



# Article Investigation of Buckwheat Hulls as Additives in the Production of Solid Biomass Fuel from Straw

Mindaugas Kulokas \*, Marius Praspaliauskas and Nerijus Pedišius

Laboratory of Heat–Equipment Research and Testing, Lithuanian Energy Institute, Breslaujos st. 3, LT-44403 Kaunas, Lithuania; Marius.Praspaliauskas@lei.lt (M.P.); Nerijus.Pedisius@lei.lt (N.P.)

\* Correspondence: Mindaugas.Kulokas@lei.lt

**Abstract:** The aim of this study was to further increase the amount of straw that can be used to produce solid biofuels, as currently only about 130–140 thousand of the 3 million tonnes of straw collected annually in Lithuania are used for solid biofuel production. Therefore, the use of buckwheat hulls as an additive in solid biofuel production was investigated. Mixtures of wheat straw and buckwheat hulls were used for this research, with an increase in buckwheat hulls from 25% to 75% of the total weight of the mixture. Results of the analysis of the chemical composition, moisture, ash, and volatile matter content of the mixtures, as well as their ash properties, were compared with the corresponding results obtained with pure buckwheat hulls, wheat straw, and wood chips. It is observed an increase in all ash melting temperatures by increasing the portion of buckwheat hulls in the mixture. Additionally, the ash shrinkage starting temperature was shown to increase as the total content of buckwheat hulls also increased in the mixture. This increase ranged from 90 °C to 210 °C. Furthermore, the Cl concentration in fuel mixtures and the corrosion risk of equipment are accordingly reduced by using buckwheat hulls, as an addition that does not contain Cl.

Keywords: wheat straw; buckwheat hulls; mixture; biofuel production; composition; ash

# 1. Introduction

The use of solid biomass fuels derived from wood or agricultural waste (agro-mass) is promoted in most energetically developed countries [1,2]. Large quantities of agro-mass, obtained in the agricultural sector as a by-product, have been used for fertilizing and other applications, but they have rarely been used in thermal conversion processes [3]. The amount of straw harvested in Lithuania fluctuates every year, although about 3 million tonnes have been collected annually on average over the last five years [3,4]. Therefore, straw can be considered as the largest source of agro-mass that can be used to produce solid biofuels. Every year in Lithuania, about 130–140 thousand tonnes of straw suitable for biofuel production are used, most of which are used for pellet production [3]. This amounts to a very small part, about 5%, of the agro-mass used in solid biofuel production [3], thus there exists great potential in the use of biomass as a fuel.

High moisture content, low raw material density, high volatile matter, non-flammable organic matter content, and low ash melting/sintering temperatures are the main reasons for the low usage of collected straw in thermal conversion processes. The main problem— ash melting characteristics—can be solved using additives (calcite, kaolin, or dolomite) to increase the melting temperature during the agro-mass combustion process [5–7]. Kaolin (Al<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>(OH)<sub>4</sub>) mainly consists of SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> compounds, which makes it less effective than dolomite [5–7]. Dolomite (CaMg(CO<sub>3</sub>)<sub>2</sub>) is predominantly composed of CaO, MgO, and CaCO<sub>3</sub> compounds, and is one of the most suitable additives for enhancing the melting characteristics of wheat straw ash [5,7]. Calcite (CaCO<sub>3</sub>), like dolomite, also enhances the melting characteristics of ash [6,7]. However, the use of additives can cause additional environmental impacts such as an increase in the amount of fly ash due to the formation of other harmful compounds.



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**Copyright:** © 2021 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/). compounds in flue gas [8,9] showed that higher concentrations of these compounds in raw materials increased the quantity of fly ash. The collected information from the references showed that the chemical composition of solid biofuels can be used to estimate its quality and influences the combustion process and ash composition [10,11]. The combustion of pure wheat straw, as with other herbaceous plants, usually results in a high ash content and is relatively dominated by the high amount of Cl, S, and alkali metals, which can cause sedimentation and corrosion on heating surfaces [12,13]. The corrosion risk, according to [14], can be divided into three groups: low corrosion risk (>8.0), medium corrosion risk (2.0 to 8.0), and high corrosion risk (<2) [15]. The high amount of K and Si, and relatively low concentration of Ca are the main reasons for low ash melting/sintering temperatures of pure wheat straw ash compared to wood fuel ash [12,13,16]. Meanwhile, alkali metals with Si become low-solubility compounds, such as salts (mainly chlorides such as KCl and NaCl) and acidic compounds, such as sulphates/sulphur compounds, which cause sedimentation processes on heated surfaces and initiate corrosion [12]. The analysis of the literature has also shown that alkali metals (e.g., K, Na) and Cl, S, and Si are mostly found in agro-mass [13,16]. It is important to note that these elements, together with heavy metals, are considered to be the main elements of fly ash, which causes local pollution of the environment when released into the atmosphere [7,12,13].

To simplify the use of additives and increase the amount of straw suitable for the production of solid biofuels, the use of buckwheat hulls was investigated. Lithuania ranks ninth among the largest buckwheat producers in the world [17] and provides particularly large quantities of buckwheat hulls. A large amount of buckwheat hulls is currently used in various industrial areas [18,19], and only a small part is used for thermal conversion processes [20]. However, judging from studies on the energetic properties of wood, wood pellets, and peat [21–23], buckwheat hulls have comparatively high energy potential [21]. This exploration of wheat straw and buckwheat hull mixtures aims to exploit the energy potential of buckwheat hulls and evaluate the ash melting characteristics by individual element impact assessments, enabling comparison with the results obtained in [24–26]. For this purpose, we compared additional pure elements from pure biomass ash (buckwheat hulls [16], straw [5,9,12,13,25,27], wood [9,12,13,25,27]) and their oxides, because of a lack of research on the use of buckwheat hulls as an additive in straw thermal conversion processes. Currently, it is possible to roughly compare the quantities of oxides formed during thermal biomass conversion processes and make assumptions about the use of buckwheat hulls as an additive based on their change.

The purpose of this research is to extend the use of residual wheat straw as a raw material for solid biofuel in thermal conversion processes by mixing it with buckwheat hulls and thus improving the incineration properties. To achieve these goals, we set the following tasks:

- 1. Determine the chemical-physical properties of pure raw materials (wheat straw, buckwheat hulls, and wood chips), mixtures of wheat straw, and buckwheat hulls in different proportions, and compare the main elements of the composition.
- 2. Evaluate the main characteristics (content, melting properties, pH, and morphology) of ash produced during the thermal decomposition of analyzed raw materials to determine the most appropriate proportions of the mixtures.

#### 2. Materials and Methods

#### 2.1. Sample Preparation

The straw used was obtained from wheat that was grown in the Kaunas district (Lithuania). The buckwheat hulls were obtained from the grain producers. Wood chips were obtained from the 7 MW Kaunas thermal power plant.

All samples of analyzed raw materials were dried in a low-temperature electric oven at 105 °C for 18 h, then cooled to room temperature and mechanically chopped to a size of 1 mm before testing. Following that, mixtures of wheat straw/buckwheat hulls in proportions of 25/75, 50/50, and 75/25 were prepared, and the proximate and ultimate analysis was completed.

## 2.2. Proximate and Ultimate Analysis

The proximate and ultimate analysis was performed by complex methods according to [15,28]. The ash content (material for the main analysis) was determined by the LST EN ISO 18122:2016 standard method. Analyses of the main organic composition matter elements C, H, N, and O were performed using the LST EN ISO 16948:2015 methodology, except for oxygen, which was calculated by difference. Chlorine and sulphur contents were determined by ion chromatography according to the LST EN ISO 16994:2016 method. The calorific value (LHV) of the dry basis for the solutions was measured by an IKA C5000 calorimeter in accordance with the LST EN ISO 18125:2017 adiabatic method for automated bomb calorimetry. Proximate and ultimate analysis results are represented in the Results section, Table 1 and Figure 1.

#### 2.3. Elemental Determination of Analysed Raw Materials and Ash

Raw materials and their mixtures (including their ashes) were mineralized. Approximately 0.2–0.4 g of sample was prepared with concentrated nitric, hydrochloric, and hydrofluoric acids in a proportion of 3 mL:3 mL:1 mL. Three replicates of each sample were prepared according to the selected method of [28] by Anton Par Multiwave 3000. After mineralization, the selected elements (Al, Ca, Fe, K, Mg, Na, P, and Si) were determined by ICP-OES, Optima 8000.

## 2.4. Determination of Ash Fusion Temperatures

Ash samples were prepared at 550 °C according to the EN ISO 18122 standard. The main procedure of ash melting temperatures was carried out using the CEN/TS 15370-1 standard. Prepared ashes were ground with a ball mill to a homogenous fraction until the maximum particle size reached approximately 0.075 mm, then moistened with ethanol (purity 95%), and pressed into a cylindrical shape ( $5 \times 5$  mm). All cylindrical shapes were left to dry at room temperature for approximately 24 h. Finally, samples were placed in an ash melting furnace. The temperature was raised to 550 °C at a rate of 5 °C/min until the ashes melted. Characteristic ash melting temperatures were identifying by visual inspection using a high-definition camera, which captured images at every 2 °C increase.

#### 2.5. Determination of Ash Morphology and pH

Additionally, the morphology of all particles was analyzed using an S-3400N scanning electron microscope (SEM) operating at 5–15 kV accelerating voltage. The pH level was determined by the hydrogen ion concentration in a solution using an ionometer, according to standard LST EN 12176:2000.

#### 3. Results

Contents of the major elements (C, H, N, S) of wood chips, wheat straw, buckwheat hulls, and mixtures as raw materials were determined. The composition of pure wheat straw and buckwheat hulls (Table 1) have a similar amount of C, H, and S, however the wheat straw has four times less N and five times more Cl compared to buckwheat hulls. Consequently, the composition of mixtures showed a significant change in N and Cl concentrations, which may be related to their formation and other chemical compounds. Figure 1 shows a strong correlation of element quantities presented in [9,12,13,21,22,25] with measurement results, which are presented in Table 1.

#### 3.1. Chemical Composition of Analysing Raw Materials

Variances in the quantities of Cl, N, P, and S in pure wheat straw and buckwheat hulls may be due to the type of biomass or the type of fertilizer used, which is dominated by N and P compounds, the nature of the soil, and the substances absorbed during growth. Comparison of (75/25), (50/50), and (25/75) wheat straw/buckwheat hull mixtures showed a significant change in N and S (Table 1). The change in N, S, and Cl concentrations correlates with the classical agro-mass composition. A comparison of agro-mass and widely used coniferous wood fuel composition showed that all analyzed biomass was suitable for solid biomass fuel production. The total amount of ash produced by burning the analyzed biofuel was reduced by mixing straw with buckwheat hulls. In the case of wood fuel, the difference in ash content compared with the results presented in [9,12,13,22] is likely because the stem contained less ash-forming elements compared to the bark. Additionally, from Table 1 it is clear that C, H, and O mad up >90% of the raw material composition, with N, S, Cl, and other elements making up most of the rest of the raw material composition.

| Parameter                | Buckwheat<br>Hulls (B) | Wheat Straw<br>(A) | 75% (A) +<br>25% (B) | 50% (A) +<br>50% (B) | 25% (A) +<br>75% (B) | Wood Chips |  |  |
|--------------------------|------------------------|--------------------|----------------------|----------------------|----------------------|------------|--|--|
| Ultimate analysis (wt.%) |                        |                    |                      |                      |                      |            |  |  |
| C, %                     | 41.82                  | 46.05              | 46.49                | 44.84                | 45.49                | 49.77      |  |  |
| Н, %                     | 5.22                   | 5.93               | 5.78                 | 6.23                 | 5.91                 | 5.9        |  |  |
| N, %                     | 2.51                   | 0.58               | 0.56                 | 1.0                  | 1.39                 | 0.38       |  |  |
| S, %                     | 0.11                   | 0.12               | 0.07                 | 0.1                  | 0.11                 | < 0.005    |  |  |
| Cl, %                    | 0.014                  | 0.07               | 0.024                | 0.028                | 0.020                | < 0.005    |  |  |
| O *, %                   | 46.47                  | 42.95              | 43.09                | 43.80                | 43.02                | 41.91      |  |  |
|                          |                        | Prox               | ximate analysis (w   | t.%)                 |                      |            |  |  |
| ash, %                   | 3.87                   | 4.31               | 3.99                 | 4.01                 | 4.07                 | 2.04       |  |  |
| H/C                      | 0.12                   | 0.13               | 0.12                 | 0.14                 | 0.13                 | 0.12       |  |  |
| N/C                      | 0.06                   | 0.01               | 0.01                 | 0.02                 | 0.03                 | 0.01       |  |  |
| 2S/Cl                    | 15.71                  | 3.43               | 5.83                 | 7.14                 | 11.0                 | 2.0        |  |  |
| O/C                      | 1.11                   | 0.93               | 0.93                 | 0.98                 | 0.95                 | 0.84       |  |  |
| LHV, MJ/kg               | 17.79                  | 17.64              | 17.75                | 17.71                | 17.68                | 19.16      |  |  |

Table 1. Proximate and ultimate analysis of raw materials and mixtures.

\*-determined by the difference.

It is important to note that the composition of raw biofuel feedstock (C, H, N, S, and O) may vary [9,22]; for example, C can be at a 48–50% concentration in the stem and a 51–66% concentration in the bark. The composition of wood biofuels with bark and branches correlates with the results presented in [9,22]. Table 1 shows the clear difference in C, N, and S concentrations between wood and agro-mass, which also correlates with the results presented in [9,22]. However, the N and P concentration in the composition of agro-mass may change due to the influence of fertilizers or processing technologies, whereas higher Si concentrations may result from agricultural harvesting and processing technologies. Concentrations of O and H in wood biomass and agro-mass are very similar. Meanwhile, it was found that the concentrations of Cl and S in wood were very low, while in agro-mass samples they were significantly higher.

The ratio of corresponding average concentrations ( $N_i$ ) of C, H, S, Cl, O and average concentrations ( $N_0$ ) of buckwheat hulls [21], straw<sub>1</sub> [21] straw<sub>2</sub> [22], and wood [22] are shown in Figure 1a. Figure 1b shows the ratio of corresponding average concentrations in straw and buckwheat hull mixtures. In these figures, there is a lack of determined element uncertainties because they are insignificantly small and may be related to the methodology of the used test equipment.

Figure 1a shows a very marked change in N, S, and Cl concentration for buckwheat hulls, wheat straw, and wood chips. From [9,22,23,26] it is clear that the change in the concentration of N, S, and Cl in the pure raw material was several times larger than the changes in concentration of C, H, and O. The concentration of N was 4 times higher, while concentrations of S and Cl were 1.5 times higher in buckwheat hulls compared to the concentration of the respective elements reported in [21]. Concentrations of N, S, and Cl in straw<sub>1</sub> were respectively 1.4, 1.2, and 7 times higher compared to the values in [21]. Meanwhile, the Cl concentration in straw<sub>2</sub> was 8 times lower when concentrations of N and

S were respectively 1.2 and 1.7 times higher, compared to the concentration of respective elements reported in [22]. Finally, the concentration of S in wood chips was 11 times higher, while concentrations of N and Cl were respectively 3.5 times lower, compared to the concentration of respective elements reported in [22].

Figure 1b shows that mixing straw with buckwheat hulls halved the concentrations of N and Cl, while the S concentration remained the same. Therefore, concentrations of N, S, and Cl presented in Figure 1b show a strong correlation with Figure 1a. The composition of straw and buckwheat hull mixtures strongly correlates with the pure raw materials composition and a proportional change N, S, and Cl concentrations. The comparison of straw<sub>1</sub> and straw<sub>2</sub> compositions showed a difference in Cl concentration, which may have been due to the nature of the soil.



**Figure 1.** Comparison of solid biomass element concentrations: (**a**) selected basic samples and (**b**) produced straw and buckwheat hulls.

Analysis of the composition of solid biofuels from wood and agro-mass provides additional information on the effects of ash on heated surfaces and flue gas treatment plants. Corrosion risk is usually described by a 2S/Cl index, which expresses the intensity of the boiler's corrosion. Calculated H/C and O/C ratios allow for the evaluation and comparison of the composition and calorific value of the studied raw materials. Table 1 shows that the calorific value of biofuels from wood chips was higher compared to buckwheat hulls, wheat straw, and their mixtures when the O/C and H/C ratios of mixtures changed slightly by increasing the amount of buckwheat hulls. The highest increase in the H/C and O/Cratio was observed by mixing buckwheat hulls and wheat straw in equal weight ratios. Meanwhile, the O/C ratio of pure buckwheat hulls was significantly higher than the wood chips biofuel, and confirms the high energetic potential, as the H/C ratio was the same as the wood chips. Combustion of fuels with a high corrosion risk should include additional measures such as automatic heat-exchanger cleaning systems or suitable surface materials in order to avoid corrosion problems, as mentioned in [27]. The high corrosion risk of heated surfaces is due to the formation of forest waste ash. However, the risk of corrosion during the formation of buckwheat hull ash is low, and remains average during the formation of ash from manufactured mixtures.

A detailed study of the composition of mixtures, as well as pure raw materials, made it possible to assess the possible effect of the corrosion of heated surfaces due to the concentrations of Cl and S in raw materials. At high temperatures, several chemical changes in ash minerals occur, such as the dissociation of carbonates, chlorides, and other salts. Therefore, ash from the combustion of solid biofuels usually consists of oxides, silicates, carbonates, sulphates, and phosphates. From [8,9,12,13,25] we know that Al, Ca, Fe, K, Mg, Na, P, and Si are the main elements of ash formation that influence the ash melting characteristics and the formation of sediments. These elements, together with heavy metals, form fly ash and occur in sediments and flue gases. Due to its composition, fly ash released into the atmosphere together with flue gases increases environmental pollution. Therefore, it is very important to determine the amount of mineral ash that has

been directed to the elements that affect the formation of sediment ash, as well as their melting characteristics and surface corrosion.

## 3.2. Composition and Properties of Produced Ash

The resulting ash compositions showed a predominance of Ca, K, P, and Si, as these elements account for the largest proportion of all elements in compounds and have the greatest influence on ash production. K, Ca, Mg, P, Al, and Fe in wheat straw ash accounts for 50% of the ash composition, and P, K, Mg, Na, Ca, S, and Cl for 50% in buckwheat hull ash. It is evident that the use of fertilizers, as for the type of agro-mass, had a significant influence on the elemental composition of the produced ash. An example is the soil contamination of fuels, which results in higher Si concentrations in agricultural waste and grass ash. Meanwhile, K is one of the most important nutrients of plants, especially fast-growing one-year rotation plants, which are absorbed from the salts dissolved in the soil. It is evident that alkaline and alkaline earth metal salts, mainly KCl, K<sub>2</sub>SO<sub>4</sub>, and CaCO<sub>3</sub>, have the greatest influence on the ash composition. Si reacts with other ash-forming elements and usually forms alkali metal silicates with portions of K and Na. The remaining part of alkali metals, similar to heavy metals, then become volatile and evaporate.

It should be noted that the composition of the produced ash depends on the pure elements and various oxides [24–26]. Thus, the total content of the elements presented in Table 2 at their oxide (Figure 2) content ranges from 70% to 86% of the ash composition, with pure elemental concentrations between 45% and 51% of the elemental composition of the ash. Additional evaluation of other elements (e.g., Zn, Mn, and Ba) gives an overall view of the elemental ash composition, and the total concentration up to 100%. Therefore, ash melting characteristics can be compared according to the correlations of major ash-forming elements composition, such as wheat straw ash [5–7] and wood ash [9,22,27].

| Parameter | Buckwheat<br>Hulls (B) | Wheat Straw<br>(A) | 75% (A) +<br>25% (B) | 50% (A) +<br>50% (B) | 25% (A) +<br>75% (B) | Wood Chips |
|-----------|------------------------|--------------------|----------------------|----------------------|----------------------|------------|
| Al, mg/kg | 2813                   | 991                | 3694                 | 5045                 | 5395                 | 27,887     |
| Ca, mg/kg | 142,610                | 120,586            | 99,415               | 100,961              | 120,853              | 215,286    |
| Cl, mg/kg | 0.014                  | 0.07               | 0.034                | 0.038                | 0.02                 | < 0.005    |
| Fe, mg/kg | 3311                   | 1831               | 6659                 | 6365                 | 6155                 | 6908       |
| K, mg/kg  | 126,525                | 159,622            | 135,022              | 139,474              | 117,266              | 57,505     |
| Mg, mg/kg | 98,048                 | 29,227             | 49,054               | 52,523               | 68,367               | 28,557     |
| Na, mg/kg | 828                    | 554                | 330                  | 1176                 | 1171                 | 2280       |
| P, mg/kg  | 102,783                | 16,696             | 26,953               | 40,332               | 61,902               | 15,659     |
| S, mg/kg  | 0.11                   | 0.12               | 0.07                 | 0.1                  | 0.11                 | < 0.005    |
| Si, mg/kg | 22,527                 | 116,924            | 168,635              | 160,802              | 124,232              | 80,215     |

Table 2. The concentrations of main elements in prepared ash samples.

From a comparison of determined quantities of elements in mixtures of buckwheat hulls and wheat straw, which are presented in Table 2, it can be seen that Al, Ca, Fe, Mg, Na, and P increased, K and Si decreased, while Cl and S concentrations were similar. The same change in the total amount of elements can be seen from a comparison of their oxides. The measured and reference value ratio of oxides of pure buckwheat hulls, straw, their mixtures, and forest waste elements shows pronounced MgO and P<sub>2</sub>O<sub>5</sub> and similar amounts of Fe<sub>2</sub>O<sub>3</sub>, K<sub>2</sub>O, and SiO<sub>2</sub>, while Al<sub>2</sub>O<sub>3</sub>, CaO, and Na<sub>2</sub>O were almost the same (Figure 3). Determined elements and their oxides contained in the ash from pure biomass and mixtures correlated with the reference results and showed differences in fertilizers, soil nature, and materials absorbed during growth. Figure 3 and the correlation of the results from the literature indicates a constant change in the ash composition which was more stable compared to the change in the ash composition of buckwheat hulls, straw, and their mixtures.



Figure 2. Concentrations of the main ash constituent oxide forms.



Figure 3. Comparison of the oxide concentration of elements in ash.

Ash melting characteristics (shrinkage starting temperature (SST), deformation temperature (DT), hemisphere temperature (HT), and flow temperature (FT)) are important properties which are affected by the type of plant, the site of growth, the fertilizer used, and the composition of the soil. Changes in the ash content of mixtures of wheat straw and buckwheat hulls were determined by a comparison with the ash content of pure materials.

Experimentally determined ash-melting characteristics of logging waste (chips) (Table 3) were similar to the ranges given in [22,27]—SST: 1150–1210 °C; DT: 1180–1225 °C; HT: 1200–1250 °C; FT: 1225–1275 °C, at higher HT and FT temperatures. Meanwhile, the melting characteristics of wheat straw ash differed from the stated temperature range [22,27]—DT: 840–1050 °C; HT: 1150–1350 °C; FT: 1330–1400 °C. The melting characteristics of buckwheat hull ash in Table 3 were similar to those of wood chips, and reflect the energy value that can be utilized in the production of solid biofuels. Table 3 shows that the mixing of wheat straw with buckwheat hulls resulted in an increase in ash melting characteristics and an increase in SST temperature of 100 °C. The highest temperature difference was found in the analysis of ash from a fuel mixture consisting of 25% wheat straw and 75% buckwheat hulls.

| Parameter | Buckwheat<br>Hulls (B) | Wheat Straw<br>(A) | 75% (A) +<br>25% (B) | 50% (A) +<br>50% (B) | 25% (A) +<br>75% (B) | Wood Chips |
|-----------|------------------------|--------------------|----------------------|----------------------|----------------------|------------|
| SST, °C   | 1210                   | 839                | 927                  | 957                  | 1047                 | 1149       |
| DT, °C    | 1371                   | 875                | 960                  | 964                  | 1095                 | 1291       |
| HT, °C    | 1392                   | 1010               | 1076                 | 1065                 | 1129                 | 1326       |
| FT, °C    | 1451                   | 1068               | 1085                 | 1080                 | 1145                 | 1379       |

Table 3. Melting characteristics of the produced ash.

When explaining and validating differences in ash melting characteristics, the elemental composition and potential influence of a particular element must be taken into account. The results of Tables 2 and 3 correlate with the results of [24–26], and suggest that Ca, Mg, and Al increase the ash melting temperature, while K, Na, P, and especially Si decrease it. This can be observed from the low melting temperatures of pure straw ash as they contained high K and Si concentrations and low Ca concentrations. The increase in temperature is visible when comparing the melting temperatures of pure buckwheat hulls with high concentrations of K, Mg, and low concentrations of Cl. The ash melting characteristics and composition of wood chip ash correlate with the buckwheat hull composition, resulting in similar ash melting characteristics. As a result, it is clear that the ash-forming compounds differ greatly in terms of the type of agro-mass, and complex chemical processes occur during the combustion of solid biofuels, which result in the formation of various compounds that affect fuel combustion efficiency. Established ash melting characteristics correlate with the use of additives in the wheat straw combustion process to increase the combustion temperature, according to research results in [5–7], because of the high concentrations of Ca and Mg in buckwheat hulls.

Additional measurements were performed to determine the pH of solid biofuel ash, which varied from 12.9 to 13.3, hence the difference between individual ash samples was insignificant. The same result was obtained for the morphology of individual ash sample analysis using the S-3400N scanning electron microscope. Figure 4 presents the morphology of wood fuel, wheat straw, and buckwheat hull ash, which is analogous to the ashes of the produced solid biofuel mixtures since no specific solid biofuel mixture could be distinguished according to SEM photos.



Figure 4. Morphology of the ash resulting from solid biofuel combustion: (a) wood chips; (b) wheat straw; (c) buck-wheat hulls.

The obtained photos of ash morphology showed similarities with the results of previous research results and are characteristic of agro-mass ash morphology. There was no significant difference in the ash morphology of analyzed raw materials, as well as that of the thermally affected ash, and as a result, photos of the ash produced during the combustion of different raw materials are presented.

## 4. Conclusions

The composition of pure straw, as well as buckwheat hulls, had a significant influence on the biomass of fertilizers dominated by N and P compounds, soil nature, and substances absorbed during growth.

The mixtures of straw and buckwheat hulls produced had a similar composition, similar energy properties, and a lower ash content compared to the pure straw ash content. The H/C and O/C ratios of mixtures were also similar, and the O/C ratio of pure buckwheat hulls was higher compared to wood chips, thus it is clear that burning pure buckwheat hulls produces a high amount of energy.

A mixture of 25% by weight of buckwheat hulls is sufficient to increase the amount of straw suitable for the production of solid biofuels, as the composition, H/C and O/C ratios, and S and Cl concentrations coincide with a mixture of 50% by weight of buckwheat hulls.

Analysis of ash composition confirmed that high concentrations of K, Si, P, and Na decreased the ash melting temperature, and high concentrations of Ca, Mg, and Al increased the ash melting temperature. The melting characteristics of wheat straw ash increased when straw was mixed with buckwheat hulls, the ash melting characteristics of which are strongly correlated with wood chip ash. The same change has been achieved with additives because they contain high concentrations of Ca, Mg, and Al. An Analysis of changes in the concentration of corrosive elements in heated surfaces showed a significant decrease in Cl after the addition of buckwheat hulls, which are free of Cl, in this way reducing Cl concentration in the fuel mixture as well as reducing the risk of corrosion of the equipment.

The SST temperature rose by 88 °C to 208 °C as the weight of buckwheat hulls ranged from 25% to 50% and approached the melting properties of wood chip ash. The composition of buckwheat hulls correlates with the composition of coniferous wood, and during the comparison of ash melting characteristics an analogous correlation between buckwheat hulls and coniferous wood was found. Meanwhile, a comparison of the ash morphology and pH of raw materials and mixtures did not reveal sufficient differences to distinguish a specific type of solid biofuel.

Shredder, mixer, and extruder or granulator are sufficient equipment for the production of straw and buckwheat hull mixtures, and after further study it will be possible to recommend the optimal mixture and equipment for the production of industrial biomass mixtures.

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