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Original scientific paper

FUEL POTENTIAL AND PROPERTIES OF GRAPE POMACE HYDROCHAR

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Increasing fossil fuel depletion that leads to air pollution and global warming have become serious environmental problem. For this reason, a numerous of alternative biofuels have been developed and investigated as potential energy sources to substitute them. One of promising and highly effective technology for conversion of wet and waste biomass into multi-functional materials is a hydrothermal carbonization. In this study grape pomace was hydrothermally carbonized at different temperatures (180, 200 and 220 °C). Produced hydrochars were characterized in order to investigate its potential application as an alternative and energy-efficient renewable fuels. The carbon, fixed carbon, sulphur and volatile matter contents were determined in all hydrochar samples. Obtained results showed that temperatures play significant role on the structural characteristics of produced materials. As expected, the carbon content and fixed carbon content in hydrochars were increased with temperature increasing. Higher yields of carbon and fixed carbon observed in hydrochars indicated that intensive carbonization of biomass occurred. On the contrary, sulphur and volatile matter content were decreased. Observed reduction may be a result of dehydration and decarboxylation of grape pomace during hydrothermal treatment. These reductions are highly beneficial and improve the efficiency of solids' direct combustion. Decreased volatile matter content can potentially reduce the release of inorganic vapours and pollutant emission during combustion, while decreased sulphur content preventing generation and emission of harmful sulphur oxides, SO_x, compared to the parent biomass. The present study showed that hydrothermal carbonization mproved fuel qualities and potential of grape pomace hydrochars among different reaction temperatures.

Keywords: grape pomace, hydrochar, hydrothermal carbonization, fuel

INTRODUCTION

Over the years, increased energy demand and global coal consumption become one of important environmental issues. To solve these problems, production of energy from renewable sources to meet the fast-growing fossil fuel depletion is urgent (1). In recent decades, biomass was considered as potential and sustainable energy source. However, utilization of biomass during direct combustion shows some disadvantages, which include low bulk and energy density, hygroscopic nature, inconsistent heat production and extremely release of volatiles during combustion. Besides, increased amount of specific inorganic elements in parent biomass can cause ash issues such as corrosion, clogging and/or clinkers formation. Mentioned problems increase maintenance costs as well as affect the combustion efficiency of the fuel, and thus hindered motivation for biomass reuse. Therefore, multiple thermochemical pre-treatment methods are considered as promising solution to overcome these limitation, including: torrefaction, pyrolysis, gasification and pelletizing (2). In recent years, thermochemical carbonization (HTC) becomes

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very attractive for conversion of waste biomass into carbon-rich, energy dense solid material. HTC utilises relatively mild reaction temperatures (180-280 °C) under autogenous pressure in water medium. Primary reactions that occured during HTC process, such as hydrolysis, dehydration, decarboxylation, condensation, polymerization and aromatization coused carbonization of parent biomass into a coal-like solid, named hydrochar and organic-rich process water (2,3,4).

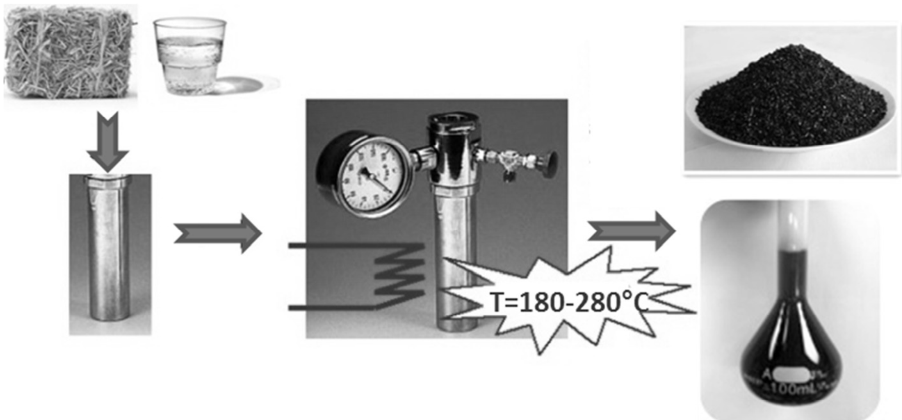

Figure 1. Simplified HTC process scheme (5)

The main advantages of HTC in comparison to traditional conversion technologies is consumption of milder reaction conditions and short reaction time (several hours) and thus less energy with high conversion efficiency, as well as direct application to biomass with high moisture content without pre-drying treatment (6). The process converts all the carbon from biomass to the coal, with no methane or CO_2 release into the atmosphere (7). Besides, structure and characteristics of the obtained products (hydrochar and process water) mainly depend on the applied reaction conditions (i.e. temperature, pressure, reaction time, solid/liquid ratio) and the starting biomass.

The resulting hydrochar, is hydrophobic, porous, solid material with high carbon and oxygen-containing functional groups (OFGs) (e.g., hydroxyl and carboxylic) content. This material expose superior performance relative to the parental biomass such as higher mass and energy density, better dewaterability, abundance of reactive groups on its surface and improved combustion performance. By adjusting the reaction parameters, a hydrochar with targeted characteristics for further application, such as adsorbent of different pollutants, energy sources, soil supplement, catalysts etc., can be produced (1-3). So far various types of biomass, from wood and agricultural residues to municipal waste and sewage sludge, were utilized as precursor for hydrochar production (2,3). On the other side, the process water from HTC so far is not considered in details. It is known that process water is mostly composed of organic fragments and inorganics incorporated in raw biomass, but its detailed characterization is very complex and so far undetermined (2,3). Some authors propose reuse of process water during HTC treatment, while others suggest extraction of value-added chemicals that left behind (2,3,8).

In this paper, hydrochar obtained from grape pomace at tree different temperatures (180, 200 and 220 °C) were characterized in order to investigate its potential for further application as alternative and energy-efficient renewable biofuels. For this purpose total carbon, fixed carbon, sulphur and volatile matter contents were determined in all hydrochar samples and compared to raw grape pomace. Particular interest of this study was to

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explore the suitability of grape pomace as a precursor for production of biofuels, since this type of biomass is largely available in Serbia.

MATERIALS AND METHODS

Biomass

The used feedstock was left behind after the wine processing at open landfill sites at a test plot Radmilovac, from witch was randomly collected. To obtain homogeneity of the sample, biomass was air-dried to constant weight and grinded. Sieved fraction of 0.5 mm was used in further hydrothermal carbonization experiments.

Hydrochar preparation and characterization

Preparation of hydrochar was carried out in laboratory autoclave (Carl Roth, Model II, 250 mL) that is equipped with temperature controller and thermocouple. For carbonization experiments, 10 g of biomass and 150 mL of ultrapure water (1:15 ratio) was carbonized at selected temperature (180, 200 and 220 °C) within 1 h. After reaction period hydrochar was separated from proces water by filtration. Obtained solid material (HC-180, HC-200 and HC-220) was rinsed with ultrapure water and dried in an oven at 105 °C to constant weight.

Total carbon and sulphur contents in all samples were detemined using Vario EL III; C, H, N, S/O Elemental Analyzer equipped with a thermal conductivity detector (TCD), while volatile matter (VM) and fixed carbon content (C_{fix}) were determined by standard ASTM D1762-84 (2007) procedure.

RESULTS AND DISSCUSION

In order to evaluate the effect of process temperature, as one of dominant carbonization parameter, on the structural and fuel properties of produced hydrochars, selected parameters were determined in HC-180, HC-200 and HC-220, and compared to raw parental biomass (GP).

The results of the total C, C_{fix} and VM contents in GP and hydrochars are given at Figure 2.

According to our results presented at Figure 2. can be seen that the raw GP has high VM content (75.49 %). A high amount of VM content is one of characteristics of different biomass feedstock. The high VM content caused higher reactivity and lower enthalpies during direct combustion of GP, which is a contrary effect in comparison to fossil coal, and unfavourable for direct combustion of raw biomass because a higher VM content leads to low combustion efficiency and emission problems (9,10). Therefore, the GP is not suitable to be utilized as an effective fuel source. Compared to raw GP, the VM content got decreased after HTC in all hydrochar samples. Upon increasing the reaction temperature from 180 to 220 °C, the VM content was reduced to 62.79 % (HC-220), resulting in an overall decrease of 12.70 %. Decrease of the VM content in grape pomace hydrochars with increasing of temperature from 180 °C to 220 °C is a result of chemical dehydration and decarboxylation of lignocellulosic constituents of GP during carbonization process that become more intensive at higher temperatures (11). The decrease in VM content upon increase of reaction temperature confirms that this reaction parameter has significant influence onto produced hydrochar characteristics. The similar observation

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was previously reported by Shama et al. (9) and Makela et al. (12) during carbonization of yard waste and recycled paper mill sludge, respectively.

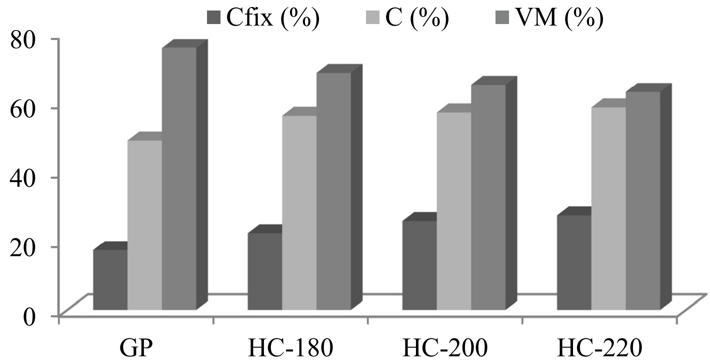

Figure 2. The total C, C_{fix} and VM contents in GP and tested hydrochars

Moreover, with the simultaneous lowering of the volatiles, the significant increase in C_{fix} content was observed. The C_{fix} was increased from 17.29 % (GP) up to 27.27 % (GP-220). Higher C_{fix} content in hydrochars than in the GP confirms the high carbonation efficiency, which is is in agreement with the results previously reported for palm branch hydrogens (11) and michanthus (3). Simultaneous hydrothermal reduction of VM and increase of the C_{fix}, improves the efficiency of hydrochar direct combustion and boosting of its energetic potential in comparison to raw biomass. These characteristics promote GP hydrochar as an easily accessible and energy-rich carbon material.

Another significant hydrochar characteristic which governs the quality of fuel other than C_{fix} is total C content. In addition to previous observation, the increase of reaction temperature during HTC from 180 °C to 220 °C led to a gradual increase of the total C content in relation to the GP. It is noticeable that the content of total C got increased from 48.87 %, in starting material, up to 58.38 % in the HC-220. Higher yields of carbon and fixed carbon observed in hydrochars indicated that intensive carbonization of biomass occurred. This trend is in agreement with the result obtained by Pala et al. (13) for the GP hydrochars carbonated at 225 °C (63.05 %). According to our findings can be conclude that higher reaction temperatures provide intensier carbonization of parental biomass and formation of more aromatic, carbon-rich, coal-like hydrochar and thus improves fuel quality of starting material.

Furthermore, if the obtained hydrochars are planned to be used as potential solid fuel, an important indicator is the sulphur content. The sulphur content (S) in the GP and tested hydrochars is shown on the Figure 3.

As can be noted, HTC treatmen promote reduction of S content in all hydrochars, as a result of dissolution of sulfides under hydrothermal conditions. The results showed that almost 40 % of sulphur content was removed from the hydrochar after HTC at 220 °C. Observed decrease of S content in hydrochar is a very significant aspect of the HTC process, especially due to prevention of the formation and emission of harmful SO_x oxides during direct combustion of hydrochars. The similar results was previosly reported by Kim et al. (14) for hydrothermaly carbonized digested sludge.

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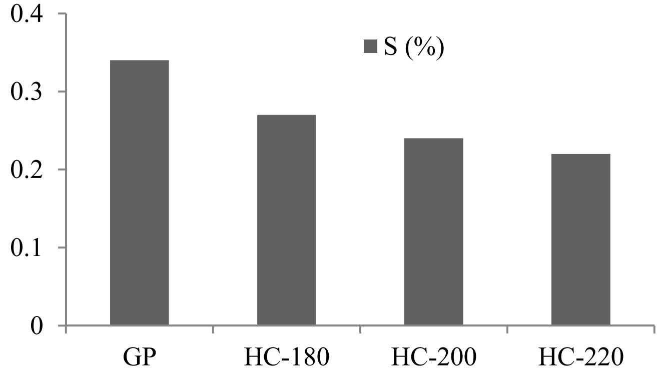

Figure 3. Sulphur content in GP and obtained hydrochars

CONCLUSIONS

According to results from this study, can be concluded that hydrothermal carbonization represents a promising method for the conversion of waste biomass into value-added hydrochars. Preliminary results of fuel properties show that temperature play significant role on structural characteristics of produced materials. Temperature increment caused a decrease in VM and S content and simultaneous increase of total C and C_{fix} content. Lower VM and S contents caused reduced emission of greenhouse gases during direct combustion of produced hydrochars, while increased C and C_{fix} contents boosting its energetic potential. These advantages of novel carbonaceous materials in comparison to raw biomass, makes obtained hydrochars highly desirable, sustainable materials that can be used as potential energy sources.

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