THE ENERGY POTENTIAL OF THE PRODUCTS OBTAINED BY PYROLYSIS OF AGRICULTURAL WASTE

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Abstract: *As the consumption of fossil fuels increases, the demand for alternative energy sources is growing. Current research focuses on alternative energy sources. Significant importance is given on renewable energy sources, such as waste biomass of agricultural origin, which is thermally processed through pyrolysis, producing products that can have further applications. Serbia, an agricultural country with great potential for using waste biomass as energy, such as corn, could significantly reduce environmental pollution by managing agricultural waste and decreasing greenhouse gas emissions from the combustion of fossil fuels through the utilization of pyrolysis technology.While biomass in its raw form may not be suitable for energy production due to its high oxygen and moisture content and lower calorific value, the process of pyrolysis emerges as a pivotal solution. This thermal processing method transforms biomass into solid, liquid, and gaseous products, the quality of which is determined by the initial biomass and process parameters. The critical aspect is that optimizing these pyrolysis conditions can significantly improve the quality of the products, thereby increasing their potential for energy applications.This study investigated two types of corn and their liquid and solid pyrolysis products obtained at a temperature of 400 °C. The following parameters were compared between the initial biomass and the liquid and solid products: calorific value, pH, moisture content, ash content, and metal ions affecting energy efficiency, such as K, S, Mg, and Al.Based on the obtained results, it can be concluded that the liquid and solid pyrolysis products hold potential as energy sources. However, certain modifications are necessary to enhance their energy potential. For instance, increasing the calorific value can be achieved by increasing the carbon and hydrogen content. This can be done by* *adding materials abundant in these elements, such as plastic waste. Consideration should also be given to the quality of the products and their subsequent applications, both for energy purposes and other uses such as chemical production (from the liquid fraction) or use as adsorbents or fertilizers (solid fraction).*

Key words: FUEL, CORN, BIO-OIL, BIO-CHAR, CHARACTERIZATION

INTRODUCTION

Biomass as a renewable energy source is gaining increasing importance due to growing concerns about climate change and the depletion of fossil fuels [1]. Agricultural waste, particularly corn biomass, represents a significant portion of potential biomass that can be utilized for energy purposes, with pyrolysis emerging as an efficient process for converting these materials into valuable energy products such as bio-oil and biochar [2]. This paper aims to explore the energy potential of bio-oil and biochar derived from the pyrolysis of agricultural waste, focusing on corn biomass and its characteristics and potential applications compared to fossil fuels and raw biomass [3].

Biomass, including corn stalks and leaves, is a renewable resource that can significantly contribute to reducing greenhouse gas emissions when used as a substitute for fossil fuels [4]. According to the latest data, around 1.2 billion tons of corn biomass are produced annually worldwide, a large portion of which remains unused or is burned in the fields, contributing to air pollution and greenhouse gas emissions [5]. This waste material can be effectively utilized through pyrolysis processes, reducing its negative environmental impact and creating additional value in the form of bio-oil and biochar [6].

Pyrolysis products such as bio-oil and biochar offer several advantages over raw biomass, including higher energy density, easier storage and transportation, and better stability [7]. When corn biomass is used for pyrolysis, it can produce bio-oil with an energy value comparable to that of fossil fuels, while biochar provides high carbon content and stability, making it suitable for use as a fuel or as a soil amendment [8]. Although bio-oil has a high energy value, its drawbacks, such as high viscosity and water content, can affect its efficiency compared to conventional fossil fuels [9]. On the other hand, biochar has a higher energy content compared to raw biomass and can be used as an environmentally friendly energy source [10].

Compared to fossil fuels, bio-oil and biochar have several benefits, including a smaller carbon footprint and the potential to reduce emissions of sulfur oxides and other harmful gases [11]. However, both bio-oil and biochar face challenges in terms of economic feasibility and the need for further research to optimize production processes and increase competitiveness relative to fossil fuels [12]. This paper will also explore opportunities to enhance the properties of bio-oil and biochar and potential synergies with existing energy systems.

The use of corn biomass for bio-oil and biochar production through pyrolysis has the potential to reduce dependence on fossil fuels and provide a sustainable solution for managing agricultural waste, which can have a significant positive impact on the economy and the environment [13]. Therefore, the research and development of technologies for the efficient conversion of corn biomass into energy-rich products become crucial in the context of a global transition to renewable energy sources [14].

EXPERIMENTAL

In this study, two types of domestic corn sampled from the vicinity of Šabac were used. The samples were cut into pieces and then air-dried for 30 days, after which they were ground in a mill to obtain particle sizes smaller than 5 mm. The prepared samples were pyrolyzed in a carbolite tube furnace (MTF 10/15/130, Carbolite, UK) at 400 °C for 30 minutes, and heating rate 100 °C/min. Nitrogen gas (99.999 %) was used to ensure an inert atmosphere, with a flow rate of 150 ml/min. The liquid fraction was collected in an HPLC- grade acetone, while the solid fraction was washed with acetone after pyrolysis to remove any residual bio-oil. Based on the initial biomass and the obtained liquid and solid fractions, the yield of each fraction was determined (Figure 1). The obtained products were subjected to physicochemical characterization, which included the determination of moisture and ash content, pH value, calorific value, and metal content. The pH value of the initial biomass and the obtained liquid and solid fractions was measured according to standard ASTM E70 method. Additionally, the calorific value was determined on an instrument IKA C400 (IKA, Germany), using the standard SRPS CEN/TS 16023:2014. The moisture content of biomass and biochar samples were determined by drying in an oven according to the ASTM E871 standard, and for bio-oil samples was used the standard procedure outlined in SRPS EN ISO 12937:2011, “Petroleum products- Determination of water- Coulometric Karl Fischer titration method” on an 831 KF Coulometer (Metrohm, Switzerland). The ash content of bio-oil were determined using the ASTM D482 standard, and for biomass and biochar samples were used ASTM D2584 and ASTM D5630. The metal content was determined using inductively coupled plasma-optical emission spectroscopy (ICP-OES) on a instrument „Spectroblue TI’’ICP-OES (Spectro, Germany) and method EPA M 200.7. The samples of bio-oil were prepared using a microwave digestion oven CEM Mars 5 (MARS, USA) according to the standard method EPA 3052 and for biomass and biochar using method EPA 3052/ISO 2598-1. The calorific value for all samples were determined on a instrument IKA C400 (IKA, Germany), using the standard SRPS CEN/TS 16023:2014.

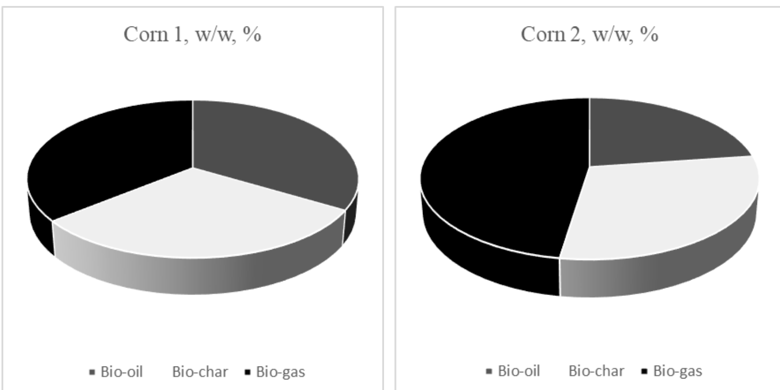

Figure 1, Yield of bio-oil, bio-char and bio-gas fraction

RESULTS AND DISCUSSION

For Corn 1, it can be concluded that the yield of each fraction is approximately the same, while the distribution for Corn 2 is slightly different (Figure 1). Biogas was not analyzed, but for bio-oil, it can be seen that the yield for Corn 1 is higher compared to the yield for Corn 2. This is due to the different composition of the initial biomass, where Corn 2 has a higher lignin content, resulting in a lower yield of the liquid fraction obtained by pyrolysis. According to the literature, the yield of the liquid fraction obtained from corn pyrolysis is correspond with literature, between 30 and 33% [15]. The biochar yield for both samples is approximately the same, which is according to the literature data, 21- 30 % [13]. The results of moisture and ash content, pH and calorific values are shown in Figure 2. These parameters are some of the key factors for the use of the obtained products as potential fuels. The obtained values for bio-oil and biochar were compared with the values for the biomass. According to Figure 2 a, it can be seen that the moisture content of bio-oil is much higher compared to the initial biomass, which may suggest that water is produced during the pyrolysis process as a result of the complex reactions that occur. In contrast to bio-oil, the moisture content of biochar does not change significantly. Moisture content is important due to the corrosive effect that bio-oil or biochar can cause if used as fuels. Additionally, high moisture content can negatively affect thermal efficiency by reducing the calorific value of the potential fuel.

The ash content for bio-oil is almost negligible compared to the initial biomass, while for biochar it is significantly higher, which is a result of the composition of the fractions themselves. Ash is an important parameter of energy efficiency. For bio-oil to be used as a liquid fuel, it is desirable for the ash content to be low, which, as seen in Figure 2b, a value of less than 1%. Biochar is generally considered as a good fuel source when its ash content is low, typically below 5%. Low ash content is desirable because high levels of ash can reduce the heating value of biochar and cause issues such as slagging and fouling during combustion. The lower the ash content, the higher the energy density and overall quality of the biochar as a fuel [16]. Elements that can contribute the ash content are silicon an the form of silica, alkali metals, such as potassium and sodium, then calcium and magnesium, and sulfur [17].

The pH value (Figure 2c) was around 6 for the initial biomass, while for the liquid fractions it dropped to around 2, and for the solid fractions, it increased to around 8. The acidic environment of the bio-oil is a result of the formation of compounds with acidic functional groups, such as phenolic, carboxylic, and alcoholic groups, which contribute to a lower pH. The pH value can also contribute to an increased corrosive effect. The higher pH value of biochar, slightly basic, is a consequence primarily due to the presence of mineral components such as alkali and alkaline earth metals (e.g., sodium, potassium, calcium, magnesium) that remain in the biochar after pyrolysis. Additionally, the formation of carbonate compounds in the biochar can also contribute to its basicity [17].

Figure 2d shows that the calorific value of the biomass is the lowest, while its pyrolysis products have slightly higher values. Compared to literature data, calorific values for bio-oil fit the values compared to litearture data [15]. For biochar calorific values depend on the pyrolysis conditions and feedstock properties [18]. Compared biochar with coal, generally, coals have calorific values range from 25 - 35 MJ/kg [19]. For both, bio-oil and biochar need upgrading. It can be concluded that the pyrolysis process produces products with better calorific values than biomass, suggesting that further development should move in this direction. As mentioned earlier, the reduction in calorific value can be influenced by high moisture content and low pH, which can be reason for lowest values for bio-oil, and high ash content. High ash content is a consequence of the presence of non-combustible elements such as sodium, potassium, calcium, magnesium, sulfur, silicon, and others. The metal content is presented in Table 1, which, in addition to some elements affecting the calorific value, also shows the content of metals considered toxic, such as Pb, Cd, Hg, Cr, and As. It can be seen that the content of these metals is below the threshold values, which can be considered to have no harmful effects. Regarding the metal content that affects ash content, we can see that for bio-oil, only sulfur and potassium for Corn 2 could contribute to this effect, which is insignificant as there is almost no ash. In contrast, for biochar, a high content of K, Ca, Mg, S, and Si can be seen, which is why the ash content is also high.

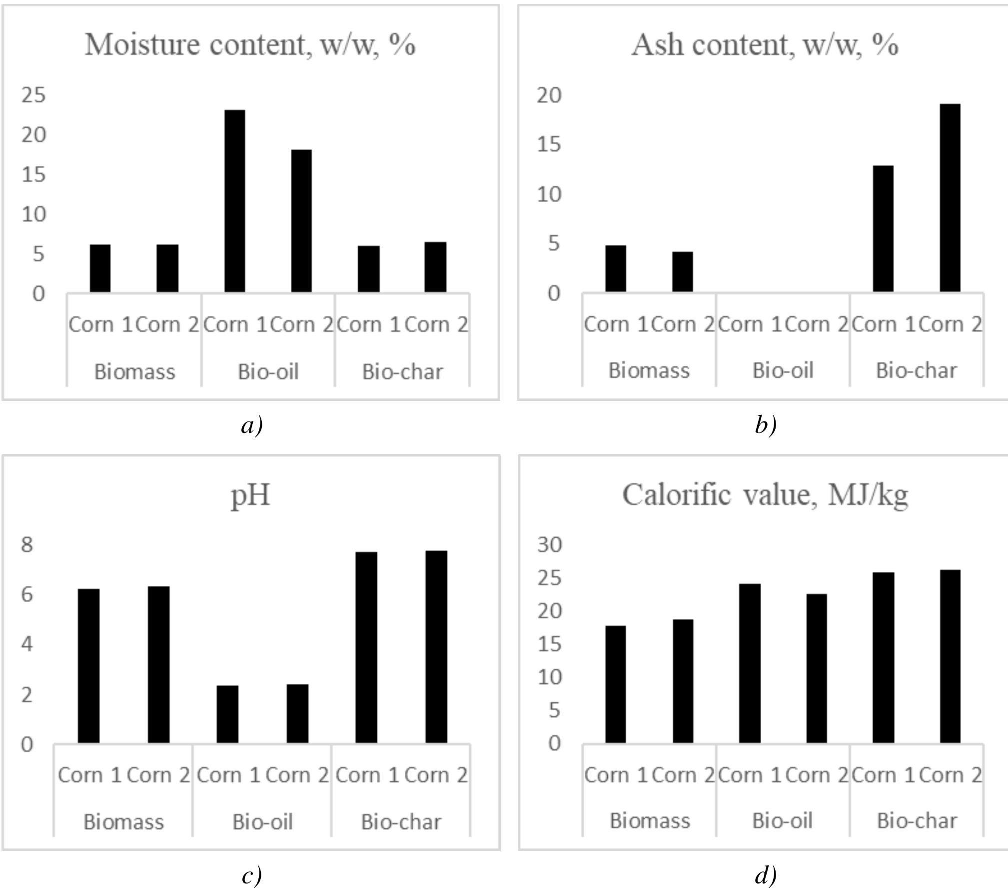

Figure 2, Moisture (a) and ash content (b) and pH (c) and calorific value (d) of obtained bio-oil and bio-char compared with biomass

Table 1, Metal content in bio-oil and biochar

Metal content, mg/kg	**Sample**			
	Bio-oil		**Bio-char**	
	Corn 1	**Corn 2**	**Corn 1**	**Corn 2**
K	<100	155.94	16654	18930
S	154.29	722.38	974.03	594.42
Mg	<100	<100	5440	4385
Al	<100	<100	391.46	250.8
Na	<100	<100	<100	<100
Cu	5.64	4.69	17.48	17.65
Ca	<100	<100	12949	9474
Si	<100	542.5	37198	31705
Pb	<0.25	<0.25	0.94	<0.25
Cd	<0.15	<0.15	<0.15	<0.15
Cr	<0.15	<0.15	<0.15	<0.15
As	<0.25	<0.25	<0.25	<0.25
Hg	<0.15	<0.15	<0.15	<0.15

CONCLUSION

Two types of corn biomass were pyrolyzed, and the liquid and solid pyrolysis products were characterized. Moisture and ash content, pH value, heating value, and metal content were determined. Based on the results, it can be seen that the obtained products have the potential to be used as fuel with certain improvements, such as reducing moisture content and increasing pH to reduce corrosive effects and increase heating value. Some potential solutions include the introduction of compounds with high carbon and hydrogen content, such as plastic waste. The possibility of using catalyzed co-pyrolysis should also be considered to achieve the best possible effect.

LITERATURE

[1] Smith, P., Adams, J., Beerling, D. J., Beringer, T., Calvin, K. V., Fuss, S., Griscom, B., Hagemann, N., Kammann, C., Kraxner, F., Minx, J. C., Popp, A., Renforth, P., Vicente Vicente, J. L., & Keesstra, S., Land-Management Options for Greenhouse Gas Removal and Their Impacts on Ecosystem Services and the Sustainable Development Goals. In Annual Review of Environment and Resources, Vol. 44, Issue 1, 2019, pp. 255–286. Annual Reviews. DOI: https://doi.org/10.1146/annurev-environ-012420-045920.

[2] Bridgwater, A. V., Review of fast pyrolysis of biomass and product upgrading. In Biomass and Bioenergy Vol. 38, 2012, pp. 68–94. Elsevier BV. DOI: https://doi.org/10.1016/j.biombioe.2011.01.048.

[3] Foster, W., Azimov, U., Gauthier-Maradei, P., Molano, L. C., Combrinck, M., Munoz, J., Esteves, J. J., & Patino, L., Waste-to-energy conversion technologies in

the UK: Processes and barriers – A review. In Renewable and Sustainable Energy Reviews Vol. 135, 2021, p. 110226, Elsevier BV, DOI: https://doi.org/10.1016/j.rser.2020.110226

[4] Zhang, D., Liu, G., Chen, C., Zhang, Y., Hao, Y., & Casazza, M., Medium-to-long-term coupled strategies for energy efficiency and greenhouse gas emissions reduction in Beijing (China). In Energy Policy Vol. 127, 2019, pp. 350–360 Elsevier BV, DOI: https://doi.org/10.1016/j.enpol.2018.12.030.

[5] Statista, (www.statista.com) Last accessed: 4.9.2024.

[6] Harris, Z. M., Spake, R., & Taylor, G., Land use change to bioenergy: A meta-analysis of soil carbon and GHG emissions. In Biomass and Bioenergy Vol. 82, 2015, pp. 27–39. Elsevier BV, DOI: https://doi.org/10.1016/j.biombioe.2015.05.008.

[7] Valizadeh, S., Oh, D., Jae, J., Pyo, S., Jang, H., Yim, H., Rhee, G. H., Khan, M. A., Jeon, B.-H., Lin, K.-Y. A., Show, P. L., Sohn, J. M., & Park, Y.-K., Effect of torrefaction and fractional condensation on the quality of bio-oil from biomass pyrolysis for fuel applications. In Fuel Vol. 312, 2022, p. 122959, Elsevier BV. DOI: https://doi.org/10.1016/j.fuel.2021.122959.

[8] González, R., González, J., Rosas, J. G., Smith, R., & Gómez, X., Biochar and Energy Production: Valorizing Swine Manure through Coupling Co-Digestion and Pyrolysis. In C Vol. 6, Issue 2, 2020, p. 43. MDPI AG. DOI: https://doi.org/10.3390/c6020043.

[9] Kumar, A., Jones, D. D., & Hanna, M. A., Thermochemical Biomass Gasification: A Review of the Current Status of the Technology. In Energies Vol. 2, Issue 3, 2009, pp. 556–581. MDPI AG. DOI: https://doi.org/10.3390/en20300556.

[10] Lee, U., Han, J., & Wang, M., Evaluation of landfill gas emissions from municipal solid waste landfills for the life-cycle analysis of waste-to-energy pathways. In Journal of Cleaner Production Vol. 166, 2017, pp. 335–342, Elsevier BV. DOI: https://doi.org/10.1016/j.jclepro.2017.08.016.

[11] Laird, D. A., Brown, R. C., Amonette, J. E., & Lehmann, J., Review of the pyrolysis platform for coproducing bio-oil and biochar. In Biofuels, Bioproducts and Biorefining Vol. 3, Issue 5, 2009, pp. 547–562. Wiley, DOI: https://doi.org/10.1002/bbb.169.

[12] Zilberman, D., Laird, D., Rainey, C., Song, J., & Kahn, G., Biochar <scp>supply-chain</scp> and challenges to commercialization. In GCB Bioenergy Vol. 15, Issue 1, 2022, pp. 7–23, Wiley, DOI: https://doi.org/10.1111/gcbb.12952.

[13] Mullen, C. A., Boateng, A. A., Goldberg, N. M., Lima, I. M., Laird, D. A., & Hicks, K. B., Bio-oil and bio-char production from corn cobs and stover by fast pyrolysis. In Biomass and Bioenergy Vol. 34, Issue 1, 2010, pp. 67–74, Elsevier BV. DOI: https://doi.org/10.1016/j.biombioe.2009.09.012.

[14] Mignogna, D., Szabó, M., Ceci, P., & Avino, P., Biomass Energy and Biofuels: Perspective, Potentials, and Challenges in the Energy Transition. In Sustainability Vol. 16, Issue 16, 2024, p. 7036, MDPI AG, DOI: https://doi.org/10.3390/su16167036.

[15] Maulinda, L., Husin, H., Arahman, N., Rosnelly, C. M., Andau, E., Lestari, W., & Karo-Karo, J. (2021). Fast pyrolysis corn husk for bio-oil production. In IOP Conference Series: Materials Science and Engineering Vol. 1098, Issue 2, 2021, p. 022007, IOP Publishing. DOI: https://doi.org/10.1088/1757-899X/1098/2/022007.
[16] Alfattani, R., Shah, M. A., Siddiqui, M. I. H., Ali, M. A., & Alnaser, I. A., Bio-Char Characterization Produced from Walnut Shell Biomass through Slow Pyrolysis: Sustainable for Soil Amendment and an Alternate Bio-Fuel. In Energies ,Vol. 15, Issue 1, 2021, p. 1, MDPI AG, DOI: https://doi.org/10.3390/en15010001.
[17] Yuan, J.-H., Xu, R.-K., & Zhang, H., The forms of alkalis in the biochar produced from crop residues at different temperatures. In Bioresource Technology, Vol. 102, Issue 3, 2011, pp. 3488–3497. Elsevier BV, DOI: https://doi.org/10.1016/j.biortech.2010.11.018.
[18] Li, W., Dang, Q., Brown, R. C., Laird, D., & Wright, M. M.,The impacts of biomass properties on pyrolysis yields, economic and environmental performance of the pyrolysis-bioenergy-biochar platform to carbon negative energy. In Bioresource Technology Vol. 241, 2017, pp. 959–968, Elsevier BV. DOI: https://doi.org/10.1016/j.biortech.2017.06.049.
[19] Kendall, R., Brown, T., & Hetherington, L., Coal, British Geological Survey, Natural Environmental Research Council, 2010.