

Article

Energetic Properties and Biomass Productivity of Switchgrass (*Panicum virgatum* L.) under Agroecological Conditions in Northwestern Croatia

Božidar Matin ¹, Josip Leto ², Alan Antonović ^{1,*}, Ivan Brandić ², Vanja Jurišić ², Ana Matin ², Tajana Krička ², Mateja Grubor ², Mislav Kontek ² and Nikola Bilandžija ²

¹ Faculty of Forestry and Wood Technology, University of Zagreb, Svetošimunska Cesta 23, 10000 Zagreb, Croatia

² Faculty of Agriculture, University of Zagreb, Svetošimunska Cesta 25, 10000 Zagreb, Croatia

* Correspondence: alan.antonovic@gmail.com

Abstract: Biomass as a renewable energy source includes energy crops that are not used for food but solely for biomass production with the goal of conversion to various forms of biofuel. Switchgrass, a perennial grass native to North America, has been explored as an energy crop for many years. It is suitable because it does not require much agrotechnical input, is highly resistant to pest infestation and disease development, and can provide very high biomass yields. The aim of this work was to determine the biomass quality of the mentioned plant in relation to the autumn and spring harvest, considering its use in direct combustion processes. Significant differences were found in the percentages of ash, carbon, nitrogen, sulfur, oxygen, and water, as well as in the percentages of micro and macro elements, in the harvest dates studied. Compared to the autumn, the moisture content decreased from 33.88% to 10.95% and ash content from 4.59% to 3.1% in the spring harvest, while the carbon content increased from 47.02% to 47.49%, dry matter from 38.91% to 89.22%, and heating value from 18.60 MJ kg⁻¹ to 18.73 MJ kg⁻¹. Shifting the harvest date from autumn to spring resulted in the production of higher quality biomass for use in combustion processes.

Keywords: switchgrass; biomass; energy crop; harvest date; energy properties

Citation: Matin, B.; Leto, J.; Antonović, A.; Brandić, I.; Jurišić, V.; Matin, A.; Krička, T.; Grubor, M.; Kontek, M.; Bilandžija, N. Energetic Properties and Biomass Productivity of Switchgrass (*Panicum virgatum* L.) under Agroecological Conditions in Northwestern Croatia. *Agronomy* **2023**, *13*, 1161. <https://doi.org/10.3390/agronomy13041161>

Academic Editors: Ralf Pude and Hongliang Wang

Received: 31 January 2023

Revised: 8 April 2023

Accepted: 18 April 2023

Published: 19 April 2023



Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

The strategy of using renewable energy sources is to reduce greenhouse gases, which is why they are playing an increasingly important role in the energy industry. According to the International Energy Agency, in 2016 they accounted for almost two-thirds of the world's net energy capacity. Energy from renewable sources is expected to be the fastest growing primary energy source at the global level over the next 20 years, with about 2/3 of investments going to bioenergy plants by 2040 [1]. According to the basic definition, biomass is an organic solid that occurs in nature, is of plant, wood, or animal origin, and is suitable for energy conversion. It is divided into several main types: agricultural biomass, wood biomass, water biomass, human and animal waste, industrial waste and contaminated biomass, and a mixture of biomasses. Biomass processing produces liquid, solid, and gaseous biofuels that can be used for energy production [2].

Agricultural biomass includes residues from primary and secondary production and energy crops. These are crops that are not suitable for human or animal consumption, require little investment, and are grown on soils that are unusable for food production, only to produce a high yield of biomass for energy purposes. They also have positive ecosystem impacts by preventing soil erosion and nutrient leaching, sequestering carbon in the soil, and providing habitat for wildlife [3]. Energy crops are classified into two groups: perennial herbaceous plants and short-rotation coppice. Perennial plants are

mostly herbaceous grasses that can be harvested on average once per year without the need to re-till and replant for several years (e.g., reed canary grass, switchgrass, miscanthus, perennial ryegrass—*Lolium perenne*, giant reed) [4]. The goal of short-rotation coppice cultivation is to obtain high biomass yields in a very short time, and this includes plants and fast-growing tree species that can be used for energy purposes (e.g., willow, poplar, ash, eucalyptus, sycamore maple, *Nothofagus*—southern beech). However, these plants must be replanted after harvest (eucalyptus, black locust) or grow as new shoots at the interface (willow, poplar) [5].

One of the energy crops mentioned earlier is switchgrass, a perennial grass that can reach a height of over 2.5 m, originates from the North American prairies, and provides high biomass yields with little agrotechnical input. Switchgrass is a plant suitable for erosion control because it grows on poorer, degraded soils and removes excess nitrogen and phosphorus generated by fertilization from the water and soil on which it resides [6]. The C₄ photosynthetic system gives it a higher biomass production efficiency than other grasses that have a C₃ photosynthetic system [7]. Depending on habitat and morphological characteristics, two ecotypes are distinguished in this species: lowland and upland [8]. The lowland ecotype is taller, grows faster, has strong, thick stems with many branches, and usually grows in swampy areas. The upland ecotype is grown in drier areas with cooler climates, is shorter, has fewer branches on a thinner stem, and forms a specialized sward [9–11]. The beginnings of switchgrass cultivation date back to the United States in the 1930s and 1940s, where many cultivars were grown along with cultivars adapted to the European climate: Alamo, Kanlow, and Cave-in-Rock [12].

Switchgrass productivity depends on the soil type, temperature, climatic conditions, and seeding method and timing [13]. Optimal seeding is at a depth of 2 cm at soil temperatures above 18 °C, usually in late April to early May, to minimize seed loss and weed infestation [14]. Nitrogen fertilization is not required in the year of sowing, while the supply of phosphorus and potassium depends on soil deficiencies [15]. Harvesting occurs thirty days after the first frost [12], with yield losses in the spring of up to 40% compared to the fall harvest [16]. Summer harvesting is not recommended, and the moisture content should be below 15% at harvest [7]. Shifting the harvest from fall to late winter or early spring reduces yield, but also the ash, moisture, and macronutrient content [17,18]. A comprehensive model is needed to optimize harvest timing considering nutrient losses, quality, and yield [19]. Switchgrass biomass has the greatest potential when considering the potential for energy use to produce biofuel, biogas, electricity, and thermal energy through the combustion process. However, biomass processing releases CO, CO₂, NO_x, and other polluting particles during combustion, and if these are not properly disposed of, energy production in this way could become a greater polluter than fossil fuels [20].

The quality of biomass during the biomass combustion process is evaluated by ultimate and proximate analysis and HHV. Parameters such as moisture, ash, volatiles, fixed carbon, and others can provide an estimate of how a particular type of biomass will behave during direct combustion and, although not sufficient for such an assessment, are necessary [21]. Biomass properties are also affected by micro and macro elements, so their analysis is also important for biomass quality assessment. During biomass combustion in furnaces, harmful chemical compounds are formed, and their deposition leads to combustion problems, formation of slag that is difficult to remove, and corrosion of mechanisms [22].

The main objective of this study is to systematically investigate and evaluate the variations in composition, yield, and energetic properties of *Panicum virgatum*, a perennial grass species commonly used for biomass production, in two different harvest seasons. This comparative analysis aims to shed light on the potential impact of seasonal variation on the overall performance of the biomass feedstock. Additionally, this study explores the assumption that changes in harvest deadlines could significantly influence the quality and quantity of biomass produced, ultimately affecting the efficiency and sustainability of *Panicum virgatum* as an energy source.

2. Materials and Methods

The experiment was established on the field of the Šašincev Experimental Station of the Faculty of Agriculture of the University of Zagreb in the eastern part of the city of Zagreb, i.e., in the northwestern region of Croatia (N 45°85'00.01", E 16°17'67.00"). The experimental field was sown in spring 2019 and consisted of 12 plots (2.4 × 8 m) laid out according to a random block scheme. The sampled biomass was harvested during two periods (November 2021 and March 2022) on each basic plot of 2 m² (1 × 2 m) by cutting the plants at a height of 10 to 15 cm above the ground with a chainsaw.

The chemical analyses were carried out in the laboratory of the University of Zagreb, Faculty of Agriculture, according to standard methods. Prior to the analyses, the biomass was dried by convection at a temperature of 60 °C for 48 h to achieve moisture and pressure equilibrium in the material. After drying, the biomass was comminuted using a Retsch GM 300 laboratory mill (RETSCH GmbH, Haan, Germany) [23]. Each sample was analyzed in triplicate.

2.1. Ultimate Analysis

In the ultimate analysis, the percentages of total hydrogen, nitrogen, and carbon (HRN EN ISO 16948:2015) [24] and the percentage of sulfur (HRN EN ISO 16994:2015) [25] were determined by the dry combustion method on a Vario, Macro CHNS analyzer (Elementar Analysensysteme GmbH, Langenselbold, Germany) [26]. The oxygen content (HRN EN ISO 18123:2015) [27] was determined by calculation.

2.2. Proximate Analysis

Proximate analysis of the samples was performed according to standard methods and determined as follows: Moisture content (HRN EN 18134-2:2017) [28] in a laboratory dryer (INKO ST-40, Croatia) [29], while coke (HRN EN ISO 18123:2015) [27] and ash (HRN EN ISO 18122:2015) [30] were determined in a muffle furnace (Nabertherm Controller B170, Lilienthal, Germany) [31]. The proportions of fixed carbon (HRN EN ISO 18123:2015) [27] and volatile matter were determined by calculation.

2.3. Heating Value

The higher heating value (HHV) was determined by the method HRN EN ISO 18125:2017 [32] using an IKA C200 adiabatic calorimeter (IKA Analysentechnik GmbH, Staufen im Breisgau, Germany) [33], while the lower heating value (LHV) was calculated [34]:

$$\text{LHV} = \text{HHV} \cdot \left(1 - \frac{w}{100}\right) - r \cdot \frac{w}{100} - r \cdot \frac{h}{100} \cdot \frac{18.2}{2} \cdot \left(1 - \frac{w}{100}\right)$$

where: LHV (MJ kg⁻¹)—lower heating value, HHV (MJ kg⁻¹)—higher heating value, r (MJ kg⁻¹)—heat of vaporization, $r = 2.445$ MJ kg⁻¹ at 25 °C, w (%) (kg/kg)—water content in the fuel $w = mw/(mw + ms)$, mw (kg)—mass of water, ms (kg)—mass of dry fuel, h (%) (kg/kg)—mass fraction of hydrogen in the fuel

2.4. Micro and Macro Elements

After the previous preparation of the samples by combustion in a microwave oven, the presence of microelements Cd, Fe, Mn, Ni, Zn, Cr, Co, Pb (HRN EN ISO 16968:2015) [35] and macro elements K, Na, Ca, Mg (HRN EN ISO 16967:2015) [36] was determined. Elemental analysis was performed using an atomic absorption spectrometer, model AAAnalyst 400 (PerkinElmer, Inc., Waltham, MA, USA) [37].

2.5. Statistical Analysis

All sample analysis results were analyzed using PROC MIXED from the SAS software package (SAS Institute Inc., SAS 9.1.2 Help and Documentation, Cary, NC: SAS Institute Inc., 2002–2004, Raleigh, NC, USA, North Carolina State University) [38].

3. Results and Discussion

Table 1 shows the yield and percent dry matter of the switchgrass biomass studied from the autumn and spring harvests conducted in November 2021 and March 2022.

Table 1. Yield and percentage of dry matter of the studied biomass.

Harvest Time	Yield DM (t/ha)	Dry Matter (%)
Autumn	19.08 ^a	38.91 ^b
Spring	13.27 ^b	89.22 ^a
Statistical difference	***	***

DM—Dry matter. Values in the column with the same letter are not statistically significantly different with $p < 0.05$. Statistical difference: *** $p < 0.001$.

The statistical analysis in Table 1 shows the differences in yield of DM (t/ha) and dry matter in relation to the two harvest periods. The average yield in the autumn harvest was 19.08 t/ha, while the average in the spring was 13.27 t/ha. The proportion of dry matter was significantly higher after the spring harvest and amounted to 89.22%, while the proportion after the autumn harvest was 38.91%.

Table 2 shows the ultimate analytical values of the percentages of the mentioned substances from the studied biomass obtained in the two harvests.

Table 2. Ultimate analysis of the studied biomass (%).

Harvest Time	C (%)	H (%)	O (%)	S (%)	N (%)
Autumn	47.02 ^b ± 0.227	5.99 ^a ± 0.014	46.70 ^a ± 0.229	0.14 ^a ± 0.011	0.16 ^a ± 0.008
Spring	47.49 ^a ± 0.113	6.01 ^a ± 0.040	46.27 ^b ± 0.156	0.11 ^b ± 0.003	0.11 ^b ± 0.013
Statistical difference	***	NS	***	***	***

C—Carbon; H—Hydrogen; O—Oxygen; S—Sulfur; N—Nitrogen. Values in the column with the same letter are not statistically significantly different with $p < 0.05$. Statistical difference: *** $p < 0.001$, NS—not significant.

Table 2 shows the differences in the percentages of C, H, O, N and S in relation to the two harvest periods. After harvesting in autumn, the percentages of carbon (47.02%) and hydrogen (5.99%) were lower on average than after harvesting in spring (47.49%; 6.01%). The average percentages of O (46.70%), S (0.14%), and N (0.16%) were significantly higher after the autumn harvest, comparing to 46.27% (O), 0.11% (S), and 0.11% (N) after spring harvest.

Table 3 shows the values of proximate analysis of the proportions of the above-mentioned substances from the studied biomass collected in the two harvests.

Table 3. Proximate analysis (%) and LHV (MJ kg⁻¹) of the studied biomass.

Harvest Time	Ash (%)	Fixed Carbon (%)	Volatiles (%)	LHV (MJ kg ⁻¹)
Autumn	4.59 ^a ± 0.252	10.16 ^a ± 0.789	79.78 ^a ± 0.562	17.29 ^a ± 0.123
Spring	3.71 ^b ± 0.066	10.23 ^a ± 0.642	80.86 ^a ± 0.707	17.42 ^a ± 0.252
Statistical difference	***	NS	NS	NS

LHV—Lower heating value. Values in the column with the same letter are not statistically significantly different with $p < 0.05$. Statistical difference: *** $p < 0.001$, NS—not significant.

Table 3 shows the differences in the proximate analysis according to the autumn and spring harvests. The percentage of ash was significantly higher after the autumn harvest (4.59%), while the average percentage was lower after spring harvest (3.71%). The average percentage of fixed carbon (10.16%; 10.23%), volatiles (79.78%; 80.86%), and LHV (17.29 MJ kg⁻¹; 17.42 MJ kg⁻¹) did not differ significantly with respect to the two harvest periods.

In the samples obtained from the switchgrass biomass, the presence of the following micro and macro elements was determined: zinc (Zn), iron (Fe), sodium (Na), potassium (K), manganese (Mn), calcium (Ca), magnesium (Mg), chromium (Cr), cadmium (Cd), nickel (Ni), cobalt (Co), and lead (Pb), the presence of which is shown in Table 4. The above elements react with each other during biomass combustion and cause significant problems in combustion chambers in the form of deposits of dirt and slag, which inevitably lead to corrosion.

Table 4. Analysis of micro and macro elements of the studied biomass (mg kg⁻¹).

Harvest Time	Autumn	Spring	Statistical Difference
Zinc (Zn)	5.77 ^a ± 0.006	4.14 ^b ± 0.089	***
Iron (Fe)	199.06 ^a ± 0.009	47.22 ^b ± 0.002	***
Sodium (Na)	99.68 ^a ± 0.005	67.67 ^b ± 0.005	***
Potassium (K)	4781.68 ^a ± 0.943	748.76 ^b ± 0.009	***
Manganese (Mn)	8.89 ^a ± 0.007	3.82 ^b ± 0.002	***
Calcium (Ca)	2353.50 ^b ± 0.005	2401.25 ^a ± 0.005	***
Magnesium (Mg)	487.67 ^a ± 0.943	464.13 ^b ± 0.047	***
Chromium (Cr)	4.38 ^a ± 0.005	2.99 ^b ± 0.002	***
Nickel (Ni)	42.85 ^a ± 0.008	2.58 ^b ± 0.004	***
Cobalt (Co)	(<0.25 mg kg ⁻¹) n.d.	(<0.25 mg kg ⁻¹) n.d.	n.d.
Lead (Pb)	(<0.25 mg kg ⁻¹) n.d.	(<0.25 mg kg ⁻¹) n.d.	n.d.

Values in the column with the same letter are not statistically significantly different with $p < 0.05$. Statistical difference: *** $p < 0.001$, n.d.—not determined.

Across the two harvests, the proportion of microelements differed significantly. After the autumn harvest, the proportions of zinc (5.77 mg kg⁻¹), iron (199.06 mg kg⁻¹), sodium (99.68 mg kg⁻¹), potassium (4781.68 mg kg⁻¹), manganese (8.89 mg kg⁻¹), magnesium (487.67 mg kg⁻¹), chromium (4.38 mg kg⁻¹), and nickel (42.85 mg kg⁻¹) were higher, while the proportion of calcium (2401.25 mg kg⁻¹) was higher on average after the spring harvest.

4. Discussion

The characteristics and quality of biomass can be influenced by several factors such as soil and tillage, seeding, fertilization, species diversity, geographic location, climate, plant parts used, and different harvesting, collection, and storage methods. These factors include the availability and cost of the resources used, the size of the plant, and the availability of equipment for the technological processing of biomass [39]. In this way, technologies can be developed and deployed to enable efficient combustion while ensuring that emissions of pollutants and gases remain within acceptable limits [40]. When evaluating biomass in the combustion process, its energetic properties are defined on the basis of proximate and ultimate analysis, with the calorific value and the proportions of micro and macro elements also having a significant influence [41]. Studies in Ukraine have shown that the dry matter content increases during the growing season in all the switchgrass genotypes studied except one. The highest dry matter content was observed in the flowering period, while during the growing season it varied from 28.62% (stem formation) to 65.28% (mature seeds) [42].

In southern Europe, studies have been conducted in Italy and Greece. The average yield in Greece was about 15 t DM/ha with the highest yield of 23.6 t DM/ha in the second

year of sowing, while the average yield in Italy was about 7 t DM/ha with the highest yield of 17.96 t DM/ha in the third year of sowing. Total precipitation for these two sites averaged about 400 mm per year, so irrigation was required. Over four years, the site in Greece was irrigated with a total of 1525 mm of water, while the site in Italy was irrigated with 2400 m³ ha⁻¹ per year [43].

Wullschleger et al. (2010) [44] reported an average of 12.9 t DM/ha for the lowland ecotype and 8.7 t DM/ha for the upland ecotype. Fike et al. (2006) [45] reported an average harvest per year of 12.8 t DM/ha for nine sites in the U.S. with the highest yield of 21.9 t ST/ha. Comparing the obtained yields of the studied biomass with the data from the literature, it can be concluded that they are within the limits of the literature data.

The moisture content of biomass at the time of harvest should not exceed 15% if harvested in early autumn or winter, as this leads to a loss of dry matter and mold growth [7]. The total moisture content of some biomasses can be as high as 90.0%. An excessively low moisture content at harvest is also not good as it leads to a loss of dry matter due to breakage and an increase in dust content [7].

In the literature, the moisture content of switchgrass biomass from autumn harvests is reported to be 47.4 to 53.4% by Ashworth et al. (2017) [17] and 30.0 to 48.0% by Kemmerer and Liu (2014) [46]. Ashworth et al. (2017) [17] also reported 12.5 to 17.9% for early winter, 12.6 to 19.6% for January and February, and 80.0 to 81.3% at the beginning of the growing season in May.

Ultimate analysis analyzes the elemental composition of the organic part of the biomass, i.e., the proportion of hydrogen, carbon, sulfur, nitrogen, and oxygen. Hydrogen and carbon are the main fuel elements of biomass and have a positive effect on its calorific value, while the influence of nitrogen and oxygen is somewhat less. Hydrogen has a calorific value seven times higher than carbon, and the higher the ratio of hydrogen to carbon, the more energy is released by oxidation in an exothermic reaction that produces H₂O and CO₂. As the proportion of C and H in biomass increases, so does the HHV. The main fuel element of biomass is carbon and as such it produces heat energy which can then be converted to other forms of energy such as electricity [47].

The results presented in Table 2 show that the harvest date has a significant effect on the carbon content in the biomass and therefore it is better to postpone the harvest to spring. In the literature, for autumn harvests, Pilon and Lavoie (2011) [48] reported 44.5%, Clarke et al. (2011) [49] 45.5%, and David and Ragauskas (2010) [50] 42.33% to 47.53%, while Kumar and Ghosh (2018) [51] reported 38.0% for a January harvest. For *Miscanthus*, Clarke et al. (2011) [49] reported a carbon content of 47.9%.

Hydrogen is the second most important fuel element in biomass after carbon and has a higher calorific value than carbon. The hydrogen content in biomass ranges from 3.0 to 11.0%, with an average of 6.3%, which is higher than fossil fuels (which average 5.4%), although it should be emphasized that biomass contains less carbon and four times more oxygen, resulting in a lower heating value [47]. The results of this study show that there is no significant difference in hydrogen content between autumn and spring harvests. In the literature, David and Ragauskas (2010) [50] reported hydrogen contents between 5.31% and 6.81% for the autumn harvest, Pilon and Lavoie (2011) [48] reported 5.8%, and Clarke et al. (2011) [49] and Sadaka et al. (2014) [52] reported 6.2%, while Kumar and Ghosh (2018) [51] reported 6.2% for the January harvest.

Biomass analysis has shown that by postponing harvesting to spring, the oxygen content decreases significantly. According to the literature, Sadaka et al. (2014) [52] reported an oxygen content of 44.0% for the autumn harvest, Pilon and Lavoie (2011) [48] reported 45.7%, David and Ragauskas (2010) [50] reported 37.58% to 42.54%, and Clarke et al. (2011) [49] reported 41.7%, while Kumar and Ghosh (2018) [51] reported 50.6% for the January harvest. The oxygen content determined in this study is above the upper limit of the literature values.

The combustion of biomass with higher sulfur and nitrogen contents leads to the emission of harmful gasses (SO₂, NO_x), and the calorific value also decreases. A small

portion of the SO_2 produced during combustion forms SO_3 , which, at lower temperatures in the smokestack, combines with water vapor to form sulfuric acid, which can lead to the severe corrosion of equipment [53]. Sadaka et al. (2014) [52] reported 0.13%, while Kumar and Ghosh (2018) [51] reported a content of 0.3% for the January period. Comparison of the determined sulfur contents shows that they are within the limits of the values reported in the literature.

For the nitrogen content at the spring harvest, Elbersen et al. (2013) [7] reported 0.56%. Comparison with the results obtained in this study shows that the determined values for the nitrogen content of switchgrass are significantly lower than the literature values.

Biomass storage and handling is one of the most important factors, as contamination during these operations can result in a higher ash content in the raw material than at harvest [54]. Ash with a high potassium content is very corrosive to boilers at combustion temperatures, and silicon can react with potassium or calcium to form alkali silicates with low melting points that can contaminate equipment with slag [55]. The research results showed that the biomass from the autumn harvest had a higher ash content, while this content decreased significantly in the spring harvest. The research values obtained were within the values reported in the literature.

Depending on how biomass is used for energy, the fraction of solid carbon and volatiles provides information on the degree of flammability, i.e., the impact on biomass combustion characteristics [56] and subsequent options for gasification or oxidation [57]. Solid carbon is the solid fraction that remains after the volatiles are evaporated. It consists of carbon, but also contains smaller proportions of oxygen, hydrogen, sulfur, and nitrogen that were not excreted with the gases [58]. A higher content of fixed carbon in biomass has a positive effect on its energy value [59].

The results of the statistical study show that there is no significant difference between the autumn and spring harvests in terms of fixed carbon content. However, the research results differ from those in the literature, with Pilon and Lavoie (2011) [48] reporting 15.3% for the autumn harvest and Sadaka et al. (2014) [52] reporting 23.1%. Kumar and Ghosh (2018) [51] reported 12.3% for the January harvest and Jackson et al. (2016) [60] reported 13.37% for the late winter harvest.

The thermal decomposition of biomass produces volatiles. Many types of biomass have relatively high levels of volatiles, which make the biomass highly flammable. The amount of volatiles depends mainly on the structure of the material, the heating rate, and the pyrolysis temperature [61]. However, the high content of volatiles in biomass does not necessarily guarantee a high calorific value because certain volatiles are formed from non-combustible elements such as CO_2 and H_2O [59]. The percentages of volatiles obtained by the analysis show that there is no statistical difference between the autumn and spring harvests (Table 3). The obtained research values are within the range of the literature data, where for the autumn harvest Sadaka et al. (2014) [52] reported a proportion of 73.1% and Pilon and Lavoie (2011) [50] 81%, while Kumar and Ghosh (2018) [51] reported a proportion of 83.2% for January harvest and Jackson et al. (2016) 83.65% for late winter harvest.

The LHV represents the heat energy available in biomass but does not include the energy for water evaporation [62]. In determining the quality of biomass, LHV is one of the most important parameters, and its value is lower than the value of HHV [63]. The results of this study (Table 3) show that there is no statistical difference between the autumn and spring harvests and the values are in the range of the literature data.

One of the most important properties of biomass in the context of energy use is the calorific value, which indicates the total amount of energy (MJ kg) of the potential raw material [64]. The calorific value, expressed by the HHV, represents the heat energy available in the biomass, including the energy for water evaporation [62].

The values of the biomass studied show that there is no statistically significant difference in HHV between the autumn and spring harvests. According to the literature data for autumn harvests, Clarke et al. (2011) [49] reported an HHV value of 18.0 MJ kg⁻¹, Pilon

and Lavoie (2011) [47] 19.5 MJ kg⁻¹, and David and Ragauskas (2010) [50] 18.75 MJ kg⁻¹. Kumar and Ghosh (2018) [51] reported a value of 19.7 MJ kg⁻¹ for the January harvest, while Jackson et al. (2016) [60] reported 18.61 MJ kg⁻¹ and Siggia et al. (2020) [65] reported values between 17.98 and 18.36 MJ kg⁻¹ for late winter harvests. It can be concluded that the values obtained in this study are almost consistent with those reported in the literature.

As the statistical analysis shows, the two harvest dates had the greatest influence precisely for the micro and macro elements, as significant differences were found for all elements. In the available literature for autumn harvests, Gorlitsky (2012) [54] reported a potassium content of 3211.0 to 4415.0 mg kg⁻¹, David and Ragauskas (2010) [50] 8112.0 to 10 894.0 mg kg⁻¹, and Mitchell et al. (2014) [66] 844.0 mg kg⁻¹. Monti et al. (2008) [55] reported a range of 1504.0 to 2126.0 mg kg⁻¹ for leaves and 2628.0 to 3555.0 mg kg⁻¹ for stems for the February harvest. The potassium values determined in this analysis are mostly in the range of the listed literature values.

Monti et al. (2008) [55] reported sodium contents ranging from 317.0 to 326.0 mg kg⁻¹ for leaves and 870.0 mg kg⁻¹ for stems, suggesting that the sodium contents of the biomass studied were lower. This study showed a lower proportion of calcium in the biomass samples studied than the proportions reported in the literature, where for the autumn harvest David and Ragauskas (2010) [50] reported values of 3512.0 to 3792.0 mg kg⁻¹ and Mitchell et al. (2014) [66] 3900.0 mg kg⁻¹.

For magnesium, values of 1085.0 to 1593.0 mg kg⁻¹ [60] and 2370.0 mg kg⁻¹ [66] for autumn harvests have been reported in the literature. Monti et al. (2008) [55] reported values of 2626.0 to 2706.0 mg kg⁻¹ for leaves and 1020.0 to 1171.0 mg kg⁻¹ for stems for the February harvest. This suggests that the magnesium content of the biomass studied is within the limits of literature values.

Samples from the spring harvest had lower zinc and manganese contents, which is a desirable characteristic. Massey et al. (2020) [67] reported manganese contents in above-ground biomass ranging from 24.7 to 98.5 mg kg⁻¹ in 2008 (five harvests from June to December) and 2009 (five harvests from February to November), while contents ranging from 6.76 to 34.5 mg kg⁻¹ were reported for zinc.

The iron content in the biomass samples from the two harvest dates is statistically different and more favorable in the spring harvest. Monti et al. (2008) [55] reported iron contents ranging from 83.0 to 319.0 mg kg⁻¹ for the February harvest, and it is evident that the iron contents from this study are within the range of data reported in the literature. Massey et al. (2020) [67] reported nickel contents in aboveground biomass ranging from 0.13 to 83.7 mg kg⁻¹ (five harvests from June to December) and from 0.13 to 75.5 mg kg⁻¹ for 2009 (five harvests from February to November). Significantly lower nickel levels were found in the spring harvest of the biomass studied, so harvesting should be postponed until then.

A statistically significant difference was found for chromium, where the spring harvest was more favorable due to a lower content. The levels of lead and cobalt could not be measured in any of the samples obtained from the biomass because their concentrations were extremely low, i.e., the levels of these elements were below the sensitivity limit of the instrument used for these studies (<0.25 mg kg⁻¹).

Considering that biomass can be used as a raw material for direct combustion and energy production, it is necessary to take into account the possibilities of the process and the selection of desirable and undesirable properties of biomass. Petrović et al. (2021) [68] conducted a study in which they investigated the combustion characteristics of hydrochars produced from waste biomass by hydrothermal carbonization (HTC). The study found that hydrochars produced at higher carbonization temperatures had better fuel properties compared to feedstocks. The results suggest that HTC technology has the potential to use waste biomass as a feedstock for novel energy sources with improved com-

bustion properties. Brown et al. (2022) [69] found that hydrochars produced by the hydrothermal carbonization of grass have a different combustion profile than grass, with a lower mass loss at about 300 °C and a larger mass loss peak at about 450 °C.

5. Conclusions

After examining the differences in yields, elemental composition, and energetic properties in relation to the two harvest periods, the following main results were found:

- The average yield of dry matter (DM) was 19.08 t/ha for the autumn harvest, while it was 13.27 t/ha for the spring harvest.
- The percentage of dry matter was 89.22% in the spring harvest and 38.91% in the autumn harvest.
- The carbon content was 47.02% in the autumn harvest and 47.49% in the spring harvest, while the hydrogen content was 5.99% and 6.01%, respectively.
- The oxygen content was 46.70% for the autumn crop and 46.27% for the spring crop, while the sulfur content was 0.14% and 0.11% and the nitrogen content was 0.16% and 0.11%, respectively.
- The ash content was 4.59% in the autumn crop and 3.71% in the spring crop.
- The potassium content was higher in the autumn harvest (4781.68 mg kg⁻¹) than in the spring harvest.
- The percentages of zinc, iron, sodium, potassium, manganese, magnesium, chromium, and nickel were generally higher in the autumn harvest, while the calcium content was higher in the spring harvest.

Based on these results, it can be concluded that the harvest period significantly influences the yield, dry matter proportion, elemental composition, and ash content of switchgrass biomass. These factors should be considered when optimizing switchgrass utilization for various applications, such as combustion or bioenergy production.

Author Contributions: Conceptualization, B.M.; methodology, N.B.; software, I.B.; validation, A.A., V.J., T.K. and A.M.; formal analysis, J.L. and M.G.; data curation, M.K.; writing—original draft preparation, B.M.; writing—review and editing, A.M.; supervision, A.A.; project administration, A.A. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the European Regional Development Fund, under the Operational program competitiveness and cohesion 2014–2022, project no. KK 01.2.1.02.0286, “Development of innovative pellets from forest and/or agricultural biomass—INOPELET”.

Data Availability Statement: Not applicable.

Conflicts of Interest: The authors declare no conflicts of interest.

References

1. Pickl, M.J. The renewable energy strategies of oil majors—From oil to energy? *Energy Strategy Rev.* **2019**, *26*, 100370.
2. Vassilev, S.V.; Baxter, D.; Andersen, L.K.; Vassileva, C.G.; Morgan, T.J. An overview of the organic and inorganic phase composition of biomass. *Fuel* **2012**, *94*, 1–33.
3. Mitchell, R.B.; Schmer, M.R.; Anderson, W.F.; Jin, V.; Balkcom, K.S.; Kiniry, J.; Coffin, A.; White, P. Dedicated energy crops and crop residues for bioenergy feedstocks in the central and eastern USA. *Bioenergy Res.* **2016**, *9*, 384–398.
4. Scordia, D.; Cosentino, S. Perennial energy grasses: Resilient crops in a changing European agriculture. *Agriculture* **2019**, *9*, 169.
5. Allen, B.; Kretschmer, B.; Baldock, D.; Menadue, H.; Nanni, S.; Tucker, G. *Space for Energy Crops—Assessing the Potential Contribution to Europe’s Energy Future*; Report Produced for BirdLife Europe, European Environmental Bureau and Transport & Environment; IEEP: London, UK, 2014; p. 61.
6. Sanderson, M.A.; Adler, P.R. Perennial forages as second generation bioenergy crops. *Int. J. Mol. Sci.* **2008**, *9*, 768–788.
7. Elbersen, H.W.; Poppens, R.P.; Bakker, R.R.C. *Switchgrass (Panicum virgatum L.): A Perennial Biomass Grass for Efficient Production of Feedstock for the Biobased Economy*; NL Agency: The Hague, The Netherlands, 2013.
8. Young, H.A.; Sarath, G.; Tobias, C.M. Karyotype variation is indicative of subgenomic and ecotypic differentiation in switchgrass. *BMC Plant Biol.* **2012**, *12*, 117.
9. Zhang, Y.; Zalapa, J.; Jakubowski, A.R.; Price, D.L.; Acharya, A.; Wei, Y.; Brummer, E.C.; Kaeppler, S.M.; Casler, M.D. Natural hybrids and gene flow between upland and lowland switchgrass. *Crop Sci.* **2011**, *51*, 2626–2641.

10. Morris, G.P.; Grabowski, P.P.; Borevitz, J.O. Genomic diversity in switchgrass (*Panicum virgatum*): From the continental scale to a dune landscape. *Mol. Ecol.* **2011**, *20*, 4938–4952.
11. Casler, M.D. Switchgrass breeding, genetics, and genomics. In *Switchgrass: A Valuable Biomass Crop for Energy*; Springer: Berlin/Heidelberg, Germany, 2012; pp. 29–53.
12. McLaughlin, S.B.; Kszos, L.A. Development of switchgrass (*Panicum virgatum*) as a bioenergy feedstock in the United States. *Biomass Bioenergy* **2005**, *28*, 515–535.
13. Giannoulis, K.D.; Karyotis, T.; Sakellariou-Makrantonaki, M.; Bastiaans, L.; Struik, P.C.; Danalatos, N.G. Switchgrass biomass partitioning and growth characteristics under different management practices. *NJAS-Wagening. J. Life Sci.* **2016**, *78*, 61–67.
14. Hancock, D.W. *The Management and Use of Switchgrass in Georgia*; The University of Georgia: Athens, GA, USA, 2009.
15. Samson, R.; Delaquis, E.; Deen, B.; DeBruyn, J.; Eggimann, U. *A Comprehensive Guide to Switchgrass Management*; Ontario Biomass Producers Cooperative (OBPC): Markdale, ON, Canada, 2019.
16. Adler, P.R.; Sanderson, M.A.; Boateng, A.A.; Weimer, P.J.; Jung, H.J.G. Biomass yield and biofuel quality of switchgrass harvested in fall or spring. *Agron. J.* **2006**, *98*, 1518–1525.
17. Ashworth, A.; Rocateli, A.; West, P.C.; Brye, R.K.; Popp, M.P. Switchgrass growth and effects on biomass accumulation, moisture content, and nutrient removal. *Agron. J.* **2017**, *109*, 1359–1367.
18. Serapiglia, M.J.; Boateng, A.A.; Lee, D.K.; Casler, M.D. Switchgrass harvest time management can impact biomass yield and nutrient content. *Crop Sci.* **2016**, *56*, 1970–1980.
19. Kiniry, J.R.; Cassida, K.A.; Hussey, M.A.; Muir, J.P.; Ocumpaugh, W.R.; Read, J.C.; Reed, R.L.; Sanderson, M.A.; Venuto, B.C.; Williams, J.R. Switchgrass simulation by the ALMANAC model at diverse sites in the southern US. *Biomass Bioenergy* **2005**, *29*, 419–425.
20. Tillman, D.A.; Duong, D.N.B.; Harding, N.S. Chapter 4—Blending Coal with Biomass: Cofiring Biomass with Coal. In *Solid Fuel Blending*; Tillman, D.A., Duong, D.N.B., Harding, N.S., Eds.; Butterworth-Heinemann: Oxford, UK, 2012; pp. 125–200.
21. Greinert, A.; Mrówczyńska, M.; Grech, R.; Szefer, W. The use of plant biomass pellets for energy production by combustion in dedicated furnaces. *Energies* **2020**, *13*, 463.
22. Finney, K.N.; Akram, M.; Diego, M.E.; Yang, X.; Pourkashanian, M. Carbon capture technologies. In *Bioenergy with Carbon Capture and Storage*; Academic Press: Cambridge, MA, USA, 2019; pp. 15–45.
23. *Retsch GM 300 Laboratory Mill*; RETSCH GmbH: Haan, Germany.
24. *HRN EN ISO 16948:2015*; Solid Biofuels—Determination of Total Content of Carbon, Hydrogen and Nitrogen. HZN: Zagreb, Croatia, 2015.
25. *HRN EN ISO 16994:2016*; Solid Biofuels—Determination of Total Content of Sulfur and Chlorine HZN: Zagreb, Croatia, 2016.
26. *Vario, Macro CHNS Analyzer*; Elementar Analysensysteme GmbH: Langenselbold, Germany.
27. *HRN EN ISO 18123:2015*; Solid Biofuels—Determination of the Content of Volatile Matter. HZN: Zagreb, Croatia, 2015.
28. *HRN EN ISO 18134-2:2017*; Solid Biofuels—Determination of Moisture Content—Oven Dry Method—Part 2: Total Moisture—Simplified Method. HZN: Zagreb, Croatia, 2017.
29. Laboratory Dryer, INKO ST-40, Inkolab d.o.o., Zagreb, Croatia.
30. *HRN EN ISO 18122:2015*; Solid Biofuels—Determination of Ash Content. HZN: Zagreb, Croatia, 2015.
31. Muffle Furnace (Nabertherm Controller B170, Germany).
32. *HRN EN ISO 18125:2017*; Solid Biofuels—Determination of Calorific Value. HZN: Zagreb, Croatia, 2017.
33. *IKA C200 Adiabatic Calorimeter*; IKA Analysentechnik GmbH: Staufen im Breisgau, Germany.
34. *HRN EN 14918:2010*; Solid Biofuels—Determination of Calorific Value. HZN: Zagreb, Croatia, 2010.
35. *HRN EN ISO 16968:2015*; Solid Biofuels—Determination of Minor Elements. HZN: Zagreb, Croatia, 2015.
36. *HRN EN ISO 16967:2015*; Solid Biofuels—Determination of Major Elements—Al, Ca, Fe, Mg, P, K, Si, Na and Ti. HZN: Zagreb, Croatia, 2015.
37. *AAAnalyst 400*; PerkinElmer, Inc.: Waltham, MA, USA.
38. SAS Institute Inc. *SAS 9.1.2 Help and Documentation*; SAS Institute Inc.: Cary, NC, USA, 2004.
39. Williams, C.L.; Emerson, R.M.; Tumuluru, J.S. Biomass compositional analysis for conversion to renewable fuels and chemicals. In *Biomass Volume Estimation and Valorization for Energy*; IntechOpen: London, UK, 2017; pp. 251–270.
40. Caraschi, J.C.; Goveia, D.; Dezajacom, G.; Prates, G.A. Evaluation of biomass properties for the production of solid biofuels. *Floresta E Ambiente* **2019**, *26*, e20180433.
41. Bilandžija, N.; Leto, J.; Fabijanić, G.; Sito, S.; Smiljanović, I. Harvesting techniques of agricultural energy crops. *Glas. Zaštite Bilja* **2017**, *40*, 112–119.
42. Rakhmetova, S.O.; Vergun, O.M.; Kulyk, M.I.; Blume, R.Y.; Bondarchuk, O.P.; Blume, Y.B.; Rakhmetov, D.B. Efficiency of *Switchgrass* (L.) Cultivation in the Ukrainian Forest-Steppe Zone and Development of Its New Lines. *Open Agric. J.* **2020**, *14*, 273–289.
43. Alexopoulou, E.; Sharma, N.; Papatheohari, Y.; Christou, M.; Piscioneri, I.; Panoutsou, C.; Pignatelli, V. Biomass yields for upland and lowland switchgrass varieties grown in the Mediterranean region. *Biomass Bioenergy* **2008**, *32*, 926–933.
44. Wullschleger, S.D.; Davis, E.B.; Borsuk, M.E.; Gunderson, C.A.; Lynd, L.R. Biomass production in switchgrass across the United States: Database description and determinants of yield. *Agron. J.* **2010**, *102*, 1158–1168.
45. Fike, J.H.; Parrish, D.J.; Wolf, D.D.; Balasko, J.A.; Green, J.T., Jr.; Rasnake, M.; Reynolds, J.H. Switchgrass production for the upper southeastern USA: Influence of cultivar and cutting frequency on biomass yields. *Biomass Bioenergy* **2006**, *30*, 207–213.

46. Kemmerer, B.; Liu, J. Effect of harvesting time and moisture content on energy consumption of compressing switchgrass. *Am. J. Plant Sci.* **2014**, *5*, 3241.
47. ; Adamovics, A.; Platace, R.; Gulbe, I.; Ivanovs, S. The content of carbon and hydrogen in grass biomass and its influence on heating value. *Eng. Rural Dev.* **2018**, *17*, 1277–1281.
48. Pilon, G.; Lavoie, J.M. Characterization of Switchgrass char produced in torrefaction and pyrolysis conditions. *BioResources* **2011**, *6*, 4824–4839.
49. Clarke, S.; Eng, P.; Preto, F. *Biomass Burn Characteristics*; Ministry of Agriculture, Food and Rural Affairs: Guelph, ON, Canada, 2011; p. 11-033.
50. David, K.; Ragauskas, A.J. Switchgrass as an energy crop for biofuel production: A review of its ligno-cellulosic chemical properties. *Energy Environ. Sci.* **2010**, *3*, 1182–1190.
51. Kumar, S.; Ghosh, P. Sustainable bio-energy potential of perennial energy grass from reclaimed coalmine spoil (marginal sites) of India. *Renew. Energy* **2018**, *123*, 475–485.
52. Sadaka, S.; Sharara, A.M.; Ashworth, A.; Keyser, P.; Allen, F.; Wright, A. Characterization of biochar from switchgrass carbonization. *Energies* **2014**, *7*, 548–567.
53. Vainio, E. Fate of Fuel-Bound Nitrogen and Sulfur in Biomass-Fired Industrial Boilers. Ph.D. Thesis, Åbo Akademi University, Turku, Finland, 2014.
54. Gorlitsky, L.E. Management of Switchgrass for the Production of Biofuel. Ph.D. Thesis, University of Massachusetts Amherst, Amherst, MA, USA, 2012.
55. Monti, A.; Di Virgilio, N.; Venturi, G. Mineral composition and ash content of six major energy crops. *Biomass Bioenergy* **2008**, *32*, 216–223.
56. Rybak, W.; Moroń, W.; Ferens, W. Dust ignition characteristics of different coal ranks, biomass and solid waste. *Fuel* **2019**, *237*, 606–618.
57. GowriShankar, G. *Proximate and Ultimate Analysis of Cotton Pod Used in the Updraft Gasifier—A Review*; Akshaya College of Engineering and Technology: Tamil Nadu, India, 2016.
58. Sarkar, D.K. *Thermal Power Plant: Pre-Operational Activities*; Elsevier: Amsterdam, The Netherlands, 2016.
59. Özyuğuran, A.; Yaman, S. Prediction of calorific value of biomass from proximate analysis. *Energy Procedia* **2017**, *107*, 130–136.
60. Jackson, J.; Turner, A.; Mark, T.; Montross, M. Densification of biomass using a pilot scale flat ring roller pellet mill. *Fuel Process. Technol.* **2016**, *148*, 43–49.
61. Caillat, S.; Vakkilainen, E. Large-scale biomass combustion plants: An overview. In *Biomass Combustion Science, Technology and Engineering*; Woodhead Publishing: Sawston, UK, 2013; pp. 189–224.
62. Gupta, G.K.; Mondal, K.M. Bioenergy generation from agricultural wastes and enrichment of end products. In *Refining Biomass Residues for Sustainable Energy and Bioproducts*; Academic Press: Cambridge, MA, USA, 2020; pp. 337–356.
63. Bilandžija, N. Potencijal Vrste Miscanthus × Giganteus kao Energetske Kulture u Različitim Tehnološkim i Agroekološkim Uvjetima. Ph.D. Thesis, Agronomski Fakultet Sveučilišta u Zagrebu, Zagreb, Croatia, 2015.
64. Basu, P. *Biomass Gasification and Pyrolysis: Practical Design and Theory*; Academic Press: Cambridge, MA, USA, 2010.
65. Siggia, D.; Lasorella, M.V.; Kolte, A.; Pawar, A. Management of Energy Production with Thermochemical Combustion: The Case of Switchgrass Perennial Crop in Mediterranean Environment. *J. Crit. Rev.* **2020**, *7*, 1185–1192.
66. Mitchell, R.B.; Lee, D.K.; Casler, M. Switchgrass. In *Cellulosic Energy Cropping Systems*; Wiley: Hoboken, NJ, USA, 2014; pp. 75–89.
67. Massey, J.; Antonangelo, J.; Zhang, H. Nutrient dynamics in switchgrass as a function of time. *Agronomy* **2020**, *10*, 940.
68. Petrović, J.; Simić, M.; Mihajlović, M.; Koprivica, M.; Kojić, M.; Nuić, I. Upgrading fuel potentials of waste biomass via hydrothermal carbonization. *Hem. Ind.* **2021**, *75*, 297–305; Erratum in *Hem. Ind.* **2021**, *75*, 381. <https://doi.org/10.2298/HEMIND211227032P>.
69. Brown, A.E.; Hammerton, J.M.; Camargo-Valero, M.A.; Ross, A.B. Integration of Hydrothermal Carbonisation and Anaerobic Digestion for the Energy Valorisation of Grass. *Energies* **2022**, *15*, 3495. <https://doi.org/10.3390/en15103495>.

Disclaimer/Publisher’s Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.