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ENERGY PROPERTIES OF AGRICULTURAL BIOMASS AFTER THE PYROLYSIS
ENERGETSKA SVOJSTVA POLJOPRIVREDNE BIOMASE NAKON PIROLIZE

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ABSTRACT

At the beginning and during the development of civilization, natural sources were the only available source of energy. With the development of society and industry, they were replaced by intensive use of fossil fuels. Non-renewability and negative impact on the environment called into question the rationality of using such sources. Therefore, natural sources of energy are becoming more and more important, especially biomass, which is becoming an important source of energy due to its ecological advantages. There are numerous ways to convert agricultural biomass into different forms of biofuel. Thermochemical conversion includes a process of pyrolysis in which, under the influence of a high temperature of 400 to 600 °C without the presence of oxygen, very valuable products are obtained in the form of biochar. The aim of this research is to evaluate the energy properties of agricultural biomass (corn, wheat, barley, oats, triticale, rye, soybeans, rapeseed and sunflower) by thermochemical conversion by pyrolysis and analysis of biochar for the evaluation of value-added products and to suggest its application. The mentioned raw materials are characterized by significant pyrolytic conversion potential, i.e. biochar production ranged from 30.03% to 47.0%. Similarly, the heating value (HHV) of biochar after the pyrolysis process increased to 27.11 MJ/kg, which proves that agricultural biomass is a good source of energy per unit mass.

Keywords: *agricultural biomass; pyrolysis; biochar*

REZIME

Na početku i tokom razvoja civilizacije, prirodni izvori su bili jedini raspoloživi izvor energije. Razvojem društva i industrije zamenila ih je intenzivna upotreba fosilnih goriva. Neobnovljivost i negativan uticaj na životnu sredinu doveli su u pitanje racionalnost korišćenja ovakvih izvora. Stoga prirodni izvori energije postaju sve značajniji, a posebno biomasa, koja zbog svojih ekoloških prednosti postaje značajan izvor energije. Postoje brojni načini za pretvaranje poljoprivredne biomase u različite oblike biogoriva. Termohemijska konverzija obuhvata proces pirolize u kome se pod uticajem visoke temperature od 400 do 600 °C bez prisustva kiseonika dobijaju veoma vredni proizvodi u obliku biouglja. Cilj ovog istraživanja je procena energetskih svojstava poljoprivredne biomase (kukuruz, pšenica, ječam, ovas, tritikale, raž, soja, uljana repica i suncokret) termohemijskom konverzijom pirolizom i analizom biouglja za ocenu proizvoda sa dodatom vrednošću i predlog njegove primene. Pomenute sirovine karakteriše značajan potencijal pirolitičke konverzije, odnosno proizvodnja biouglja se kretala od 30,03% do 47,0%. Slično, toplotna vrednost (HHV) biouglja nakon procesa pirolize porasla je na 27,11 MJ/kg, što dokazuje da je poljoprivredna biomasa dobar izvor energije po jedinici mase.

Ključne reči: *poljoprivredna biomasa; piroliza; biougalj*

INTRODUCTION

Due to the steady growth of the world's population and the economic development of the industry, there is an ever-increasing demand for energy (*Dutta et. al., 2014*). Huge amounts of natural resources are consumed and the environment is damaged as a result. Biomass is the first and oldest source of energy that people used in the form of various wood residues that they collected and used for heating and other purposes. Until the beginning of intensive use of fossil fuels, whose use influenced the development of civilization, biomass was the primary and almost the only source of energy (*Kiš et. al., 2017*). Due to the negative impact of fossil fuels on the environment, biomass is again becoming an important source of energy and interest in it is increasing again. The use of biomass and biofuels has been shown to reduce dependence on external energy sources while helping to reduce greenhouse gas emissions (*Matin et. al., 2023*). Biomass is a complex, heterogeneous mixture of organic structural components such as cellulose, hemicellulose, and lignin. Characterization of these components in a given biomass is crucial for determining the biomass processing approach (*Antonović et al., 2016*) and for understanding the reaction mechanism in biofuel production. Agricultural biomass as a part of lignocellulosic biomass has significant energy potential as it is residue that is produced after agricultural production and is available at relatively low prices (straw, corn husks, stalks, hulls, seeds) (*Matin et. al, 2019*). There are a number of techniques for converting biomass into usable forms of energy. The type, characteristics, and quantity of available biomass, the intended final energy form, environmental standards, and economic conditions all influence the conversion process. (*Saxena et al., 2009; Krička et al., 2012; Bilandžija et al., 2018*). Thus, there are biochemical, thermochemical, biotechnological, and physicochemical conversion processes used to convert biomass into various forms of energy (heat, electricity, fuels, chemicals, and other value-added products) (*Muh et. al, 2020*). The most commonly used thermochemical processes are the use of thermal energy and chemical catalysts to break down biomass into valuable energy-rich products, including gasification, pyrolysis, and direct liquefaction (*Demirbas, 2001*). Pyrolysis is the basic thermochemical process for converting biomass into a more useful fuel. Biomass is heated in the absence of oxygen or partially burned with a limited oxygen supply to produce a mixture of bio-oil, biochar, and hydrocarbon-rich gas (*Goyal et. al., 2008; Jahirul et. al., 2012*). Bio-oil is used to produce fertilizers and resins and in boilers and turbines to generate heat and electricity (*Uzun and Sarioglu, 2009*). Biochar is used for soil amendment and as a heating source in boilers (*Laird et al., 2009; Yin et al., 2018*). The heat from produced gas by pyrolysis can be effectively used for the energy needs of pyrolysis plants (*Jahirul et al., 2012*). Pyrolysis produces energy fuels with a high fuel-to-commodity ratio, making it the most efficient biomass conversion process and the method most capable of competing with and eventually replacing nonrenewable sources of fossil fuels (*Chhiti and Kemiha, 2013*). It is influenced by temperature, environment, and biomass type (*Guizani et al., 2017*). In general, there are two main types of pyrolysis depending on the heating rate: slow pyrolysis and fast pyrolysis. In general, there are two main types of pyrolysis depending on the rate of heating: slow pyrolysis and fast pyrolysis. In slow pyrolysis, the biomass is heated more slowly to the pyrolysis temperature and the heating time is longer than the time the substrate remains at the characteristic pyrolysis reaction temperature. This method usually results in a higher yield of biochar, a carbon-rich solid material (*Harussani et. al., 2020*). In contrast, fast pyrolysis involves heating the feedstock rapidly, with the initial heating time being shorter than the final residence time at the peak pyrolysis temperature. This process results in a higher yield of liquid products, especially bio-oil, which can be used as a renewable energy source or as a precursor for the production of chemicals and materials. For all these reasons, the aim of this study is to evaluate the energetic properties of agricultural biomass through thermochemical conversion by pyrolysis and the analysis of biochar in order to identify value-added products and propose their use.

MATERIAL AND METHOD

Agricultural biomass (corn, wheat, barley, oats, triticale, rye, soybeans, rapeseed and sunflower) grown on the territory of continental Croatia and collected during the harvest of 2021 in dry weather was used for this research. Prior to analyses, biomass was comminuted using a Retsch GM 300 laboratory mill (RETSCH GmbH, Germany) according to (*EN ISO 14780:2017*). Each sample of the row and pyrolyzed biomass (biochar) was analysed in triplicate. The energetic properties consisted of the determination of the properties of the non-combustible, combustible, lignocellulosic composition and macroelements.

The analyses of non-combustible properties were performed according to standard methods and determined as follows: moisture content (*EN ISO 18134-2:2017*) in a laboratory dryer (INKO ST-40, Croatia), while ash (*EN ISO 18122:2015*) and coke (*EN ISO 18123:2023*) were determined in a muffle furnace (Nabertherm Controller B170, Germany). The fixed carbon content (*HRN EN ISO 18123:2023*) was determined by calculation. Combustible analyses were performed according to standard methods and determined as follows: combustible and volatiles matter was determined by calculation, and the higher heating value (HHV) was determined according to the method (*HRN EN ISO 18125:2017*) using an IKA C200 adiabatic calorimeter (IKA Analysentechnik GmbH, Germany). Lignocellulosic composition of cellulose, hemicellulose and lignin content was determined according to the modified standard procedure by *Antonović et. al. (2010)* under laboratory conditions. Finally, the amount of macroelements (sodium (Na), magnesium (Mg), potassium (K) and calcium (Ca)) in the samples was determined according to the method (*HRN EN ISO 16967:2015*) in an atomic absorption spectrometer (Perkin Elmer, Analyst 400), with the samples previously prepared in a microwave oven (*HRN EN ISO 16968:2015*). The input raw materials of agricultural biomass particles with a size of 360 μm were subjected to a laboratory pyrolysis process at a temperature of 500 °C in the absence of oxygen. The pyrolysis process involved direct heating of the biomass, after which the volatiles were passed through the cooler, where the condensing gases turned into liquid, i.e., bio-oil, while the synthetic gases were released into the atmosphere. After the pyrolysis process, the yield of the obtained biochar was calculated. The data obtained were processed using SAS version 9.3 (USA). To show the changes in the observed variables, i.e. the composition of the biomass after the pyrolysis process, the values after the measurements are given and the last column shows the mean value and the standard deviation to be able to compare the differences between the mean values of the individual biomass types.

RESULTS AND DISCUSSION

To gain insight into the effects of pyrolysis on the energy potential of agricultural biomass, it was necessary to determine its content of non-combustible, combustible, lignocellulosic composition and macroelements. For the process of biomass combustion, it is important to have raw materials with reduced content of water, ash and mineral composition, as they reduce the efficiency of boilers, and fermentation of organic content (lignin, cellulose, hemicellulose) changes the overall efficiency of conversion from solid to other fuels.

Therefore, Table 1 presents the results regarding the content of non-combustible and structural properties in agricultural biomass. Water is a non-combustible component of the fuel and directly affects the calorific value of biomass due to the amount of heat expended for its evaporation (*Francescato et al., 2008*). According to *Ross et al. (2008)*, the optimal moisture content for biomass combustion is 15%. From the data in Table 1, it can be seen that the moisture content of all the agricultural biomasses studied was below the maximum written limit for combustion of 15%, so it can be said that the biomass studied is a good raw material for energy production by the pyrolysis process from the point of view of water content. Ash has a catalytic effect on thermal decomposition, and with increasing ash concentration, coal and gasses also increase (*McKendry, 2002*). Fuels with lower ash content are more suitable for thermal utilization because smaller ash volumes facilitate removal, transportation, storage, utilization, and disposal. Ash content is usually between 0.5 and 3%, depending on the type of agricultural biomass and biomass components, although it can vary in a very wide range from 0.1% to 46% (*Vassilev et al., 2010*), values that are consistent with this study, where the highest ash content in sunflower biomass is 12.04 %. Coke content represents the residue of dry distillation, and the higher its content, the higher the quality of biomass (*Boboulos, 2010*; *Krička et. al., 2017*), and accordingly, a higher coke content of 21.46% was found in sunflower biomass. Increasing the fixed carbon content of biomass increases its heating value, and at the same time improves the quality of the biomass itself (*McKendry, 2002*). *Das et al. (2021)* report the fixed carbon content of agricultural biomass to be 17.3%, which is much higher than the values obtained in this study. The structural content of biomass is important because biomass with a higher lignin content is more suitable for energy production by direct combustion, while in the production of second-generation biofuels, the content is as low as possible (*Hodgson et al., 2010; Bilandžija et al., 2016*). Cellulose has a higher oxygen concentration compared to lignin, so the calorific value of cellulose is lower than that of lignin (Lewandowski et al., 2003). For this reason, a lower percentage of cellulose is desirable for direct combustion. Like cellulose, hemicellulose also has a higher oxygen concentration compared to lignin, so the calorific value of hemicellulose is lower than that of lignin; therefore, a lower proportion of hemicellulose in the biomass is also desirable for the combustion process. From Table 1, it can be seen that the cellulose composition is different for all biomasses studied and is best for corn biomass. Based on the results from agricultural biomass, it can be observed that a high percentage of biochar was obtained after pyrolysis, ranging from 30.03% in triticale to 47.0% in rapeseed. It can be concluded that the choice of an agricultural crop, i.e. its biomass, is very important during the pyrolysis process, i.e. the production of biochar. As for biomass, the prerequisite for the energetic use of biochar is a low percentage of ash and fixed carbon (*Jurišić et. al, 2016*). When analyzing the ash content as well as other properties of biochar (coke and fixed carbon), a very high ash content was found in all samples, from 7.91% in soybeans to 17.98% in oats. Coke content is also high, ranging from 35.72% in corn to 75.11% in barley. However, in all this, it must be taken into account that larger amounts of ash cause soot formation and corrosion in biomass combustion plants (*Biedermann et al., 2013*).

The results of combustibles properties from agricultural biomass before and after pyrolysis are shown in Table 2. The highest value of combustible substances was obtained in corn biomass with 91.47%, and the lowest in sunflower with 75.54%. Volatiles are associated with fuel components that are released when the fuel is heated to high temperatures, so it is desirable that their content in biomass is as low as possible (*Mc Kendry, 2002; van Loo and Koppejan, 2008; Vassilev et al., 2010; Bilandžija, 2017*). The volatile content in raw agricultural biomass ranged from 69.54 % in sunflower to 87.64% in rapeseed, while according to *Vassilev et al. (2010)*, the volatile content ranged from 60 to 80%. Heating value is the basic parameter for biomass energy calculation. The heating value is influenced by moisture, chemical composition and density of biomass. By decreasing the moisture content of biomass, the calorific value increases sharply. The calorific value is a measure for determining the energy content of the fuel, and for the studied feedstocks it ranged from 16.16 MJ kg^{-1} for barley straw to 19.36 MJ kg^{-1} for soybean, which is consistent with available data (*Bilandžija et al., 2012; Grubor et al., 2015*). Temperature and the type of pyrolysis have an effect on the structure of biochar due to the release of volatiles (Shaaban et al. 2014). Increasing the temperature results in lower volatile matter content (*Crombie et al., 2013; Tag et al., 2016*). The heating value (HHV) of biochar ranged from 24.21 MJ kg^{-1} for triticale to 27.11 MJ kg^{-1} for soybean, making it an even better energy source per unit mass. These values are consistent with those obtained by *Sohaib et al. (2017)* in their research on biomass.

The content of elements in biomass is influenced by morphological characteristics and environmental conditions such as soil properties (soil fertility, pH), weather conditions, and agrotechnical treatments - mainly fertilization (*Barglowicz, 2014*). Knowledge of the content of various elements can be useful in choosing the method of processing biomass into energy (*Borkowska and Lipinski 2008*). Sodium (Na), in combination with chlorine (Cl) and sulfur (S), is involved in the formation of corrosion and partially evaporates during combustion, forming sulfates and releasing chlorine. Therefore, the lower the proportion of sodium (Na), the better the quality of the fuel (*Masià et al., 2007; Khan et al., 2009*). Magnesium (Mg), as an alkaline element lowers the melting point and usually increases the ash melting temperature (*Porbatzki et al., 2011*).

Table 1. Non-combustibles and structural properties of raw and pyrolyzed (biochar) agricultural biomass

Raw material										
Biomass	Corn	Wheat	Barley	Oat	Triticale	Rye	Soybean	Rapeseed	Sunflower	$\bar{X}$ ± S.D.
Moisture (%)	5.94	8.65	8.67	9.87	5.89	7.73	8.18	8.90	10.54	8.26±1.57
Ash (%)	3.90	3.34	8.28	9.69	5.88	4.71	5.76	4.49	12.04	6.45±2.94
Coke(%)	13.46	15.91	19.49	20.92	17.76	20.23	14.27	12.39	21.46	17.33±3.43
Fixed Carbon (%)	8.34	11.44	9.56	9.27	11.49	14.62	8.70	5.82	6.61	9.54±2.69
Cellulose (%)	42.19	56.12	47.05	56.30	45.98	51.97	58.25	46.96	53.52	50.93±5.58
Hemicellulose (%)	21.88	22.67	32.18	14.91	35.63	18.29	15.23	33.06	19.42	23.7±7.93
Lignin (%)	27.67	20.05	18.99	26.42	24.64	31.88	24.12	18.41	26.07	24.25±4.44
Biochar										
Share (%)	37.80	36.39	47.02	34.92	30.03	36.28	37.82	47.09	33.93	37.92±5.69
Ash (%)	8.92	10.58	13.09	17.98	9.36	9.86	7.91	8.52	15.84	11.34±3.53
Coke(%)	35.72	55.62	58.39	75.11	41.34	65.14	54.02	38.70	63.48	54.17±13.27
Fixed Carbon (%)	27.23	60.96	45.32	57.13	31.97	59.33	46.12	28.18	50.64	45.21±13.27

Table 2. Combustibles properties of raw and pyrolysed (biochar) agricultural biomass

Raw material										
Biomass	Corn	Wheat	Barley	Oat	Triticale	Rye	Soybean	Rapeseed	Sunflower	$\bar{X}$ ± S.D.
Combustible matter (%)	91.47	87.82	83.41	80.20	89.79	87.91	87.18	83.77	75.54	85.23±5.03
Volatile matter (%)	82.63	76.62	73.97	70.89	77.95	73.88	86.31	87.64	69.54	77.71±6.52
HHV MJ kg^{-1}	16.36	16.58	16.16	16.72	16.20	16.98	19.36	18.99	18.56	17.32±1.28
Biochar										
Combustible matter (%)	94.19	90.08	86.94	82.11	90.64	90.14	92.30	91.48	87.26	89.46±3.57
Volatile matter (%)	64.02	40.12	42.01	39.25	58.68	29.81	44.75	61.31	43.52	47.05±11.6
HHV MJ kg^{-1}	24.77	25.02	24.99	24.89	24.21	25.36	27.11	26.08	26.33	25.42±0.91

Potassium (K), in combination with chlorine (Cl) and sulfur (S), is involved in corrosion and partially evaporates during combustion, forming sulfates and releasing chlorine (Cl). Therefore, the lower the proportion of potassium (K), the better the quality of the fuel. Calcium (Ca) reacts with potassium (K) and silicon (Si) and affects the appearance of slag in furnaces. However, its increased content contributes to a lower probability of slag occurrence but also lowers the melting point (*Monti et al., 2008*). Table 3 shows that for agricultural biomass, the lowest values for sodium (Na), magnesium (Mg), potassium (K), and calcium (Ca) were obtained with rye biomass, while the highest values were obtained with sunflower biomass. For biochar, the results are slightly different and the percentage of sodium (Na) from oat biomass is 472.11 mg/kg, magnesium (Mg) from corn biomass is 1038 mg kg^{-1}, while the highest percentage of potassium (K) is 28430 mg kg^{-1} and calcium (Ca) is 33450 mg kg^{-1} from sunflower biomass. A similar study on agricultural biomass was conducted by *Le et al. (2014)* and found magnesium content of 176-891 mg kg^{-1}, potassium content of 864-2111 mg kg^{-1} and calcium content of 194-4143 mg kg^{-1}, which are slightly lower values than in this study. Many factors that can affect the concentration of different elements in plants result in variations in the content of the elements and large differences. These include the type of element, its content and form in the soil, soil type, plant variety, proximity to external sources of pollution, and many other factors (*Femenia et al., 1995*).

Table 3. Macroelements of raw and pyrolysed (biomchar) agricultural biomass

Raw material										
Biomass	Corn	Wheat	Barley	Oat	Triticale	Rye	Soybean	Rapeseed	Sunflower	$\bar{X}$ ± S.D.
Na mg kg^{-1}	103.61	70.11	77.59	97.31	58.33	43.53	92.03	86.76	161.77	87.89±33.68
Mg mg kg^{-1}	498.80	511.62	506.59	163.89	484.95	90.58	523.31	515.90	514.63	423.36±169.25
K mg kg^{-1}	1116	791.58	861.16	702.50	742.20	560.80	1356	787.70	15170	2454.22±4774.31
Ca mg kg^{-1}	1003	304.60	979.30	758.20	666.10	225.80	2236	7695	7280	2349.78±2971.64
Biochar										
Na mg kg^{-1}	368.80	289.40	304.94	472.11	117.64	269.10	367.90	270.28	168.70	292.1±106.58
Mg mg kg^{-1}	1038	1032	1020	1026	974.75	1016	1038	1023	990.10	1017.54±21.62
K mg kg^{-1}	2313	2491	2379	5975	17800	4105	4632	1591	28430	7746.22±9211.56
Ca mg kg^{-1}	7065	3814	4923	5354	3716	7140	6278	14420	33450	9573.33±9510.28

CONCLUSION

In this research, it was demonstrated that agricultural biomass can be used in the pyrolysis process and that pyrolysis can be an effective method to increase the energy concentration of biomass materials. The influence of the type of agricultural biomass on increasing the energy concentration is different. It can also be found that a large part of biochar is obtained from cereal straw by pyrolysis. At the same time, there is a very large difference in the percentage obtained in relation to the species. The main advantage of this method is the increase in the calorific value of biomass compared to the raw material.

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