Investigation of Pellet Properties Produced from a Mix of Straw and Paper Sludge

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Abstract: Global energy consumption is increasing every year, and, despite their many negative impacts, fossil fuels are a major source of energy, but their reserves are gradually depleting. One of the promising but underutilized resources is plant biomass (phytomass). The main problem of plant biomass combustion is the low melting temperature of ash, but there are also problems with corrosion of heat exchangers and clogging of heat-exchanging surfaces. This work is concerned with the production of straw pellets in order to increase the melting temperature of ash by adding an additive. The paper sludge contains substances that can increase the melting point of ash and was therefore added to the pellet samples. This additive was mixed with straw in ratios from 90:10, 80:20 and 70:30 (straw/paper sludge). The use of paper sludge showed positive effects on increasing the melting temperature of the ash samples. The deformation temperature of the ash has already risen from 1020 to 1260 °C after the addition of 10% sludge, which is comparable to wood pellets.

Keywords: straw; paper sludge; ash; melting temperature

1. Introduction

The advantage of straw is in its wide availability in almost all parts of the world, which is related to its low price. Along with its rapid renewability, these factors are the reason for the high potential of straw. The main problems of plant biomass combustion include low energy density, potentially high moisture contents, problems in terms of availability, and in combustion the low melting point of biomass can pose problems with corrosion. Nowadays, due to the growing awareness of greenhouse gas emissions, plant biomass as part of biomass is expected to be a very important element in achieving Europe’s 20-20-20 climate and energy targets [1]. Therefore, the combustion of plant biomass has enormous potential in terms of sustainable electricity and heat production. Its disadvantage compared to dendromass is the relatively high content of alkali metals, potassium, nitrogen, sulfur, silicon, chlorine and other ash-forming elements. The higher content of these elements generally leads to increased concentration of emissions and particulate matter, as well as operational problems related to ash behavior during combustion [2]. The already mentioned low melting temperature of ash causes problems during the operation of burners. This includes slagging, fouling and in some cases corrosion
of heat exchangers. Among other things, these problems reduce the efficiency of combustion systems, incur additional cleaning and maintenance costs for boilers, and in some cases even prevent the use of certain types of plant biomass for combustion [3]. Various methods have been investigated to prevent or reduce ash sintering during phytomass combustion. These approaches include: (1) application of additives; (2) fuel mixing; (3) decreasing the problematic compounds by leaching the fuel [4–15]. The use of additives and blending of plant biomass with another type of fuel has proven to be an effective solution to these difficulties. The various waste materials are of particular interest as additives, especially if they contain active chemical compositions for economically attractive costs. In the studies of Wang et al. the low cost additives (sewage sludge and marble sludge) were analyzed and proved able to abate biomass ash sintering and slagging [7,9]. Paper sludge is a by-product of the paper recycling process, which can be considered as either a biofuel of poor quality due to its high water content or a waste product. On the other hand, the sludge was used as an effective additive to wheat straw due to the high content of calcite and kaolin [16]. According to the literature review, kaolin was successfully tested to increase the ash melting point during the combustion of wheat pellets with kaolin [5]. The reduction in slagging was noticed by blending kaolin and calcite in wood pellets [17]. The sintering temperatures of barley straw and husk ashes were considerably increased by adding kaolin and calcite [18].

The agricultural residues are usually pelletized in order to obtain higher energy and bulk densities. Application of additives into plant biomass before pelletization is an effective option to include the additives into the combustion process. In addition, the entire contact of fuel and additives can be achieved during the mixing and pelletization process. It may positively support the effects of the additives on plant biomass’ ash chemistry [18–23].

To better understand the process of obtaining energy from plant biomass, it is crucial to know the chemical composition of this energy source. This composition is a unique base code that characterizes and determines the characteristics, quality, potential applications, as well as the environmental problems of a fuel. The ultimate analysis of the individual plant biomass species reference is presented in Table 1.

| Table 1. Ultimate analysis of different plant biomass [24]. |
|------------------------------------------------------------|
| **Fuel**         | **C (%)** | **O (%)** | **H (%)** | **N (%)** | **S (%)** |
| Miscanthus grass | 49.2      | 44.2      | 6.0       | 0.4       | 0.15      |
| Switchgrass     | 49.7      | 43.4      | 6.1       | 0.7       | 0.11      |
| Barley straw    | 49.4      | 43.6      | 6.2       | 0.7       | 0.13      |
| Rape straw      | 48.5      | 44.5      | 6.4       | 0.5       | 0.10      |
| Wheat straw     | 49.4      | 43.6      | 6.1       | 0.7       | 0.17      |
| Straw           | 48.8      | 44.5      | 5.6       | 1.0       | 0.13      |

The carbon content of plant biomass is up to 50% of this element. A higher carbon content leads to a higher calorific value of the fuel. Hydrogen also contributes to the higher calorific value of the fuel, the proportion of this element in plant biomass is usually 5–6% [25].

This work dealt with the possibility of effective energy use of plant biomass and the influence of an additive on ash melting problems. The aim was to test the paper sludge as additive with the purpose to raise the melting point of ash during combustion processes, to analyze the ash formation process at elevated temperatures and to investigate the effects of various proportions of paper sludge on the ash melting characteristics. The properties of straw pellets with the addition of sludge were analyzed as well.
2. Materials and Methods

2.1. Additives

Additives refer to a group of materials that can alter the ash properties of the burned fuel. In this case, it means reducing the concentration of problematic compounds and increasing the melting point of ash in plant biomass combustion processes [10]. In recent decades, many studies of potential additives have been carried out to solve the problems associated with plant biomass combustion. An overview of the most commonly used additives with anticipated effects is shown in Table 2.

| No. | Predicted Effects                                      | Additives                                                                 |
|-----|--------------------------------------------------------|---------------------------------------------------------------------------|
| 1.  | Capture of problematic ash species via chemical adsorption and interaction | kaolin, halloysite, cat litter, emathlite, clay minerals, clay sludge, illite, detergent zeolites, ammonia sulfate, aluminum sulfate, iron sulfate, limestone, lime, marble sludge, ammonia phosphate, phosphoric acid, sewage sludge, paper sludge, peat ash, coal fly ash, dolomite, bauxite, quartz, titanium oxide |
| 2.  | Physical adsorption and eliminating troublesome ash species from combustion facilities | kaolin, zeolite, halloysite, clay sludge, sewage sludge, paper sludge, clay minerals, lime, limestone, dolomite, calcined dolomite, bauxite, gibbsite |
| 3.  | Increasing the ash melting temperature by adding inert elements | bauxite, lime, limestone, silicon oxide, marble sludge                      |
| 4.  | Restraining ash sintering by diluting and powdering effects | lime, limestone                                                            |

The company Metsä Tissue from Slovakia produces an average of 60,000 tons of paper sludge per year as waste. In order to utilize the positive properties of this waste product, the sludge was used as an additive in this work. Chemical analysis of the paper sludge used is presented in Table 3.

| Parameter | Value (%) |
|-----------|-----------|
| Na₂O      | 0.031     |
| K₂O       | 0.053     |
| CaO       | 54.990    |
| MgO       | 1.020     |
| Al₂O₃     | 3.292     |
| SiO₂      | 4.488     |
| TiO₂      | 0.094     |
| Fe₂O₃     | 0.205     |
| MnO       | 0.012     |

The Na₂O and K₂O were analyzed by atomic absorption spectrometry on a Varian SpectrAA300 device at 550 °C. The rest of the parameters were measured by inductively coupled plasma optical emission spectrometry (OES-ICP) on a Varian Liberty 200 device at 480 °C.

2.2. Plant Biomass and Paper Sludge

The primary raw material for the production of experimental samples in the form of pellets was wheat straw. The paper sludge was used as an additive in various proportions in order to increase the melting temperature. The average measured moisture content of the sludge was 25% as a result of its storage in the open air. Therefore, it had to be dried in a laboratory oven MEMMERT UFP 500 at 100 °C for 12 h. The resulting average moisture content of the paper sludge after drying was about...
which shows a gradual decrease in the carbon content of the produced samples with the addition of paper sludge (PS100) and 100% of paper sludge (PS100) were produced as well for comparison. The pelleting process was carried out on a pellet press KAHL 33–390/500 with a vertical die and the input material was crushed before compaction. The three samples as the mixtures of wheat straw with paper sludge in the following proportion were produced: 70% straw–30% paper sludge (SPS–70/30), 80% straw–20% sludge (SPS–80/20), 90% straw–10% sludge (SPS–90/10), (see Figure 1). In a previous study, the influence of paper sludge on melting temperature was investigated and the increased melting point of produced samples was already reached at 50% of sludge content [26]. In order to reduce the ash from combustion and elevate the melting point at the same time, the range of paper sludge for the production of wheat straw pellets was analyzed from 10% to 30%. The reference pellets from 100% of wheat straw (S100) and 100% of paper sludge (PS100) were produced as well for comparison.

![Produced samples: (a) S–100 (b) SPS–70/30 (c) SPS–80/20 (d) SPS–90/10 (e) PS–100.](image)

**Figure 1.** Produced samples: (a) S–100 (b) SPS–70/30 (c) SPS–80/20 (d) SPS–90/10 (e) PS–100.

### 2.3. Ultimate Analysis of Samples

In this work, the CHN628 series analyzer LECO with dual stage furnace system, operating at temperatures of up to 1050 °C, was used to determine the carbon, nitrogen and hydrogen content in the samples. Each sample was tested three times and the averaged data are presented in Figure 2, which shows a gradual decrease in the carbon content of the produced samples with the addition of paper sludge, and the carbon content is lower compared to straw pellets (S100). The lowest carbon concentration was measured in the sludge pellets (PS100).

![Proximate analysis of produced samples compared to wheat straw (S100) and paper sludge pellets (PS100).](image)

**Figure 2.** Proximate analysis of produced samples compared to wheat straw (S100) and paper sludge pellets (PS100).

The hydrogen content of all samples is lower than in the straw pellets (S100). For all samples, as the amount of sludge increases, there is an increased proportion of nitrogen in the fuel. The proportion of N is also relatively high in pure straw pellets, which is probably due to excessive soil fertilization.
2.4. Proximate Analysis of Samples

The TGA-701 thermogravimetric analyzer, which determines material weight loss as a function of temperature in a controlled environment, was used to analyze the composition of the produced samples and the results of measurement are summarized in Table 4. The results of dry mass are given. The first measured quantity is moisture and the highest humidity is shown by pure straw pellets (S100).

| Sample  | Moisture (%) | Volatile Matter (%) | Ash (%) | Fixed Carbon (%) |
|---------|--------------|---------------------|---------|------------------|
| SPS–90/10 | 5.81         | 69.05               | 10.32   | 14.81            |
| SPS–80/20 | 5.1          | 68.39               | 12.92   | 13.58            |
| SPS–70/30 | 6.64         | 66.93               | 13.91   | 12.51            |
| S100     | 6.87         | 71.3                | 5.02    | 16.81            |
| PS100    | 5.61         | 55.71               | 42      | 0.93             |

The paper sludge contains a negligible amount of fixed carbon, despite the relatively high proportion of volatile combustible material. In this case, the proportion of volatiles is highest for straw pellets, the value being close to that of wood pellets’ volatile matter (75%) [26]. As the amount of sludge in the samples increases, a gradual decrease in the volatiles content can be observed.

The large proportion of non-combustible components in the paper sludge causes high ash concentration and it can be noticed that sludge pellets show the highest value of ash. For the sample SPS–80/20 and SPS–70/30, the ash content is up to 2.5 times higher than that of S100 pellets. Such high values can lead to burner clogging and other operational problems.

In the study conducted by Matuš et al., the effect of various proportions of papermaking sludge mixed with wheat straw on the quality of this fuel is presented. Comparing some of the results, the deviation in the range of 1–2% was noticed in the case of carbon, hydrogen and ash content. Comparison of nitrogen values shows content fluctuations in the range of 7–16% [16]. However, this may be due to the type of straw, different composition of soil on which the straw was grown, or the harvesting period.

3. Experimental Research Results and Discussion

3.1. Calorific Values

The higher calorific value (HCV) of samples, as one of the most important fuel indicators in terms of energy, was measured on a calorimeter LECO AC 500. The lower calorific value (LCV) of the samples was subsequently determined by the following equation [27]:

\[ LCV = HCV - r_{H_2O} \left( W_p + 8.94 \cdot x_H \right) \]

where \( r_{H_2O} \) is the water heat of vaporization [kJ/kg], \( W_p \) is the water content in sample [% wt.] and \( x_H = 0.01 \cdot H_h \cdot B_p \), where \( H_h \) is the hydrogen content in the sample [% wt.], \( B_p \) is the volatile content in the sample [% wt.].

From Figure 3, it is clear that straw pellets (S100) show the highest calorific value and the LCV of the sludge pellets (PS100) is around 5 MJ·kg⁻¹. As expected, the calorific value decreases with increasing sludge content in the samples. The lowest LCV was recorded for the sample with the highest proportion of paper sludge (SPS-70/30).
The data shown above were confronted with the results presented in the work of Matúš et al. and around 1% variation was recorded in compared samples [16].

3.2. Effect of Paper Sludge on Ash Melting Temperature

The main purpose of adding paper sludge to straw pellets was to increase the melting temperature of the ash. This was analyzed on the LECO AF 700 device, which monitors the deformation of ash pyramids at a given temperature. Individual characteristic changes in ash are defined by the following temperatures: DT—deformation temperature, ST—shrinkage (softening) temperature, HT—hemisphere temperature, FT—flow (fluid) temperature.

The measurement was based on the ISO-540 standard and it was necessary to prepare three pyramids from each ash sample. Three measurements were taken and each lasted about 2 h. The furnace temperature increased at a rate of approximately 8 °C per minute, from the initially defined 750 °C to the desired 1500 °C. Samples before and after the measurement are presented in Figure 4. It is already clear that only two samples of ash, namely S100 and SPS-90/10 (the two samples in the upper left of the plate), were completely melted.

![Figure 4. Comparison of samples before (left) and after measurement (right).](image)

The characteristic ash temperatures of all samples are presented in Table 5. These results present the average values from three measurements. The table of data reports that the higher content of the paper sludge in the samples increases the melting temperature of the ash. The results are satisfactory even at a 10% share of the sludge. Thus, further increasing the sludge content is not relevant in terms of increasing the melting temperature.
Table 5. Melting points of the samples.

| Sample | DT (°C) | ST (°C) | HT (°C) | FT (°C) |
|--------|---------|---------|---------|---------|
| S100   | 1025    | 1081    | 1121    | 1205    |
| SPS–90/10 | 1261    | 1348    | 1395    | 1418    |
| SPS–80/20 | 1285    | >1500   | >1500   | >1500   |
| SPS–70/30 | 1294    | >1500   | >1500   | >1500   |
| PS100  | 1305    | >1500   | >1500   | >1500   |

The temperatures presented in Table 5 are higher than reported in the research of Matúš et al. The difference is probably caused by the shape of the specimens, since the tests in the mentioned research were based on the heating of the cylindrical samples (according to CEN/TS 15370-1 based on the ISO 540) [16]. Another factor, as already stated, is the different types of straw.

A detailed measurement of the sample S100 is shown in Figure 5. At the temperature 1025 °C, the deformation point DT was determined. The high content of potassium in straw ash significantly affects the melting temperature [5]. The sample softened at approximately 1081 °C, with a gradual melting of the ash at 1121 °C and subsequent flow at a temperature of about 1205 °C.

![Figure 5. Measurement of ash sample S100.](image1)

Figure 6, for comparison, shows the measurement of the sample SPS-80/20. Deformation of this ash was determined at a temperature of 1285 °C, a significant increase over the sample S100. This sample containing 20% sludge did not soften and a temperature higher than 1500 °C would be required.

![Figure 6. Measurement of ash sample SPS-80/20.](image2)

The explanation for the rapid increase in the melting temperatures of all samples is the higher proportion of sludge ash. This statement is demonstrated in Table 6.

Table 6. Ash content in 10 g of SPS-90/10 sample.

|                          | Straw | Paper Sludge |
|--------------------------|-------|--------------|
| Ash content (%)          | 5.02  | 42.00        |
| Weight of raw material in 10 g sample (g) | 9.00  | 1.00         |
| Ash content in 10 g of sample (g)    | 0.45  | 0.42         |
| Ash content in 10 g of sample (%)    | 51.82 | 48.18        |
In the SPS-90/10 sample, ash is formed by up to 48% sludge ash, although the paper sludge is only 10% by weight in the produced pellets. From the measured values it is obvious that the paper sludge positively influences the melting temperature of the ash and can be used as an additive in the plant biomass combustion processes. This effect is also confirmed in the work of Wang et al. where the melting temperature of the rye straw ash increased upon addition of the Ca-sludge waste from pulp and paper industry [28].

4. Conclusions

Agricultural residues contain high amounts of ash, forming matters and problematic elements like K, Cl and P, causing ash-related problems during the combustion process [29]. Therefore, this work has shown that one of the solutions to deal with the greatest deficiency of plant biomass and thus the low melting temperature of ash is the use of suitable additives and materials that can increase this temperature. The aim was to investigate the effect of paper sludge on the properties of straw pellets and its potential for combustion in small-scale boilers. Analysis of the results shows that the sludge adversely affects the calorific value of the straw pellets, due to its low carbon content. With a 10% sludge content (sample SPS-90/10), the LCV decreased by approximately 10% compared to the calorific value of the reference pellets (sample S100). In the case of ash content, after adding 10% of the sludge, its proportion in the sample increased up to two-fold. The positive effect of the sludge was manifested in its ability to increase the melting point of the ash of plant biomass pellets. The deformation temperature of the ash increased by almost 250 °C after the addition of 10% sludge, an increase of 18.97% compared to the reference pellet. Thus, in terms of fusibility, it has been shown that such an amount of sludge is sufficient to eliminate the problems that arise in the combustion of plant biomass. More sludge in the pellets would raise the melting temperature and content of ash, but it would decrease the LCV.

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