Pyrolysis of corn stalks: the potential of using bio-oil as a fuel

JELENA ISAILOVIĆ[1]*, EMILIJA VUKIĆEVIĆ[2], MALIŠA ANTIĆ[1], JAN SCHWARZBAUER[3], LJUBIŠA IGNJATOVIĆ[4], GORDANA GAJICA[5] and VESNA ANTIĆ[1]

[1]*University of Belgrade – Faculty of Agriculture, Nemanjina 6, 11080 Zemun, Serbia,*
[2]*University of Belgrade – Faculty of Chemistry, Studentski trg 12-16, 11158 Belgrade, Serbia,*
[3]*Institute for Geology and Geochemistry of Petroleum and Coal, RWTH, Lochnerstr. 4-20, Aachen, Germany,* [4]*University of Belgrade – Faculty of Physical Chemistry, Studentski trg 12-16, 11000 Belgrade, Serbia, and* [5]*Institute of Chemistry, Technology and Metallurgy, National Institute of the Republic of Serbia, Njegoševa 12, 11000 Belgrade, Serbia.*

Abstract: Due to the increasing consumption of fossil fuels, there is a growing demand for renewable energy resources. At the same time, a significant amount of agricultural waste accumulates, including corn residues, and the efficient management of this waste is a challenge. In this work, the waste biomass, which consisted of the stalks of two types of corn, was characterized and subjected to the pyrolysis process at 400 °C. The physicochemical characterization of the obtained liquid fraction (bio-oil) was performed, and the obtained data were compared with the literature data for liquid biofuel. The calorific value of bio-oil was above 22 MJ kg^{-1}, which indicates the good potential of waste corn biomass as an energy source. With appropriate further changes in the composition of waste, by adding materials with a higher carbon and hydrogen content, corn stalks can represent a significant energy source, with better regulation of disposal and storage of agricultural waste.

Keywords: agricultural biomass; pyrolysis process; physico-chemical properties; liquid fraction.

INTRODUCTION

Contemporary society encounters significant challenges due to the rising consumption of fossil fuels and the resulting environmental impacts. Therefore, there is an increasing emphasis on developing alternatives to ensure a more sustainable energy balance and reduce negative environmental impacts. In this context, the present research focuses on using corn biomass as a renewable energy source.[1]

The global corn production continues to grow and it has reached 1.2 billion tons according to the latest statistics from 2021.[2] In Serbia, the data from 2022 show an annual output of 4,283,293 tons of corn on 952,216 hectares of arable land across the country.[3]

After corn harvest, the plant residues such as stalks, leaves, cobs, and husks can be partly used as animal feed. Also, parts of plant waste remain on arable land and return to the soil.[4] The remaining amount of biomass, which is not negligible (about 30%), remains to be used as an energy source. Corn waste biomass is rich in lignocellulose material, with lignin, cellulose, and hemicellulose being the main components of these plant residues.[5] Lignin is a three-dimensional amorphous polymer consisting of aliphatic and aromatic structures, and it is considered a non-nutritive part of biomass. Lignin provides strength and hydrophobicity to plant cell walls, while protecting polysaccharides from microbial degradation. Lignin, cellulose, and hemicellulose can be converted into liquid fuel by the pyrolysis process, effectively managing this waste and yielding a significant amount of bio-oil that can be modified as a substitute for fossil fuel.[6,7] It is important to note that corn biomass is not a significant food source for the animal consumption because it has a low level of nutrients, making it waste.[7,8] Also, agricultural lignocellulosic biomass represents a cheap and readily available source of carbon that can be used.[9]

Traditionally, corn residues are often burned or disposed of as unnecessary waste in many fields worldwide.[10] However, such a practice can have profound implications for the environment, because the burning of such material releases various gases and particles into the atmosphere, contributing to air pollution and negatively impacting the quality of the environment and human health.[11]

Using biomass as an energy source has several advantages because it is renewable and can be replenished faster than used, keeping ecosystems in balance.[8] The biomass-based energy reduces greenhouse gas emissions and contributes to the reduction of the greenhouse effect, which is crucial to the climate change issue.[12] The production of the liquid fuels from biomass can help reduce dependency on fossil fuels, increase the energy independence, and reduce the economic and the geopolitical risks.[1]

This is the first study examining the characteristics of waste stalks from two types of corn, BC 398 and ZP 6263, cultivated in the municipality of Šabac, Serbia. Additionally, it provides a detailed analysis of the physico-chemical characteristics of the bio-oil obtained through the pyrolysis of corn residues under the specified conditions. The characterization of the liquid fractions obtained aims to provide a thorough understanding of the potential of this alternative energy approach. The findings of this research are expected to offer valuable insights for the advance of sustainable energy solutions and contributing to the global initiatives aimed considering the climate change.

EXPERIMENTAL

Biomass samples

Two types of corn, BC 398, designated as Kz, and ZP 6263, designated as Kn, were used for this study, collected from the vicinity of Šabac, Serbia, from two different plots. The samples were taken at a height of 5 to 10 cm above the ground surface. Before any analysis, the samples were air-dried for 30 days to achieve a less than 10% moisture content. Afterward, they were milled to achieve an average particle size ranging between 2 and 5 mm.

Thermogravimetric analysis (TGA)

The thermal degradation of corn stalk samples was studied by thermogravimetric analysis (TGA). Thermogravimetric measurements were performed on TA Instruments TGA Q500, Thermogravimetric Analyzer (Delaware, USA). The nitrogen flow was 60 cm^3 min^{-1}. About 10 mg of the sample was placed into the platinum crucible, loaded into the TG furnace, and heated from 25 to 700 °C. The applied heating rate was 5 °C min^{-1}. The signals of weight (%) and deriv. weight (% $°C^{-1}$) were presented by the package TA Advantage Universal Analysis 2000 software, version 4.5 A. The obtained TGA and their DTG curves were used to analyse the thermal properties of the biomass samples.

Pyrolysis

Air-dried samples of corns Kz and Kn, 19.61 g and 19.14 g, respectively, were pyrolyzed in a carbolite tube furnace (MTF 10/15/130, Carbolite, UK) for 30 minutes at 400 ºC under a constant flow of nitrogen (99.999%) at a rate of 150 cm^3 min^{-1}. The quartz tube was situated within the furnace. The glass joint ends of the quartz tube were outside the furnace. The tube was connected with the nitrogen supply at one side, while the other was connected with a recipient trap filled with solvent. The sample was situated in a porcelain vessel, and the vessel was transferred in the middle of a quartz tube. The heating rate was 100 ºC per minute. The liquid fraction was collected in HPLC-grade acetone. The solvent was removed after pyrolysis in an inert nitrogen atmosphere. The yield of liquid fraction was calculated according to the mass of pyrolyzed samples.

Physico-chemical characterization of biomass and bio-oil

The composition of biomass

The composition of corn stalks samples was analysed in detail to determine the lignin, cellulose, hemicellulose, and extractable material content. The extractives were isolated from the sample using acetone with heating, after which the sample was dried to a constant mass at a temperature of 110 °C. The quantity of extractives was determined from the difference between the initial and dried masses after extraction. Subsequently, the hemicellulose content was determined in the sample without extractives by extraction with a 0.5 mol dm^{-3} solution of sodium hydroxide with heating. The sample was then rinsed with distilled water until the reaction was negative for Na^+ ions and dried to a constant mass. The lignin content was obtained by extraction with 98% sulfuric acid on a sample from which extractives had been previously removed. The sample was rinsed with distilled water until a negative reaction for sulphate ions and then dried to a constant mass. The cellulose content was calculated as a difference of up to 100%.[13]

Determination of pH, moisture and ash content, elemental analysis, and calorific value for biomass and bio-oil samples

The pH value of corn biomass and bio-oil samples was measured using the standard ASTM E70 method. The moisture content of biomass samples was determined by drying in an oven

according to the ASTM E871 standard. The moisture content in bio-oil samples was determined using 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 in biomass samples was determined using the thermal analysis following the ASTM E1755 standard, while for bio-oil, the ASTM D482 standard was used. Elemental analysis of biomass and bio-oil samples was conducted on a CHNS Elementar-Vario Macro Cube (Elementar, Germany) for carbon, hydrogen, nitrogen, and sulphur analysis, using the standards SRPS ISO 13878:2005, SRPS ISO 10694:2005, and SRPS ISO 15178:2019. At the same time, the oxygen content was calculated as a difference of 100%. The calorific value of corn biomass and bio-oil samples was determined on an instrument IKA C400 (IKA, Germany), using the standard SRPS CEN/TS 16023:2014.

Density, viscosity, and the group composition of the bio-oil

The bio-oil was characterized by the parameters such as density, viscosity, the group composition, FTIR analysis, and the toxic elements content. The density was determined using the ISO 12185 standard. The rheological behaviour of bio-oil samples was investigated using shear measurements in the parallel plate geometry (diameter 25 mm; gap 500 μm) on a Discovery Hybrid Rheometer HR2 (TA Instruments, U.S.A). The experiments were conducted at 25 and 40 °C using a Peltier plate heating system, and viscosity curves were obtained within a shear rate range from 0.1 to 100 s^{-1}. To determine the group composition of the bio-oil, samples were fractionated into aliphatic, aromatic, and NSO fractions (polar fraction containing nitrogen, sulfur, and oxygen compounds). The fractionation process involved the separation of different compounds using different eluents. A 15 mg sample was dissolved in 0.100 cm^3 of acetone and transferred to silica gel. Column chromatography was performed using 2 g of dried silica gel, with the sample transferred to the top of the column. Below this column section, dry Na_2SO_4 is placed to remove moisture from the sample. The Fractions were eluted with the following solvents: aliphatic with 5 cm^3 *n*-hexane; aromatic with 5 cm^3 of a mixture of *n*-hexane/dichloromethane (40/60); and NSO fraction with 5 cm^3 of methanol. The fractions were collected in receiving vessels, and after the solvent evaporation, the vessels weights were measured. The proportions of these fractions were determined gravimetrically after elution.[14]

FTIR analysis of bio-oil

Liquid bio-oil samples (~0.01 cm^3) were placed between two KBr plates, and spectra were obtained using a transmission technique. Infrared spectra over the wavelength range 4000-400 cm^{-1} were recorded with an IRAffinity-1 FTIR spectrophotometer (Shimadzu, Japan). The measurement resolution was 4 cm^{-1}.

ICP-OES analysis of bio-oil

The samples were prepared using a microwave digestion oven CEM Mars 5 (MARS, USA) according to the standard method EPA 3052. For the bio-oil samples, 0.25 g was measured, and then 9 cm^3 of concentrated nitric acid, 3 cm^3 of hydrochloric acid, and 0.5 cm^3 of hydrofluoric acid were added. The samples were placed in a microwave digestion oven, and the heating temperature was set to 180 ± 5 °C for 5.5 minutes. After cooling, the samples were filtered through "blue band" filter paper (pores size < 2 μm) and topped up to a volume of 50 cm^3. Then they were analysed using the ICP-OES technique ("Spectroblue TI"-Spectro, Germany) following the standard method EPA 200.7.

GC-MS analysis of bio-oil

GC-MS analysis was performed in order to determine the molecular composition of liquid pyrolysates and to identify the most dominant compounds. The samples were analysed using the GC–MS technique (Varian 450-GC with 220-MS, USA). The separation of compounds was performed on FactorFour capillary column VF-5ms 30 m × 0.25 mm with 0.25 μm film thickness (Varian, USA). The injector temperature was 200 °C, and the injection volume was 1 mm^3 in split mode 90%. The carrier gas was helium at a constant flow rate of 1 cm^3 min^{-1}. The oven program started at 50 °C. Afterward, the temperature was incremented at 3 °C min^{-1} to reach 150 °C, and then immediately at 25 °C min^{-1} until it reached 280 °C, where it was held for 20 minutes. The parameters for MS analysis were as follows: EI (70 eV) temperature 200 °C, solvent cut time 3 minutes, scan 45-650 m/z. The identification was based on comparing a particular compound's mass spectra and retention time with the reference materials using the "Wiley registry of mass spectral data, 8th edition" library.

RESULTS AND DISCUSSION

The results of physico-chemical characterization of biomass

The composition of corn stalk samples, pH value, moisture and ash content, elemental analysis, and calorific value are presented in Table I. These analyses provide the key information regarding the chemical composition of corn biomass and its suitability for conversion into biofuels. The moisture content was about 6% in both samples, which was acceptable for the pyrolysis experiments. Biomass rich in cellulose and hemicellulose is a better source for obtaining bio-oil than lignin-rich biomass.[15] The lignin content was higher in the Kn sample, which indicated that this sample would give a lower yield of liquid fraction than the Kz sample. All values provided in Table I were within the range of literature values,[16,17] except for the sulphur content, which was present in significant amounts in the Kz sample. This can be explained by the specific composition of the soil where the Kz sample was grown, which is probably rich in sulphur compounds.

TABLE I. Results of the composition and physico-chemical characterization of the biomass.

P	Ext.	Lig	Cell	HC	pH	MC	AC	Elemental analysis, wt %					CV
S	%	%	%	%		%	%	C	H	N	O	S	MJ kg^{-1}
Kn	6.00	19.43	28.86	45.72	6.26	6.20	4.78	45.68	6.44	0.86	46.64	0.384	17.80
Kz	4.23	13.25	34.29	48.24	6.32	6.25	4.25	41.90	4.15	0.90	34.89	18.16	18.80

P – parameters; S – sample; Ext – extractives; Lig – lignin; Cell – cellulose;
HC – hemicellulose; MC – moisture content; AC – ash content; CV – calorific value

TGA results of two types of corn biomass

The thermogravimetric analysis was applied to monitor the thermal behaviour of corn stalk samples, which is essential for understanding the pyrolysis process and characterizing this biomass as a feedstock for biofuel production. The TGA analysis of two types of corn stalks is shown in Fig. 1. Given that corn biomass is a complex mixture mainly consisting of three major components - lignin, cellulose,

and hemicellulose, it is expected that the thermogravimetric analysis of corn stalks is more complex than the TGA of individual components. According to the information from Chen et al., each individual component exhibits different thermal stability and thermogravimetric behaviour depending on its chemical structure. Lignin, with the most stable structure compared to hemicellulose and cellulose, rapidly degrades over a wide temperature range from 311.5 to 461.3 °C. Cellulose, less stable than lignin but more stable than hemicellulose, degrades during the second phase in the 326.8 to 369.7 °C range. As the least stable of the three components, hemicellulose degrades during the second phase in the 223.4 to 332.8 °C range.[18]
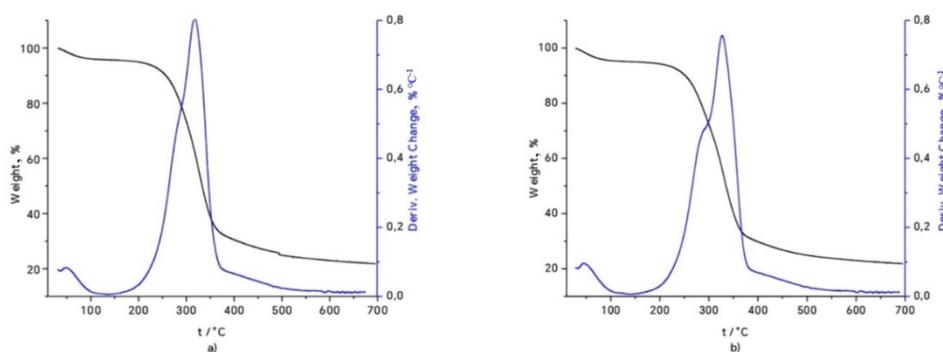

Fig. 1. Thermogravimetric curves for a corn sample a) Kn and b) Kz

The obtained thermogravimetric curves of corn stalks contained three main steps (Fig. 1). During the first degradation step, at around 120 °C, there was a minimal weight loss below 5% in both pre-dried corn stalk samples, corresponding well to a water content of about 6% (Table I). The second phase of thermal degradation (200-400 °C) involves rapid sample decomposition, resulting in the most substantial weight loss. Finally, the third step represents the slow stage where bio-char is formed (400-600 °C). The second step was more complex in the case of the Kz sample, showing a maximum of 330 °C on the DTG curve and a visible "shoulder" at 268 °C, unlike the Kn sample, where the "shoulder" was much less pronounced. This phenomenon corresponds to the chemical composition, where the "shoulder" appears due to the decomposition of hemicellulose and part of cellulose. The Kz sample contained higher amounts of hemicellulose (48.24%) and cellulose (34.29%) in comparison with the Kn sample, where the quantities of hemicellulose (45.72%) and cellulose (28.86%) were lower. It can be concluded that the higher content of hemicellulose and cellulose caused the appearance of a "shoulder" on the DTG curve of sample Kz. The maximum degradation rate corresponds to the decomposition of the mixture of cellulose and lignin. Lignin coats cellulose and hemicellulose, protecting these structures, which may influence

the thermal degradation behaviour. The total weight loss amounted to 73.2% for the Kn sample and 78.9% for the Kz sample, which can be linked to the biomass composition. Since the lignin content is higher in the Kn sample (19.43%), it was expected that the residue after TGA analysis would be larger, which was confirmed in comparison to the other sample with a lower lignin content (13.25%). Since the study aimed to obtain the highest possible bio-oil yield, we concluded that a temperature of 400 °C to perform pyrolysis is sufficient to decompose the entire sample.

Pyrolysis of two types of corn biomass

The pyrolysis of corn biomass produces three fractions: liquid, solid, and gaseous. This study focused on the liquid fraction, which was isolated and characterized in detail. The values for the amount of pyrolyzed sample are given in Table II, as well as the obtained yield of bio-oil in relation to the pyrolyzed mass of corn stalks. The obtained results were compared with the literature data for bio-oil yield. It can be noted that there is a difference in the yield of bio-oil obtained from these two types of corn stalks, where the sample Kz gave a significantly higher yield of bio-oil (33.5%) compared to the sample Kn (22.8%).

TABLE II. The yield of the liquid fraction concerning the mass of the pyrolyzed sample and comparison with literature data.

Sample	m [a]/ g	Yield of liquid fraction, wt %	Yield of liquid fraction, wt % [b, 19]
Kn	19.14	22.8	30-33
Kz	19.61	33.5	

[a] pyrolyzed biomass; [b] literature data

The difference in the bio-oil content obtained by the pyrolysis of these two samples may be attributed to their distinct chemical compositions. The difference in the content of bio-oil obtained by pyrolysis of these two samples can be attributed to their different chemical composition. As mentioned before, higher lignin content leads to lower bio-oil yield, which is the case with the sample Kn.

The results of physico-chemical characterization of bio-oil

The results obtained for density, pH, ash and moisture content, elemental analysis, calorific value, and viscosity are presented in Table III. The density of the bio-oil is slightly higher than that of crude oil, which may be attributed to the presence of a large number of oxygenated compounds, and according to the literature, it is similar to the data obtained from other authors.[19] The acidity of bio-oil can affect its corrosiveness during application, so it is desirable to modify the liquid fraction.[20] The presence of water in bio-oil increases the oxygen content and potentially leads to corrosion, so it is desirable to minimize the water content.[19] Based on the obtained results, a significant amount of water is present, so it is necessary to reduce these values by prior biomass drying or using dehydration

agents for bio-oil. The ash content is crucial for assessing the energy properties of biomass. The lower the ash content in the samples, the more energy-efficient the use of bio-oil.[21] Based on the values in Table III, it can be seen that the ash content values in bio-oil samples are lower compared to the initial biomass and according to literature data for bio-oil,[17] which correlates with the sulphur content, also lower in the bio-oil compared to the initial biomass. It can be concluded that sulphur is removed from the samples during the pyrolysis and annealing processes, most likely in the form of gases, such as sulphur dioxide, for example. The elemental analysis is vital for determining the essential chemical characteristics of biomass. The elemental analysis shows that the content of all elements, carbon, oxygen, hydrogen, and nitrogen, are within the literature values.[18,21] The difference in carbon content in the initial biomasses is not significant – 45.68% for Kn and 41.90% for Kz. However, there is a significant imbalance in the carbon content in the bio-oil, with a higher proportion in the Kn sample (43.93%) compared to Kz (26.97%). The oxygen content is also significantly different, with a higher proportion in Kz (60.19%) compared to Kn (34.14%). This variable of the elemental composition may be associated with the content of lignin, cellulose, and hemicellulose in the samples. In the Kn sample, where lignin is dominant (19.43%), containing more carbon compared to cellulose and hemicellulose, a higher carbon content was observed in the bio-oil. In contrast, in the Kz sample, where there is a higher proportion of cellulose (34.29%) and hemicellulose (48.24%), higher oxygen content was observed in the resulting bio-oil. The calorific value is a parameter used to determine biomass's energy potential and potential for energy production during the pyrolysis process. It can be concluded that bio-oil has a better energy potential compared to the initial biomass,[1] which fits with the literature values for the liquid fraction of pyrolysis products.[19] Viscosity can affect engine performance and injection processes, so determining it is essential. Viscosity was measured at temperatures of 25 and 40 °C. It can be concluded that the obtained values for viscosity also correspond to literature data.[18] Results of the ICP analysis are provided in the table in the supplementary material (Table S1). Determining the concentration of specific elements such as Si, K, and S is important for the engine operation because a higher presence of these elements results in increased ash in the engine, making such bio-oils unsuitable for use as fuels.[21] The concentration of Si for both samples and K for sample Kn was below the detection limit (< 100 mg kg^{-1}), while the concentration of K for sample Kz was 155.94 mg kg^{-1}, and the concentrations of S for the same sample were 154.29 mg kg^{-1}, and for Kn 722.38 mg kg^{-1}. Additionally, the presence of toxic elements that can harm human health, such as lead, mercury, and cadmium, was below the detection limit (< 0.25 mg kg^{-1} for Pb, and < 0.15 mg kg^{-1} for Hg and Cd), indicating that using such bio-oil as liquid fuel would not lead to emissions of these elements in the environment.

TABLE III. The results of physico-chemical parameters of bio-oil.

P / S	pH	MC %	AC %	Elemental analysis, wt %					CV / MJ kg⁻¹	ρ / g cm⁻³	η / Pa s	
				C	H	N	O	S			25 °C	40 °C
Kn	2.35	23.06	0.07	43.93	6.40	14.83	34.14	0.70	24.18	1.15	0.014	0.010
Kz	2.43	18.09	0.04	26.97	7.86	4.79	60.19	0.19	22.62	1.08	0.006	0.003

P – parameters; S – sample; MC – moisture content; AC – ash content; CV – calorific value

The results of FTIR analysis of bio-oil

The FTIR analysis was performed on the bio-oil samples; the results are presented in Fig. 2. Corn samples were subjected to infrared spectroscopy (IR) to identify and analyse functional groups and structures. A characteristic peak around 3400 cm⁻¹ of a hydroxyl group originates from water, alcohols, phenols, or their derivatives. A peak at around 1700 cm⁻¹ is associated with the axial deformation of the carbonyl group. The peak around 1400 cm⁻¹ could be attributed to the deformation of C-H in CH_2 and CH_3 groups. The presence of C-O and deformed C-OH groups is linked to a value of around 1050 cm⁻¹. The phenolic compounds were from lignin. The ketone was formatted from hemicellulose/cellulose.[22] The lower pH value of the bio-oil compared to crude oil, which typically has a pH range between 6 and 8,[23] can be attributed to the presence of carboxylic and hydroxyl groups.
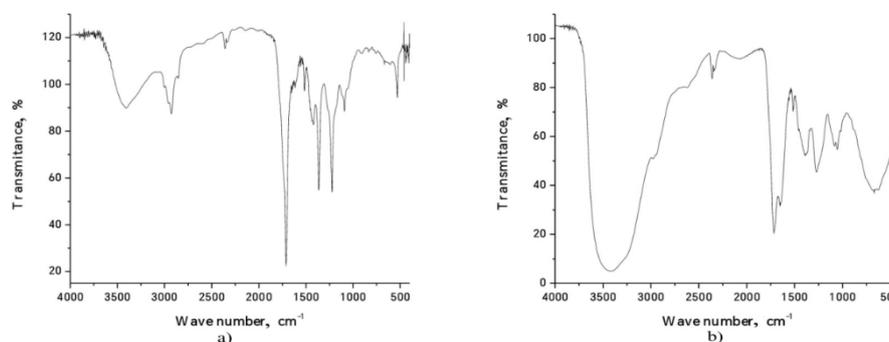

Fig. 2. The FTIR analysis for corn samples of bio-oil: a) Kn and b) Kz

Results of the compositional analysis of bio-oil

The compositional analysis of the bio-oil can show whether it is suitable or makes sense to separate fractions and utilize them for different purposes. Based on the results presented in Table IV, it is evident that the aliphatic and aromatic fractions are negligible compared to the NSO fraction, which is expected for the bio-oil derived from biomass, considering that the basic structures in biomass are cellulose, hemicellulose, and lignin, which are rich in oxygen.

TABLE IV. The group composition of the bio-oil.

Fraction / Sample	Alifatic fraction, %	Aromatic fraction, %	NSO fraction, %
Kn	2.5	2.5	95.0
Kz	1.1	0.5	98.4

Diesel and gasoline are liquid fuels consisting of linear saturated hydrocarbons, branched saturated hydrocarbons, saturated cyclic alkanes, and aromatic compounds, with a dominant aromatic fraction of up to 50 % and *iso*-paraffins of up to 35%.[24] The fractions that make up a significant part of liquid fuels are not present in bio-oil, which suggests that bio-oil in its native form is unsuitable for direct use, considering that it is similar to crude oil. Therefore, it must be processed and modified to be used as a fuel.
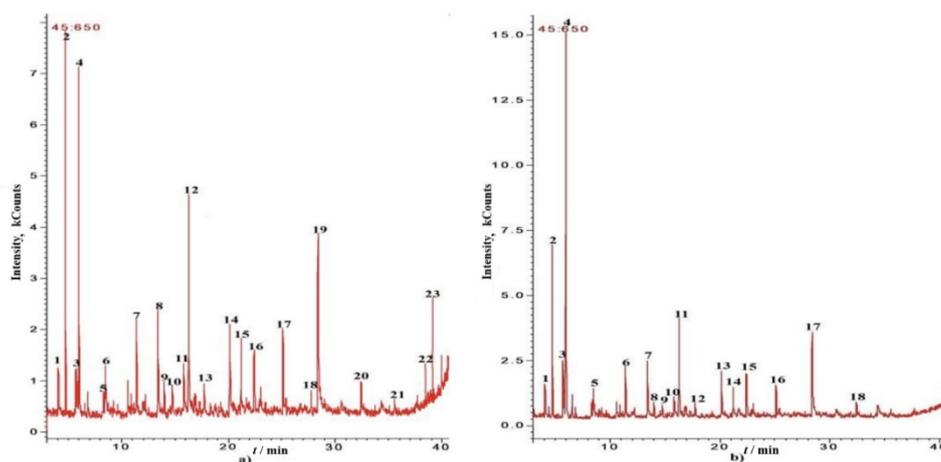
GC-MS analysis of bio-oil

Fig. 3. GC- MS analysis of bio-oil produced from two types of corn: a) Kn and b) Kz

The compounds identified in obtained bio-oil using GC-MS analysis include: 3-penten-2-one, 4-methyl-; 2-furancarboxaldehyde; 2-cyclopenten-1-one, 2-methyl-; phenol; 2-cyclopenten-1-one, 2-hydroxy-3-methyl-; 2-cyclopenten-1-one, 2,3-dimethyl-; phenol, 2-methyl-; phenol, 4-methyl-; phenol, 2-methoxy-; phenol, 3-ethyl-; guaiacol, 4-ethyl-; and phenol, 2,6-dimethoxy. The remaining compounds are isomers formed either during pyrolysis or afterward. According to the literary data, the identified compounds have also been found in bio-oil from corn, reported by other researchers, along with their isomers which include 2-furancarboxaldehyde, 2-cyclopenten-1-one, 2-methyl-; phenol; 2-cyclopenten-1-one, 2,3-dimethyl-; phenol, 2-methyl-; phenol, 4-methyl-; phenol, 2-methoxy-; 2-cyclopenten-1-one, 3-ethyl-2-hydroxy-; and phenol, 2,6-dimethoxy-.[1,25] The

results of the GC-MS analysis complement those of the FTIR analysis, group composition, and the oxygen content in the bio-oil samples. Based on the results of the FTIR analysis, the presence of hydroxyl and carbonyl groups was found, which correlates with the GC-MS analysis confirming the presence of compounds containing these groups, such as various phenols derivates and 2-furancarboxaldehyde, for example.

TABLE V. The results of GC-MS analysis of bio-oil.

No[a]	Compounds Fig. 3 a)	R.t, min[b]	Compounds Fig. 3 b)	R.t, min[b]
1	Heptane, 2,2,4,6,6-pentamethyl-	4.09	3-pentanone	4.07
2	3-penten-2-one, 4-methyl-	4.72	3-penten-2-one, 4-methyl-	4.72
3	2-furancarboxaldehyde	5.73	2-furancarboxaldehyde	5.71
4	Not identified	5.96	Not identified	5.94
5	2-cyclopenten-1-one,-2-methyl-	8.28	2-cyclopenten-1-one, 2-methyl-	8.27
6	Ethanone, 1-(2-furanyl)-	8.41	Phenol	11.38
7	Phenol	11.38	2-cyclopenten-1-one, 2-hydroxy-3-methyl	13.39
8	2-cyclopenten-1-one, 2-hydroxy-3-methyl-	13.39	2-cyclopenten-1-one, 2, 3-dimethyl-	13.98
9	2-cyclopenten-1-one, 2,3-dimethyl-	13.98	Phenol, 2-methyl-	14.77
10	Phenol, 2-methyl-	14.77	Phenol, 4-methyl-	15.83
11	Phenol, 4-methyl-	15.82	Phenol, 2-methoxy-	16.27
12	Phenol, 2-methoxy-	16.27	Cyclohexanone, 2-ethyl-2-propyl-	17.74
13	2-cyclopenten-1-one, 3-ethyl-2-hydroxy-	17.73	Phenol, 3-ethyl-	20.15
14	Phenol, 3-ethyl	20.14	Phenol, 2-methoxy, 5-methyl-	21.20
15	1-hydroxy-2-methoxy-4-methylbenzene	21.18	Not identified	22.41
16	Not identified	22.38	Guaiacol, 4-ethyl-	25.10
17	Guaiacol, 4-ethyl-	25.10	Phenol, 2,6-dimethoxy-	28.39
18	Benzenebutanitrile	27.74	Ethanone,1-(2,3,4)-tri(hydroxyphenyl)-	32.43
19	Phenol, 2,6-dimethoxy-	28.40	-	-
20	Benzene, 1,2,4- trimethoxy-	32.44	-	-
21	Ethanone, 1,1'-(1,3-propanediyl)bis-	35.58	-	-
22	Benzene, 1,1'-(1,3-propanediyl)bis-	38.45	-	-
23	Not identified	39.14	-	-

CONCLUSION

In this study, the composition of bio-oil obtained by pyrolysis of corn stalks was analysed. The ash content in the bio-oil was below 1%, consistent with the literature data and the sulphur content determined by the elemental analysis. Based on the elemental composition, the carbon and oxygen content were determined, correlating with the composition of the initial biomass. The presence of a

significant amount of oxygen, besides elemental analysis, was confirmed through other parameters, including pH, moisture content, density, FTIR analysis, and GC-MS analysis. The functional groups identified by FTIR analysis were further identified as various compounds by GC-MS analysis. Such compound classes contribute to the acidic pH, as observed here. Additionally, the high density indicates the presence of heavier compounds, such as oxygen compounds. The bio-oil exhibits a slightly higher calorific value than the original biomass, suggesting it may be a better energy source. The lower C/H ratio affects the calorific value due to the significant presence of oxygen, so this bio-oil cannot be used as a liquid fuel in its current form. Further research should focus on improving the quality of bio-oil, including increasing the carbon and hydrogen content, reducing the oxygen and water content, as well as the calorific value. Some possibilities include the addition of other waste materials with high carbon and hydrogen content, such as synthetic polymers, and the use of catalysts in pyrolysis processes, which would undoubtedly improve bio-oil characteristics and enable its more efficient and sustainable use for various purposes. In conclusion, this study highlights the need for further research and the development of biofuels that would result in a more sustainable and environmentally friendly alternative to fossil fuels.

SUPPLEMENTARY MATERIAL

Additional data are available electronically at the pages of journal website: https://www.shd-pub.org.rs/index.php/JSCS/article/view/12769, or from the corresponding author on request.

И З В О Д

ПИРОЛИЗА СТАБЉИКА КУКУРУЗА: ПОТЕНЦИЈАЛ КОРИШЋЕЊА БИО-УЉА КАО БИОГОРИВА

JELENA ISAILOVIĆ[1], EMILIJA VUKIĆEVIĆ[2], MALIŠA ANTIĆ[1], JAN SCHWARZBAUER[3], LJUBIŠA IGNJATOVIĆ[4], GORDANA GAJICA[5], VESNA ANTIĆ[1]

[1]Пољопривредни факулшеш, Универзишеш у Беоīраду, Немањина 6, Земун, Србија, [2]Хемијски факулшеш, Универзишеш у Беоīраду, Сшуденшски шрī 12-16, Беоīрад, Србија, [3]Institute for Geology and Geochemistry of Petroleum and Coal, RWTH, Lochnerstr. 4-20, Aachen, Germany, [4]Факулшеш за физичку хемију, Универзишеш у Беоīраду, Сшуденшски шрī 12-16, Беоīрад, Србија и [5]Инсшишуш за хемију, шехнолоīију и мешалурīију, Национални инсшишуш Реūублике Србије, Његошева 12, Беоīрад, Србија.

Због све веће потрошње фосилних горива, постоји растућа потражња за обновљивим изворима енергије. Истовремено, акумулира се значајна количина пољопривредног отпада, укључујући остатке кукуруза, чије ефикасно управљање представља изазов. У овом раду, отпадна биомаса, која се састојала од стабљика два типа кукуруза, окарактерисана је и

подвргнута процесу пиролизе на 400 °C. Урађена је физичко-хемијска карактеризација добијене течне фракције (био-уља), а вредности су упоређене са литературним подацима за течно биогориво. Топлотна моћ био-уља била је изнад 22 MJ kg^{-1}, што указује на добар потенцијал кукурузног отпада као енергента. Уз одговарајуће даље промене у саставу отпада, додавање материјала са већим садржајем угљеника и водоника, стабљике кукуруза могу представљати значајан извор енергије, са бољом регулацијом одлагања и складиштења пољопривредног отпада.

REFERENCES

1. G. Q. Calixto, D. M. A. Melo, M. A. F. Melo, R. M. Braga, *Braz. J. Chem. Eng.* **39** (2021) 137 (https://doi.org/10.1007/s43153-021-00099-1)
2. FAO. (2021). FAOSTAT database. Retrieved from http://www.fao.org/faostat/en/#data (accessed 25.12.2023)
3. Statistički kalendar Republike Srbije (2022) 218 https://www.stat.gov.rs/sr-Latn/calendar (accessed 25.12.2023)
4. V. Semenčenko, Dušanka Terzić, M. Radosavljević, Slađana Žilić, „Korišćenje agrorezidua kukuruza u proizvodnji biogoriva, bioapsorbenata i hrane za ljude i životinje" INDUSTRIAL WASTE 2nd International Scientific Conference on Waste Management, Tara, Serbia, 2009. (http://dx.doi.org/10.13140/2.1.4549.3769)
5. M. E. Himmel, S.-Y. Ding, D. K. Johnson, W. S. Adney, M. R. Nimlos, J. W. Brady, T. D. Foust, *Science* **315** (2007) 804 (http://dx.doi.org/10.1126/science.1137016)
6. G. Ungureanu, G. Ignat, C. R. Vintu, C. D. Diaconu, I. G. Sandu, *Rev. Chim.* **68** (2017) 570 (http://dx.doi.org/10.37358/RC.17.3.5503)
7. J. B. Sluiter, R. O. Ruiz, C. J. Scarlata, A. D. Sluiter, D. W. Templeton, *J. Agric. Food Chem.* **58** (2010) 9043 (http://dx.doi.org/10.1021/jf1008023)
8. P. McKendry, *Bioreso. Techn.* **83** (2002) 37)https://doi.org/10.1016/S0960-8524(01)00118-3)
9. D. L. Klass, *Biomass for Renewable Energy, Fuels, and Chemicals*, Elsevier, San Diego, 1998, 1-27 (https://doi.org/10.1016/B978-012410950-6/50003-9)
10. R. D. Perlack, *Biomass as Feedstock for a Bioenergy and Bioproducts Industry: The Technical Feasability of a Billion-Ton Annual Supply*, USDA, Springfield, 2005, 1-38 (https://doi.org/10.2172/885984)
11. C. Corvalan, S. Hales, A. J. McMichael, *Ecosystems and human well-being: health synthesis*, World Health Organization, Geneva, 2005, 27-49 ISBN: 9241563095
12. A. J. Ragauskas, C. K. Williams, B. H. Davison, G. Britovsek, J. Cairney, C. A. Eckert, W. J. Frederick Jr., J. P. Hallett, D. J. Leak, C. L. Liotta, J. R. Mielenz, R. Murphy, R. Templer, T. Tschaplinski, *Science* **311** (2006) 484 (https://doi.org/10.1126/science.1114736)
13. H. Yang, R. Yan, H. Chen, C. Zheng, D. H. Lee, D. T. Liang, *Energy Fuels* **20** (2005) 388 (https://doi.org/10.1021/ef0580117)
14. D. Vitorović, B. Jovančićević. *Osnovi organske geohemije.* Faculty of Chemistry University of Belgrade, Belgrade, 2005, 153 ISBN 978-8672200195
15. T. Qu, W. Guo, L. Shen, J. Xiao, K. Zhao, *Ind. Eng. Chem. Res.* **50** (2011) 10424 https://doi.org/10.1021/ie1025453

16. T. Sun, Z. Li, Z. Zhang, Z. Wang, S. Yang, Y. Yang, X. Wang, S. Liu, Q. Zhang, T. Lei, *Bioresource Technology* **301** (2020) 122739 (https://doi.org/10.1016/j.biortech.2020.122739)
17. L. Wang, W. Yi, A. Zhang, Z. Li, H. Cai, Y. Li, *Front. Energy Res.* **7** (2019) (https://doi.org/10.3389/fenrg.2019.00086)
18. D. Chen, K. Cen, X. Zhuang, Z. Gan, J. Zhou, Y. Zhang, H. Zhang, *Comb. and Flame* **242** (2022) 112142 (https://doi.org/10.1016/j.combustflame.2022.112142)
19. L. Maulinda, H. Husin, N. Arahman, C. M. Rosnelly, E. Andau, W. Lestari, J. Karo-Karo, *IOP Conf. Ser.: Mater. Sci. Eng.* **1098** (2021) 022007 (https://doi.org/10.1088/1757-899X/1098/2/022007)
20. R. Chen, L. Lun, K. Cong, Q. Li, Y. Zhang, *Energy* **183** (2019) 25 (https://doi.org/10.1016/j.energy.2019.06.127)
21. M. Praspaliauskas, N. Pedišius, D. Čepauskienė, M. Valantinavičius, *Biom. Conv. Bioref.* **10** (2019) 937 (https://doi.org/10.1007/s13399-019-00457-7)
22. S. Nizamuddin, H. A. Baloch, N. M. Mubarak, S. Riaz, M. T. H. Siddiqui, P. Takkalkar, M. M. Tunio, S. Mazari, A. W. Bhutto, *Wast. Biom. Valor.* **10** (2018) 1957 (https://doi.org/10.1007/s12649-018-0206-0)
23. J. E. Strassner, *J. of Petrol. Techn.* **20** (1968) 303–312 (https://doi.org/10.2118/1939-PA)
24. R. Marchal, S. Penet, F. Solano-Serena, J. P. Vandecasteele, *Oil and Gas Sci. and Tech.* **58** (2003) 441 (https://doi.org/10.2516/ogst:2003027)
25. H. Wei, Y. L. Liu, D. Y. Chen, *AMM* **737** (2015) 14 (https://doi.org/10.4028/www.scientific.net/AMM.737.14).