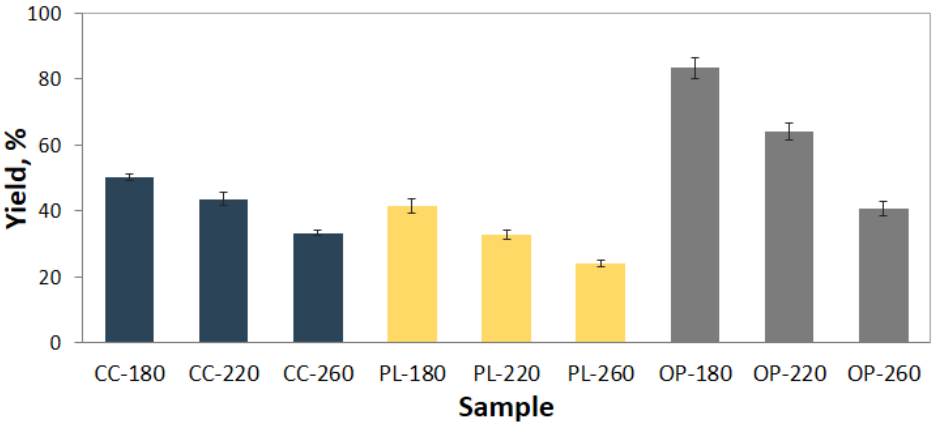

Figure 1. Yields of solid hydrochars obtained from corn cob (CC), paulownia leaf (PL), and olive pomace (OP) at different carbonization temperatures (180, 220 and 260 °C)

As it can be seen, the solid yield of all produced hydrochars decreased with the temperature increase and reached the lowest values for materials produced at 260 °C. Although this decrease is observed for all investigated biomass types, it was the most pronounced for OP, decreasing from 83.25±3.05 % at 180 °C to 40.63±2.02 % at 260 °C. This progressive weight loss upon the increase the reaction temperature can be explained by degradation of the basic constituents of lignocellulosic biomass (hemicellulose, cellulose and lignin) during the hydrothermal treatment, particularly as a result of intense dehydration and decarboxylation reactions with simultaneous leaching of organic and water-soluble components from the solid into the process water. It is known that the degradation of hemicellulose under HTC conditions begins already at 180 °C, while reaction temperatures above 200 °C are required for decomposition of cellulose and lignin into smaller constituents [4,5,18]. Therefore, it can be expected that lignin-rich biomass provides higher mass yields. Accordingly, the highest mass yield observed for the OP-180 in comparison to the CC-180 and PL-180 suggests that OP probably contains more cellulose and lignin than more easily degradable hemicelluloses. On the other hand, the lowest yields are noticed for all PL hydrochars (from 41.44±2.23 % to 24.00±1.05 %) indicating that the main constituents of this biomass are thermally unstable lignocellulosic compounds, which underwent the greatest degradation during the HTC treatment. Our results are in accordance with previous studies of the influence of temperature on the mass yield of hydrochars from different biomass precursors [2,19,20]. It was found that the biomass type directly affected the mass yields of hydrochars produced at the same hydrothermal conditions [2]. The authors stated that the mass yield from a mixed feedstock, such as olive pomace, depends not only on the lignocellulose content but also on interactions between the biomass constituents [2]. According to their observations, the achieved yield upon carbonization at 220 °C was 65.8 and 64.8 % for olive pomace and walnut shell, respectively, which is comparable to the OP-220 yield in the present study (64.00±2.46 %). Recently, in two separate studies a gradual decrease in the hydrochar yield was reported as the temperature was increased from 180 to 260 °C [19,20]. The obtained hydrochars solid yields were in the range 57.20-38.32 % for the spent mushroom substrate [19] and 53.8-35.0 % for the food waste [20]. These values are in accordance with the results of solid yields obtained in our study. Similar to our observations, the decreasing trend as a result of pronounced biomass decomposition with an increase in the reaction temperature was also noticed during carbonization (180-240 °C) of eucalyptus, giant bamboo, coffee wood and coffee parchment [21], as well as during optimization of the HTC process for production of grape pomace [4] and miscanthus [5] hydrochars.

To gain a better insight into the transformation and improvement of fuel characteristics of the obtained hydrochars, analyses of volatile substances, elemental composition, *HHV* and *ED* were performed. Table 1 summarizes the results of volatiles and elemental composition for three selected biomass types before and after carbonization treatment.

Table 1. Volatile contents and elemental compositions for initial biomass samples and hydrochars produced at different temperatures.

Sample	Content, %					
	Volatiles	C	H	N	S	O
CC	90.45±2.14	43.81±0.05	6.08±0.01	0.41±0.11	<0.01	48.86±0.16
CC-180	91.56±1.05	47.20±0.15	5.95±0.01	0.42±0.06	<0.01	46.29±0.20
CC-220	81.83±0.66	48.98±0.04	5.88±0.00	0.28±0.02	<0.01	44.59±0.06
CC-260	55.42±0.21	69.30±0.11	4.88±0.01	0.57±0.01	<0.01	25.11±0.11
PL	76.70±0.71	45.75±0.16	6.03±0.03	3.82±0.02	0.50±0.04	38.19±0.13
PL-180	75.31±1.03	55.24±0.15	6.37±0.12	3.34±0.11	0.45±0.02	29.21±0.06
PL-220	71.15±0.87	60.64±0.08	6.36±0.01	3.08±0.01	0.37±0.02	23.07±0.10
PL-260	62.10±0.58	64.54±0.16	6.34±0.01	3.18±0.20	0.35±0.08	16.72±0.08
OP	82.86±1.37	53.86±0.12	7.28±0.02	1.13±0.03	<0.01	37.53±0.11
OP-180	87.15±2.01	60.93±0.14	7.75±0.08	1.05±0.07	<0.01	30.29±0.31
OP-220	79.66±1.01	64.08±0.17	7.30±0.01	0.75±0.05	<0.01	27.89±0.22
OP-260	66.77±0.42	70.97±0.18	6.80±0.00	0.83±0.06	<0.01	21.41±0.25

From the results (Table 1) it can be concluded that hydrothermal carbonization promoted degradation of volatiles in almost all tested samples. These results vary depending on the biomass type used as a precursor. Consequently, one of the significant objectives of this study was to realize which type of biomass and which carbonization temperature are the most suitable for production of hydrochars with the best fuel characteristics. With this regard, it can be noticed that the CC has the highest content of volatile matter (90.45±2.14 %), although the other two biomass samples have also rather high contents of volatiles. High amount of volatiles is one of the peculiarities of biomass feedstock. This feature is one of the main obstacles for direct combustion of raw biomass since it causes higher reactivity and lower enthalpy, and further, leads to low combustion efficiency, evaporation and emission problems, which are the opposite effects in comparison to fossil coal [22]. Therefore, it can be concluded that CC, PL, and OP are not suitable to be exploited as efficient fuel sources. However, as it can be seen in Table 1, hydrothermal treatment at higher temperatures promoted a significant reduction in the VM content. The exception to this trend was found in OP-180 and CC-180 samples, which showed a slight increase in the VM content in comparison to the initial biomass samples. An increase in volatile matter content (from 80.7 to 82.2 %) during hydrothermal treatment of municipal solid waste at 180 °C was previously reported [23]. Since lignocellulose under HTC conditions starts to hydrolyze at 180 °C, a reason for this unexpected behavior could be accumulation of leached volatile compounds from the process water onto the formed hydrochar surface [24]. Wang *et al.* [25] also observed adsorption of volatile compounds during carbonization of sludge. The authors reveal that this phenomenon is mostly pronounced during HTC treatment at 180 °C, while a further increase in temperature promotes reduction in devolatilization rate and formation of a more stable hydrochar. Consistently, a general decrease in volatile contents upon temperature increase was also noticed during our research. The most intensive reduction in this content is observed in the CC hydrochars, and thus the CC-260 has only 55.42±0.21 % of volatiles, which is significantly lower than that in PL-260 (62.10±0.58 %) and OP-260 (66.77±0.42 %) samples. The observed significant VM content reductions in produced hydrochars upon the temperature increase from 180 to 260 °C is probably induced by hydrolysis, dehydration and decarboxylation of lignocellulosic biomass constituents. Although the mechanism of biomass conversion to hydrochar is not yet fully elucidated, numerous authors have found that it begins with the hydrolysis that causes devolatilization of biomass macromolecules into oligomers and monomers. These fragments are subject to subsequent degradation mechanisms that include dehydration and decarboxylation, followed by aromatization to the formation of carbon rich solids [2,7,9,15,16]. Simultaneous occurrence of these degradation reactions during HTC causes formation of hydrochars with lower volatile contents as compared to the corresponding starting biomasses [2,15,16]. The results (Table 1) indicate that this degradation is more pronounced at higher carbonization temperatures. In hydrothermal carbonization of olive mill wastewater, a decrease in the volatile matter content from 84.00 % to 78.21 % was also noticed during carbonization at different temperatures [15]. Besides, VM content reduction after HTC processing of wood sawdust, walnut shell, tea stalk, olive pomace, apricot seed and hazelnut husk was also observed by Kabakci and Baran [2].

Chemical transformations during HTC can be best described by the results of elemental analysis regarding C, H and O contents. It can be deduced that the hydrochars elemental content is highly dependent on the carbonization temperature. Hence, with the simultaneous lowering of the volatiles, a significant increase in the C content in hydrochar samples was observed. The increase in the reaction temperature from 180 to 260 °C promoted a gradual increase in the C content in the CC samples from the initial 43.81±0.05 % to 47.20±0.15 in CC-180 and up to 69.30±0.11 % in CC-260. Besides, both OP and PL also show an increase in the C content that ranged from 53.86±0.12 % in the OP up to 70.97±0.18 % (OP-260), and from 45.75±0.16 % for PL to 64.54±0.16 % (PL-260). The observed increase in the C content reveals that intensive carbonization of biomass occurred. On the contrary, H and O contents decreased with the increase in the reaction temperature, which further confirms dehydration and decarboxylation of biomass during the HTC process.

According to the obtained values for C, H and O contents, atomic ratios (H/C and O/C) were calculated for all biomass and hydrochar samples. The evolution of H/C and O/C atomic ratios of raw CC, OP, PL and its hydrochars could be visualized by the Van Krevelen diagram [26,27] in Figure 2.

A van Krevelen diagram (named after the Dutch chemical engineer Dirk Willem van Krevelen) represents graphical plots used to illustrate difference in chemical composition of natural fuels like biomass and fossil fuels, by plotting H/C atomic ratios as a function of O/C atomic ratios obtained from elemental analysis [26,27]. This diagram provides a clear insight into the chemical transformation and coalification of biomass to carbon-rich materials, which occur as a result of demethanation, dehydration and decarboxylation reactions during HTC [7,13]. High H/C and O/C atomic ratios indicate the presence of plant macromolecules, such as cellulose, hemicellulose and lignin, while low coefficients are typical for aromatic structures [10].

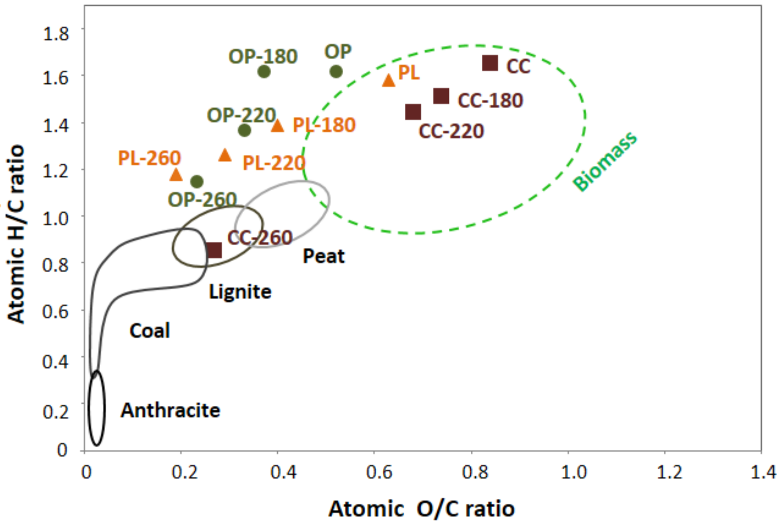

Figure 2. Van Krevelen diagram of starting biomass samples and the obtained hydrochars along with data for typical fuels (typical value range for biomass is indicated by a green circle)

It could be seen in Figure 2 that all three feedstock samples are located in the region characteristic for raw biomass [3-5,7,19,26]. On the other hand, as the carbonization temperature increases, a more progressive decrease in atomic ratios is observed, and the position of the obtained hydrochars has shifted to the lower-left corner of the Van Krevelen diagram (Fig. 2). This practically means that higher reaction temperatures promote the removal of H_2O and CO_2 from feedstock during HTC, followed by intensive condensation of polycyclic structures, whereby a more aromatic lignite-like hydrochar is formed. Thus, Figure 2 shows that the increase of the applied HTC temperature from 180 to 260 °C, induced translocation of hydrochar positions from the region of biomass, through the peat stage, all the way close to the lignite region. There, the CC-260 is on the boundary of lignite and coal, indicating CC carbonization at 260 °C to the material which is structurally similar to commercial coal. Energy sources that exhibit low H/C and O/C atomic ratios were regarded as remarkably desirable due to reduced energy loss and smoke formation during direct combustion [3]. Our results show such desired achievement since the obtained hydrochars showed lower atomic ratios in relation to the corresponding precursors.

Based on our findings, it can be concluded that hydrothermal treatment significantly improves the fuel characteristics of waste biomass, and provides potentials for further application of hydrochars as an energy source. Calculated values of *HHV* and *ED* further confirm these conclusions (Table 2).

Table 2. HHV values and energy density (ED) of waste biomass and obtained hydrochar samples

Sample	*HHV* / MJ kg^{-1}	*ED*
CC	17.31±0.03	-
CC-180	18.69±0.05	1.08±0.00
CC-220	19.41±0.01	1.12±0.00
CC-260	27.33±0.03	1.58±0.00
PL	18.99±0.08	-
PL-180	23.65±0.15	1.25±0.01
PL-220	26.13±0.02	1.38±0.00
PL-260	28.06±0.05	1.48±0.01
OP	23.45±0.06	-
OP-180	27.24±0.15	1.16±0.00
OP-220	28.07±0.06	1.19±0.01
OP-260	30.55±0.07	1.30±0.00

HHV values increased with the increase in temperature from 180 to 260 °C where the highest value was obtained for OP-260 amounting to 30.55±0.07 MJ kg^{-1}. Although the starting biomasses exhibited high *HHV* values, hydrothermal treatment further enhanced this fuel characteristic for almost 10 MJ kg^{-1} in the CC-260 and PL-260 samples while about 6 MJ kg^{-1} in the OP-260 sample. Removal of substances with low *HHV* such as hemicellulose (13.9 MJ kg^{-1}) [28] and cellulose (16.5 MJ kg^{-1}) [28] from the biomass during HTC can cause an increase in *HHV* of the produced hydrochars [1,28]. Furthermore, as the reaction temperature was elevated degradation of structure constituents was accelerated, causing higher *HHV*. Besides, when compared to lignite (16.3 MJ kg^{-1}) [29], all obtained hydrochars from exhibit better energy potentials (Table 2) than this commercial coal. The upward trend caused by the elevation of the process temperature is also noticeable for the *ED* (Table 2). The increase in the *ED* value varied depending on the biomass type, and it ranged from 1.08±0.00 to 1.58±0.00 for CC, from 1.16±0.00 to 1.30±0.00 for OP and from 1.25±0.01 to 1.48±0.01 for PL. Thus, both energy parameters increased with the increase in the process temperature. Similar findings were obtained earlier for olive pomace mill, food waste and spent mushroom substrate hydrochars in studies of potential applications as energy sources [15,19,30]. However, when comparing all of the obtained hydrochars, although the PL-260 sample shows a high *HHV* value, it is characterized by a very low yield, which significantly reduces its potential for commercial application as a solid fuel. This could represent an obstacle for the valorization of PL into a fuel source *via* the HTC technology. Therefore, it is practically very important to determine the best reaction conditions as well as the type of biomass, which will provide the material with the best characteristics for further use as a fuel. Summarizing our results, it can be concluded that the CC and OP hydrochars obtained at higher temperature can be considered as potential candidates for use as solid biofuels because these materials are characterized by good yields, satisfactory *HHV* values and energy density, while the content of volatiles is significantly reduced.

4. CONCLUSIONS

Within this study, hydrothermal carbonization was successfully utilized for valorization of waste corn cob, olive pomace and paulownia leaf into carbon-rich solid materials. Hydrochars produced at different carbonization temperatures displayed distinct structural and fuel characteristics. Results reveal that the increase in the reaction temperature causes a decrease in the solid yield due to degradation of the biomass matrix. Besides, all hydrochars showed lower volatile matter, hydrogen and oxygen contents, with a simultaneous significant increase in the carbon content and heating values. Summarizing the results obtained in this study, it can be concluded that hydrochars produced at higher carbonization temperatures show superior fuel characteristics compared to the corresponding starting raw materials. The overall results emphasize the potential of HTC technology to exploit waste biomass as a precursor for novel energy sources with upgraded combustion performance.

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SAŽETAK

Poboljšanje gorivnog potencijala otpadne biomase primenom hidrotermalne karbonizacije

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Poslednjih decenija masovna eksploatacija fosilnih goriva dovela je do sve veće potražnje za proizvodnjom energije iz obnovljivih izvora. Hidročađi dobijene hidrotermalnom karbonizacijom (engl. hydrothermal carbonization, HTC) otpadne biomase poseduju veliki potencijal kao biogorivo. U ovom radu su zato hidrotermalno karbonizovani oklasak kukuruza, listove paulovnije i kominu masline na različitim temperaturama (180, 220 i 260 °C). Glavni cilj ovog rada jeste uporedna procena uticaja HTC uslova na strukturu i gorivne karakteristie dobijenih proizvoda. Dobijeni rezultati su pokazali da se prinosi hidročađi značajno smanjuju sa porastom temperature u svim uzorcima. Sadržaj C i gornje toplotne moći rastu i dostižu najviše vrednosti u hidročađima dobijenim na 260°C, dok se sadržaj isparljivih materija smanjuje. Dalje, Van Krevelenov dijagram ukazuje da je tokom HTC procesa postignuta transformacija sirovine u proizvode slične lignitu. Naime, rezultati su pokazali da procesi dehidratacije i dekarboksilacije izazivaju intenzivnu transformaciju biomase i da hidročađi dobijene na višim temperaturama imaju značajno poboljšana gorivna svojstva i manji sadržaj isparljivih materija u poređenju sa polaznom sirovinom.

Ključne reči: konverzija biomase; hidročađ; biogorivo; oklasak kukuruza; lišće paulovnije; komina masline