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CHEMICAL COMPOSITION AS AN INDICATOR OF THE CALORIFIC VALUE OF PLANT BIOMASS

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Abstract: The aim of this study was to predict the calorific value of plant biomass based on its chemical composition. Lignin and ash contents, as well as elemental composition (C, H, N, O), were analyzed in biomass derived from tobacco, maize, and sunflower stalks. Using the obtained parameters, empirical equations were applied to estimate the calorific (heating) value of the biomass. The use of chemical indicators enables a rapid and reliable assessment of biomass energy potential without the need for direct calorimetric measurements. The results indicate that lignin and ash contents have a significant influence on calorific value, while elemental composition allows for more precise quantification. The obtained data provides a basis for optimizing the utilization of plant biomass in biofuel production and thermal energy generation, thereby contributing to the sustainable use of renewable energy sources.

Keywords: Plant biomass, Calorific value, Lignin, Ash, Elemental composition, Prediction, Biofuel

INTRODUCTION

The utilization of renewable energy sources represents one of the most relevant challenges in developed countries worldwide. In this context, biomass stands out as a particularly important renewable energy resource, with a steadily increasing share in national energy balances, including that of Serbia. Although Serbia possesses considerable renewable energy potential, available data on the economic feasibility of its large-scale application remain limited (Jevtić and Ivkov, 2021).

It is estimated that approximately 12.5 million tons of agricultural biomass are available annually in Serbia, of which about 9 million tons originate from the Autonomous Province of Vojvodina. Given that arable land accounts for around 50% of the national territory and forests approximately 30%, the largest proportion of available biomass is derived from agricultural residues (Savić and Adžić, 2013).

The Serbian energy sector is characterized by numerous structural challenges, including low energy efficiency in both production and consumption, outdated technologies, insufficient investment, relatively low electricity prices, a limited share of renewable energy sources in total energy consumption, and pronounced inefficiencies in energy use. Consequently, the broader application of biomass remains constrained by high collection and transportation costs, fragmentation of agricultural holdings, and temporal mismatches between biomass generation and utilization (Ećim-Đurić et al., 2020).

Despite these limitations, Serbia has significant potential for biomass utilization in combined heat and power (CHP) systems. Government projections for renewable energy capacity development in the period 2015-2030 emphasize the important role of renewable sources in the country's future of energy. According to the Energy Development Strategy of the Republic of Serbia until 2025, with projections to 2030, biomass represents the largest share of renewable energy potential, accounting for approximately 61% of the total available potential. For this reason, biomass has been identified as the most important renewable energy resource available in Serbia (Martinov et al., 2015).

The use of wood pellets and briquettes is already widespread, while increasing attention is being directed toward the production and utilization of biofuels derived from agricultural crop residues (Kuthe et al., 2021). In this context, tobacco stalks constitute a significant fraction of the total available agricultural biomass in Serbia (Kulić et al., 2025). According to data from the Statistical Office of the Republic of Serbia, large-leaf tobacco varieties were cultivated on an area of 4.116 ha in 2024 (Statistical Office of the Republic of Serbia, 2025). Considering an average plant density of approximately 22.500 stalks per hectare and an average stalk mass of 400 g, the total number of tobacco stalks produced is estimated at approximately 92.6 million (Radojčić, 2011).

In 2024, maize was cultivated on an area of 987.492 ha (Statistical Office of the Republic of Serbia, 2025). The number of maize stalks varies, typically ranging from 50.000 to 65.000 plants per hectare, with an average stalk mass of 350 g (Kovačević, 2001), depending on hybrid selection, soil type, and sowing method, with the aim of achieving optimal crop density and high yield. Sunflower was cultivated on an area of 248.607 ha (Statistical Office of the Republic of Serbia, 2025), with an average stalk weight of 400 g and approximately 50.000 stalks per hectare (Kovačević, 2001).

These data clearly indicate the substantial energy potential of tobacco, maize, and sunflower stalks as alternative biofuels.

Available estimates suggest that agricultural biomass can fully meet the energy demands of the agricultural sector itself. Approximately 25% of the total biomass generated in agricultural production can be utilized for thermal energy, corresponding to about 3 million tons of biomass, which is equivalent to approximately 1.05 million tons of fuel oil (Statistical Office of the Republic of Serbia, 2021).

From an environmental protection perspective, the combustion of agricultural biomass is considered environmentally justified, as it results in lower emissions of harmful substances compared to conventional fossil fuels. Notably, biomass combustion does not lead to an

increase in CO₂ emissions, while emissions of sulfur oxides are negligible (Brkić et al., 2007).

The research presented in this paper contributes to the assessment of the energy potential of tobacco stalks, with particular emphasis on Burley-type tobacco, which is distinguished by its specific stalk-curing method. Previous studies have largely overlooked tobacco stalks as a potential biofuel, especially under domestic conditions, although they are classified as non-hazardous waste under current regulations (Waste Catalogue, 2010). These considerations provided the primary motivation for the present study.

Accordingly, the aim of this research was to estimate the heating value of Burley-type tobacco stalks as a potential biofuel based on their elemental composition, lignin content, and ash content. The obtained results were compared with the heating values of maize and sunflower stalks, which represent major crops in Serbian agriculture, with all values calculated using the same methodology.

MATERIAL AND METHODS

Experimental research was conducted on three different types of biomass: Burley-type tobacco stalks, maize stalks, and sunflower stalks. The stalks were obtained from individual agricultural producers in the Stara Pazova production area. Biomass preparation involved gradual air-drying followed by grinding to obtain a homogeneous mass. In accordance with standard methods for determining the physicochemical properties of biomass, the following parameters were analyzed: ash content determined according to SRPS EN 14775:2011, and lignin content, determined using the TAPPI method (TAPPI Test Method T 222 om-02). Elemental composition (C, H, N, and S) was determined instrumentally using an Elementar Vario EL III elemental analyzer (Elementar GmbH, Germany), in accordance with EN 15104:2011 for the determination of carbon, hydrogen, and nitrogen, and EN 15289:2011 for the determination of sulfur. Oxygen content was calculated by difference.

The prediction of higher heating value (HHV), expressed as the calorific value, was calculated using three empirical equations based on the previously determined lignin content, ash content, and elemental composition of the investigated biomass.

The calculation of HHV (calorific value) was performed using the following equations:

$$\text{HHV} = 19.914 - 0.2324 (A) \quad (\text{Sheng and Azevedo, 2005}), \text{ where } A \text{ is ash content} \quad (1)$$

$$\text{HHV} = 0.0889 (L) + 16.8218 \quad (\text{Demirbas, 2001}), \text{ where } L \text{ is lignin content} \quad (2)$$

$$\text{HHV} = -1.3675 + 0.3137 (C) + 0.7009 (H) + 0.0318 (O) \quad (\text{Sheng and Azevedo, 2005}) \quad (3)$$

where C, H, and O represent the mass fractions of carbon, hydrogen, and oxygen respectively.

Equation (3) is one of the most reliable, with an estimated uncertainty of $\pm 5\%$. Using these equations, HHV values were calculated for all investigated biomass samples, and the results are presented in Table 2. To determine the presence of statistically significant differences among HHV values calculated using different empirical equations, as well as to compare HHV values between the investigated biomass samples, a one-way analysis of variance (ANOVA) was applied.

RESULTS AND DISCUSSION

Table 1 presents the results of the chemical composition analysis (lignin content, ash content, and elemental composition) of large-leaf Burley-type tobacco stalks and two additional biomass samples included for comparison of HHV values. Based on the determined lignin and ash contents, ash content and elemental composition, HHV values were calculated using the previously described equations.

The results of the chemical analysis indicate that Burley tobacco stalks have the highest lignin content (18.36%). Mijailović et al. (2014) calculated, based on lignin content, that tobacco stalks have an HHV of 18.308 MJ/kg and a relatively low ash content (4.24%), while maize stalks contain the lowest lignin content (12.75%) and the highest ash content (6.49%). According to previous research results (Badger, 1999; Mijailović et al., 2014; Malnar et al., 2015a), the expected ash content in biomass is below 10%, which was confirmed for all investigated samples. Sunflower stalks exhibited moderate lignin content (16.43%) and the lowest ash content (4.06%). With respect to elemental composition, sunflower stalks had the highest carbon content (47.50%) and the lowest oxygen content (39.62%), indicating more favorable energy characteristics compared with the other analyzed biomass samples.

Table 1. Chemical Composition of Tobacco Stalks and Other Biomass Samples (%)

| Samples | Lignin | Ash | Elemental Composition | | |
|------------------------|----------|---------|-----------------------|------|-------|
| | | | C | H | O |
| Burley stalk | 18.35694 | 4.24128 | 44.03 | 7.02 | 43.27 |
| Maize stalk | 12.75476 | 6.48624 | 44.75 | 5.80 | 41.76 |
| Sunflower stalk | 16.42938 | 4.05657 | 47.50 | 5.52 | 39.62 |

By calculating HHV values using the three aforementioned equations, results were obtained from five replicates for tobacco stalks and for the two biomass types most commonly produced in Serbia. The mean calorific values are presented in Table 2. The calculated average HHV values indicate that sunflower stalks achieve the highest HHV according to all three applied equations (18.28-18.97 MJ/kg), while maize stalks show the lowest HHV values (17.96-18.41 MJ/kg). Burley-type tobacco stalks exhibit comparable and consistent HHV values (18.45-18.93 MJ/kg), which are slightly lower than the value of 18.94 MJ/kg reported for Burley-type tobacco from the Čoka region (Radojičić et al., 2014a). This reported value lies between those obtained for sunflower and maize biomass. The observed deviations among the applied equations are small, indicating good agreement in estimating the energy value of the investigated samples.

Table 2. Average HHV Values (MJ/kg)

| | HHV (1) | HHV (2) | HHV (3) |
|------------------------|-----------|-----------|-----------|
| Burley stalk | 18.928326 | 18.453732 | 18.816846 |
| Maize stalk | 18.406598 | 17.955698 | 18.04419 |
| Sunflower stalk | 18.971252 | 18.282372 | 18.588236 |

Table 3 presents the results of the statistical analysis examining the presence of statistically significant differences in HHV estimates for individual biomass samples calculated using

different empirical equations. The results of the one-way analysis of variance (ANOVA) indicate that, for Burley-type tobacco stalks, no statistically significant differences were observed among HHV values obtained using the different equations ($F = 1.86 < F_{0.05}$), confirming good agreement among the applied models and confirms the robustness and reliability of the applied predictive approach for this type of biomass highlighting the methodological significance of ANOVA.

In contrast, for maize stalks, highly significant differences were detected between HHV values using the different equations ($F = 57.27 > F_{0.01}$), while for sunflower stalks the differences were statistically significant at the 95% confidence level ($F = 26.91 > F_{0.05}$). These results indicate that the choice of empirical equation can significantly influence HHV estimation for certain types of biomass.

Table 3. Analysis of Deviations in HHV Values Calculated Using Different Equations for Each Individual Sample

| Sources of Variation n=5; k=4; N=20 | Sum of Squares (SS) | Degrees of Freedom (v) | Variance (MS) | F-Statistic | F -Table $\alpha = 0.01$ $\alpha = 0.05$ |
|--|---------------------|------------------------|---------------|------------------------|--|
| Burley stalk | | | | | |
| HHV Values from Different Equations | 0.629997 | $v_1=3$ | 0.21 | 1.8574 ^{NS} | $F_{0.05;3;16}=3.24$ |
| Error | 1.808972 | $v_2=16$ | 0.11306 | | $F_{0.01;3;16}=5.29$ |
| Maize stalk | | | | | |
| HHV Values from Different Equations | 1.944727 | $v_1=3$ | 0.648242 | 57.27048 ^{**} | $F_{0.05;3;16}=3.24$ |
| Error | 0.181103 | $v_2=16$ | 0.011319 | | $F_{0.01;3;16}=5.29$ |
| Sunflower stalk | | | | | |
| HHV Values from Different Equations | 1.524506 | $v_1=3$ | 0.508169 | 26.9088 [*] | $F_{0.05;3;16}=3.24$ |
| Error | 0.302158 | $v_2=16$ | 0.018885 | | $F_{0.01;3;16}=5.29$ |

NS-Difference is not significant, $p < 0,05^*$, $p < 0,01^{**}$

Table 4 presents the results of the statistical analysis examining differences in higher heating value (HHV) among biomass samples for each of the three applied HHV calculation equations. When the calculated F-value exceeds the corresponding critical value, the differences in HHV among biomass types are considered statistically significant, indicating that the observed variation is not due to random errors. Conversely, when the F-value is lower than the critical value, the differences are not statistically significant.

The results of the one-way analysis of variance (ANOVA) reveal highly significant differences in higher heating values (HHV) among the analyzed biomass samples for all three equations. For HHV (1), an F-value of 6.02 was obtained, exceeding the critical value at a significance level of $\alpha = 0.01$ ($F_{0.01} = 3.90$). Similarly, the calculated F-value for HHV (2) was 7.50, while an even more pronounced difference was observed for HHV (3), with an F-value of 21.45. In all cases, the calculated F-values exceeded the corresponding critical values at $\alpha = 0.01$. These results clearly indicate that biomass type has a highly

significant effect on HHV, regardless of the empirical equation applied, with the greatest difference observed when HHV is calculated using equation (3).

Table 4. Analysis of Deviations in HHV Between Different Biomass Samples Obtained Using Different Equations

| Sources of Variation n=5; k=6; N=30 | Sum of Squares (SS) | Degrees of Freedom (v) | Variance (MS) | F Statistic | F Table $\alpha = 0.01$ $\alpha = 0.05$ |
|--|---------------------|------------------------|---------------|-------------|---|
| HHV (1) | | | | | |
| HHV of Different Biomass Samples | 1.388704 | $v_1=5$ | 0.277741 | 6.024802** | $F_{0,05;5;24}=2.62$ |
| Error | 1.10639 | $v_2=24$ | 0.0461 | | $F_{0,01;5;24}=3.9$ |
| HHV (2) | | | | | |
| HHV of Different Biomass Samples | 1.129937 | $v_1=5$ | 0.225987 | 7.5** | $F_{0,05;5;24}=2.62$ |
| Error | 0.721405 | $v_2=24$ | 0.03006 | | $F_{0,01;5;24}=3.9$ |
| HHV (3) | | | | | |
| HHV of Different Biomass Samples | 2.526018 | $v_1=5$ | 0.505204 | 21.44875** | $F_{0,05;5;24}=2.62$ |
| Error | 0.565296 | $v_2=24$ | 0.023554 | | $F_{0,01;5;24}=3.9$ |

NS-Difference is not significant, $p < 0,05^*$, $p < 0,01^{**}$

Calorific value is a key parameter in evaluating the suitability of biomass as a fuel, as it determines the amount of energy that can be obtained under given conditions (Kulić et al., 2025). It can be determined both experimentally and through computational approaches. In this study, the higher heating value (HHV) was predicted using three empirical equations proposed by different authors, based on the previously determined lignin content, ash content, and elemental composition of the investigated biomass. Estimating calorific value from chemical composition is commonly used to obtain preliminary results, particularly when planning the introduction of a new type of biofuel in a rapid and cost-effective manner.

The chemical composition of biomass represents a fundamental parameter in its characterization for bioenergy production, as it directly influences the quality of the final product as well as compliance with relevant standards a regulatory requirement.

Elemental composition of biomass defines the mass fractions of carbon, hydrogen, sulfur, nitrogen, and oxygen, and serves an important indicator of biomass quality, as well as its potential for the formation of harmful gaseous emissions during utilization (Živković and Đorđević, 2001). Burley-type tobacco was selected because, compared with other tobacco types, it is harvested and cured on the stalk, which facilitates collection and transport and reduces the energy required for subsequent drying. Maize stalks were included due to their traditional use as biofuel, while sunflower stalks were selected because they are less commonly used.

The obtained calorific values (HHV) for all investigated samples are consistent with data reported in the relevant literature, which indicate that plant biomass typically exhibits HHV values in the range of 18.0 to 24.8 MJ/kg (Demirbas, 1997; Sheng and Azevedo, 2005;

Chun-Yang, 2011). Accordingly, based on their energy characteristics, all analyzed biomass samples can be considered suitable for use as biofuel.

CONCLUSION

The results demonstrate that Burley-type tobacco stalks exhibit higher HHV values (18.45-18.93 MJ/kg), comparable to those of the other analyzed biomass types, thereby confirming their potential for use as a biofuel. Statistical analysis indicated that, for Burley-type tobacco stalks, no statistically significant differences were observed among HHV values calculated using different empirical equations, whereas for maize and sunflower stalks, statistically significant or highly significant differences were detected. Furthermore, highly significant statistical differences were observed between the HHV values of Burley-type tobacco stalks and those of the other analyzed biomass samples.

Based on the obtained results, it can be concluded that existing empirical equations can be effectively applied to predict the calorific value of new types of biomass, providing a reliable basis for further experimental investigations and potential wider utilization. The calculation of calorific value using equations based on elemental composition, ash content, and lignin content confirmed that the investigated stalks possess favorable energy characteristics and can be used as biofuels. Moreover, predicting the calorific value of Burley-type tobacco stalks enables the development of future studies focused on the economic feasibility of their utilization, either as a standalone biofuel or in combination with other available agricultural residues in Serbia.

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