



Article

The Utilization of Plum Stones for Pellet Production and Investigation of Post-Combustion Flue Gas Emissions

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Abstract: Agri-food waste is generated at various food cycle stages and is considered to be a valuable feedstock in energy systems and chemical syntheses. This research identifies the potential and suitability of a representative agri-food waste sample (i.e., plum stones) as a solid fuel. Ground plum stones containing 10, 15, and 20 wt.% of rye bran were subjected to pelletization. The pelletizer was operated at 170, 220, and 270 rpm, and its power demand for the mixture containing 20 wt.% of rye bran was 1.81, 1.89, and 2.21 kW, respectively. Such pellets had the highest quality in terms of their density ($814.6 \text{ kg}\cdot\text{m}^{-3}$), kinetic durability (87.8%), lower heating value ($20.04 \text{ MJ}\cdot\text{kg}^{-1}$), and elemental composition (C: 54.1 wt.%; H: 6.4 wt.%; N: 0.73 wt.%; S: 0.103 wt.%; Cl: 0.002 wt.%; O: 38.2 wt.%). Whole plum stones and pellets were subjected to combustion in a 25 kW retort grate boiler in order to determine the changes in the concentrations of NO, SO₂, CO, CO₂, HCl, and O₂ in the post-combustion flue gas. Collected results indicate that plum stone–rye bran pellets can serve as effective substitutes for wood pellets in prosumer installations, meeting the Ecodesign Directive requirements for CO and NO.

Keywords: agri-food waste; plum stones; pressure agglomeration; biomass combustion; flue gas emissions

1. Introduction

Improving the energy efficiencies of thermally operated waste conversion processes has lately become a trending topic worldwide [1,2]. The utilization of waste for heat and electricity production decreases the amount of land-filled waste, slows down the depletion of fossil resources, and, hence, reduces the diverse effects for the climate change [1]. According to the data obtained from the greenhouse gas inventory of the European Environment Agency (EEA) [3] and the Eurostat [4], total greenhouse gas emissions in the EU have remained stable since 2014, amounted to ca. 4483 megatons (Mt) of CO₂ equivalent in 2017. The main reason for the high CO₂ emissions is the excessive use of fossil fuels in power plants, prosumer boilers, and transportation [3,5,6]. Hence, the introduction of alternative renewable fuels, such as solid organic waste (e.g., agri-food and municipal) is mainly driven by the needs of replacing the dominant types of fossil fuels (e.g., coal, fuel oil, and natural gas), along with the disposal of post-production waste [7].

The agri-food waste can be defined as the waste biomass generated by the industrial operations of agriculture and food sectors. According to the Directive 2008/98/EC of the European Parliament and of the Council of 19 November 2008 on waste, these can also be considered to be bio-waste. Emissions associated with the agri-food waste include that of all generated/released during the

production, processing, retail, distribution, and consumption of food, together with the waste removal and disposal operations [8]. The actual trend in the management of agri-food products is described by the abovementioned EU directive and affiliated with the circular economy, which are concentrated on the reuse and utilization of resulting by-products and waste [9]. In 2016, approximations for the European Union claimed that ca. 88 million tons of food waste are created via the food production chain, yielding ca. 173 kg per inhabitant per year [10]. On the other hand, the utilization of agri-food waste as substrates in chemical syntheses and energy systems has been shown to increase [11]. According to Banaszuk et al. [12], the use of biomass for energy generation purposes should initially be associated with the management of plant origin post-production waste. One of the factors that may highly limit the use of some agricultural waste products is their high moisture content, which might overstep 50 wt.% in some cases (fruit and vegetable pulps and peelings, brewing grain, etc.) [4]. Moreover, for each biomass species, the calorific value and ash content should be determined to indicate the possibility of its use as an energy raw material and to select the appropriate technology for its energy processing [13,14]. Therefore, the abovementioned physicochemical properties of solid organic wastes are the objects of interest for many researchers.

Fruit stones can become a cheap source of bioactive peptides [15], carbon absorbents [16], activated carbon [17], or a substrate for biodiesel production [18–20]. As an example, plum stones are the by-products of plum processing industry and constitute ca. 2.8 wt.% of the total fruit weight [21,22]. As an example, plum stones are the by-products of plum processing industry and constitute ca. 2.8 wt.% of the total fruit weight [22]. According to Food and Agriculture Organization Corporate Statistical Database (FAOSTAT) [23], from 1994 to 2018, the area of plums harvesting was doubled worldwide, reaching a current value of 2.5 million ha. As a result of the ever increasing production of plums, possibilities of eco-friendly use of post-production waste are sought [20]. Ceylan [19], examining the elemental composition and heat of combustion of selected fruit seeds, states that plum stones contain 51.3 wt.% carbon, and their heat of combustion is $21.12 \text{ MJ}\cdot\text{kg}^{-1}$; this is about $5 \text{ MJ}\cdot\text{kg}^{-1}$ higher from the heat of combustion of cherry stones. Cagnon et al. [21] state that plum stones are materials with a low ash content of 0.9 wt.%. For comparison, olive stones and coconut shells contain ca. 4.4 wt.% and 2.7 wt.% of ash, respectively.

Rye bran, the by-product of flour milling process, contains 39 wt.% of fiber [24–26]. It is mainly added to food to help gut peristalsis and lower the energy density of food, which results in a longer satiety feeling [27]. Rye bran consists of carbohydrate components which are non-starch and starch polysaccharides [24]. The second of these gelatinizes to form of a sticky gel, due to the high temperatures occurring during the granulation process and the presence of moisture. Rye-bran binding properties are preferred in the agglomeration processes, where, used as additives (e.g., binder), they improve the process efficiency and reduce its energy expenditure [28–30].

Agri-food waste might be converted into energy via several thermochemical processes, the selection of which has to be based on the desired form of energy, the type and amount of material available, environmental requirements, and economic conditions [31–33]. Before being processed, agri-food solid waste may be submitted to pressure agglomeration (i.e., pelletization and granulation) and acquire a geometric shape in the form of granules (e.g., pellets and agglomerates) or briquettes [34–37]. According to an European Biomass Association (AEBIOM) report [38], worldwide consumption of pellets in 2018 was almost 53 million tons (where half of it is consumed in the EU) and increased by 14%, compared to the year 2017. According to Cincinelli et al. [39], the European Union covers only 70% of its own demand for fuel pellets, where the remaining fuel is imported from the United States of America.

The popularity of fuels produced via the pressure agglomeration increases due to their numerous advantages, such as being intermediate renewable energy carriers, having higher energy densities and their ability to adapt to the automated feeding systems. Moreover, fuels in the form of pellets may be transported and stored without packaging having improved storage conditions: reduced risks affiliated with the microbial hazards (i.e., the development of bacteria and fungi in materials of plant

origin). The agglomeration process allows the creation of a material mix consisted of components of different particle sizes (dusty materials), different particle shapes, etc., into a uniform, durable product [33,40–44]. Fuel pellets are becoming more common both in the power industry and in low- and medium-power installations; so-called prosumer energy. Combustion is the most preferred technology due to its high market availability and low installation and operating costs, compared to that of gasification and pyrolysis. Hence, both woody and non-woody biomass pellets need to meet high-quality requirements of current standards, which was, in detail, described in Reference [45]. It has to be emphasized that the method of energy generation highly depends on the type of available fuel (woody biomass and agri-food waste) [46].

The current amount of direct heating domestic installations for biomass combustion in the European Union is ca. 65 mln (e.g., stoves, fireplaces and ovens), and ca. 8 mln for indirect heating (e.g., boilers and burners mainly using wood, wood chips, and pellets) [38]. The latest European Union legislation and amendments to the Ecodesign Directive [47] are crucial for the development of more efficient units with lower emissions of harmful flue gas compounds in the following next 10 years, along with encouragement systems, to convince users to replace old installations with newer, more efficient models.

The management of waste in the form of fruit stones for heating purposes requires comprehensive studies on the optimization of pellet production and their subsequent use in thermal/thermochemical technologies. This article presents comprehensive research results regarding the utilization of agri-food waste in the form of plum stones and rye bran for the production of fuel pellets. The scope of the work included assessment of proximate and ultimate analyses, pressure agglomeration of the feedstocks and assessment of the effects of the granules' combustion in a fixed grate retort boiler where concentrations of NO, SO₂, CO, CO₂, HCl, and O₂ in the post-combustion flue gas were tested.

2. Materials and Methods

The presented research was conducted as shown in Figure 1.

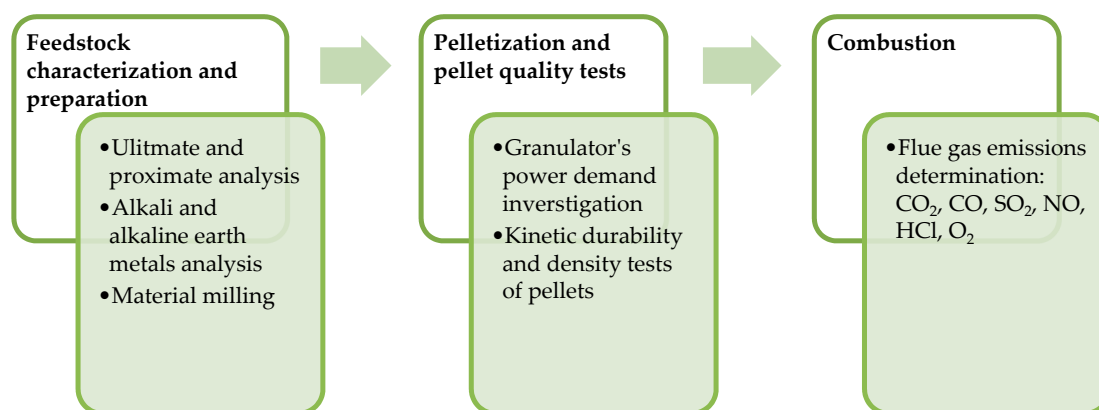


Figure 1. Schematic plan of the research.

2.1. Feedstock

Plum stones and rye bran used in this study were obtained from Greenyard Frozen Poland in Lipno (Lipno, Poland), and Młyn Rymaszówka (Korycin, Poland), respectively (Figure 2). Prior to the pelletization process, plum stones were comminuted to particle sizes of 2 to 5 mm using a concrete crusher. The particle size of rye bran was less than 1 mm (a.r.).



Figure 2. Plum stones, (a) as received from the processing plant and (b) in comminuted form for the granulation process; and (c) rye bran.

2.2. Feedstock Characterization

The elemental composition of the agri-food waste feedstocks was tested by the means of a LECO CHN628 analyzer. The contents of carbon, hydrogen, and sulfur (d.b.) were determined by high-temperature combustion with infrared radiation (IR) detection (according to the method proposed in the norm [48]), while nitrogen was determined by means of a catarometer (according to the norm [49]). The chlorine contents of the feedstocks were tested according to the method given by the producer of the fluorescence spectrometer S2 PICOFOX. Contents of moisture [50], volatile matter [51], and ash [52] in plum stones and rye bran were determined by the TGA-701 analyzer from LECO. The higher heating value (HHV) was examined in accordance with the method presented in Reference [53], with the use of the KI-12Mn calorimeter. The abovementioned methods are also presented in Reference [54]. Based on the hydrogen content of the material and its moisture content, the lower heating value (LHV) was calculated as follows:

$$\text{LHV} = \frac{\text{HHV} - 24.43 \cdot (w + 8.94 \cdot H)}{1000} [\text{MJ} \cdot \text{kg}^{-1}] \quad (1)$$

where 24.23 is the coefficient taking into account the amount of water vaporization heat at 25 °C, corresponding to 1% of water in the fuel; and 8.94 is the coefficient resulting from the stoichiometry of the hydrogen combustion reaction (occurring quantitative changes).

2.3. Pressure Agglomeration Process

The agglomeration process of the feedstocks was performed on a test setup. In this setup, the main element for agglomeration was the P-300 pelletizer from Protechnika. The pelletizer's matrix was mounted on a shaft to which the torque from the electric motor was transmitted through a bevel

gear. The pelletizer's working system contained a flat rotating matrix cooperating with two stationary bearing-mounted compacting rollers, forcing the material to be agglomerated into the matrix holes. The granulator matrix had a thickness of 28 mm, diameter of 210 mm, and hole diameter of 6 mm. Uniform supply of the raw material to be compacted to the working system of the pelletizer was ensured by the use of a vibrating feeder, dosing the raw material through a charge. Pellets were leaving the working system by the pouring out. The test setup was equipped with a recorder coupled with a computer and a universal meter for taking the measurements of the power demand of the device. Received binary signals were sent to a recorder–transmitter and were further processed in Microsoft Excel and Statistica 13.0PL software [54–57].

Pressure agglomeration of ground plum stones and rye bran was performed at various input values of materials (addition of rye bran) and process parameters (rotational speed of the pelletizer matrix). Mixtures containing a mass content of 10, 15, and 20 wt.% of rye bran were agglomerated at a rotational speed of 170, 220, and 270 rpm for each.

Tests were carried out with respect to the kinetic durability and density of the obtained pellets and to determine the power demand of the pelletizer. To verify the physical density of the pellets, ten randomly selected specimens (in order to approximate their shape to a roll as accurately as possible, their edges were ground before the measurement) were weighed with an accuracy of 0.0001 g. Besides this, their height was measured with the use of a conventional calliper with an accuracy of 0.05 mm. Pellet densities were calculated as the volume and weight quotient of each pellet, next averaged. The kinetic durability of the received pellets was tested by using the Holmen method [58]. The power demand for the granulator was measured by using an appropriate meter coupled with the recorder in the PC.

2.4. Combustion of Pellets

To verify the emission effects of produced pellets in a low-power boiler, combustion tests were performed at the laboratory of Low Emission Combustion Technologies in Białystok University of Technology.

The laboratory-scale system includes a Moderator 2 UnicaVentoEko boiler equipped with a 25 kW retort fixed grate and a MCA10 flue gas analyzer from Dr. Födisch. For each run, around 10 kg of pellets were fed to the system via an automatically controlled screw feeder. The mass flow rates of the fuel (pellets) and the air dozed to the combustion chamber were controlled automatically in the Fuzzy Logic mode. The mass flow rate of pellets to the combustion chamber was 3.2 kg·h⁻¹.

In order to compare to the Ecodesign requirements, the contents of the tested compounds (i.e., NO, SO₂, CO₂, CO, and HCl) in the post-combustion flue gases had to be normalized to an oxygen O₂ content of 10% content, and it was calculated according to the following formula:

$$Z_{s2} = \frac{21 - O'_2}{21 - O''_2} \cdot Z_{s1} [\%, \text{mg} \cdot \text{m}^{-3}] \quad (2)$$

Calculations of the excess air factor λ were based on the formula as follows:

$$\lambda = \frac{21.5}{21.5 - O''_2} [-] \quad (3)$$

3. Results and Discussion

3.1. Physicochemical Properties of the Feedstock

The results of proximate and ultimate analyses of investigated feedstock are shown in Table 1.

Table 1. Physicochemical properties of plum stones and rye bran.

| Parameter | Plum Stones | Rye Bran |
|---|-------------|----------|
| Proximate analysis (a.r.) (wt.%) | | |
| Volatile matter (PN-EN ISO 18123: 2016) | 70.4 | 69.7 |
| Moisture (PN-EN ISO 18134: 2017) | 10.7 | 10.5 |
| Ash (PN-EN ISO 18122: 2016) | 0.9 | 3.77 |
| Ultimate analysis (d.b.) (wt.%) | | |
| C | 54.2 | 46.3 |
| H | 6.4 | 6.0 |
| O [†] | 38.2 | 55.1 |
| N | 0.73 | 2.42 |
| S | 0.103 | 0.095 |
| Cl | 0.002 | 0.002 |
| AAEMs ^{††} (d.b.) (wt.%) | | |
| K | 0.151 | n.d. |
| Na | 0.004 | n.d. |
| Mg | 0.045 | n.d. |
| Ca | 0.057 | n.d. |
| Ni | 0.003 | n.d. |
| Si (g·kg ⁻¹) | 3.56 | n.d. |
| Hg (g·kg ⁻¹) | 0.011 | n.d. |
| HHV (a.r.) (MJ/kg) ^{†††} | 22.26 | 16.77 |
| HHV (d.b.) (MJ/kg) | 22.46 | 18.86 |
| LHV (d.b.) (MJ/kg) | 20.76 | 17.24 |

[†] Calculated by difference. ^{††} Alkali and alkaline earth metals. ^{†††} Calculated by using the Milne formula [59]. LHV = lower heating value. HHV = higher heating value.

Both feedstock samples were originally characterized by similar moisture contents of ca. 10 wt.% (d.b.). However, due to the design and processing requirements of the agglomeration system, prepared feedstock mixtures were moistened to a moisture content of ca. 20 wt.%, prior to their pressure agglomeration. After the process, the produced pellets were kept at room conditions to cool and dry.

The amount of volatile components is a significant parameter when assessing the suitability of solid fuels for their utilization as the key sources of energy generation. According to Kaczmarczyk [60], solid fuels containing significant amounts of volatile components (>60 wt.%) give a long flame during combustion and require additional air supply for complete smokeless combustion. Saxena [61] and Chmielniak et al. [62] claim that the dynamics of the combustion of volatile components depends not only on their share in fuel, but also on the speed and manner of their release from the porous structure of the resulting carbonizate; it is important for their even release of volatiles, giving a diffusion flame, and ejecting them under high pressure causes the formation of streams (torch flame). Both materials tested in this work are characterized by an almost identical content of volatile parts of ca. 70 wt.%, which is similar to that of woody biomass [62].

Ash is one of the by-products formed during the combustion of biomass [14]. As Obernberger [63] reports, the ash content in the fuel is crucial for choosing the right technologies for combustion and flue gas purification. Some of the ash-forming compounds evaporate during combustion, becoming a part of the gas phase [64]. The volatile amount of ash depends on the fuel characteristics, the combustion technology, and the atmosphere surrounding the particle [65]. The reducing atmosphere and high combustion temperature improve the volatilization of environmentally relevant elements like heavy metals (Pb, Zn, etc.) [66]. At high temperatures, metals and metal oxides are partially evaporated in the fuel particles, and then become a part of the gas phase as so-called “fly ash” (particle size <1 µm). Due to the processes of nucleation, reoxidation, and coalescence, these particles agglomerate, forming ash with a particle size larger than 10 µm, known as coarse fly ash [33].

Non-volatile ash compounds, which remain in the already burning fuel particles, can melt and be combined on or in the surface of the particle, the chemical structure of these particles, temperature,

and the surrounding gases [33]. This in consequence results in the formation of ash particles that have a vast range of ingredients, different sizes, and features associated with the original mineral. Depending on the density and size of these particles, as well as the combustion technology and exhaust gas velocity used, some of them may be entrained in the exhaust stream, but most of them remain on the boiler grate [67]. Woody biomass usually contains relatively small amounts of ash (ca. 1–2 wt.%) compared to coal; the latter may contain ash in the range of 6 to 30 wt.%. Higher values of ash are usually found in straw, bark, grains, grasses, and fruit residues [68,69]. The amount of ash in biomass is significantly lower than in coal; nevertheless, its different origin and chemical structure can affect the operation of the boiler installation, where they might influence the settling of ash and slag in the furnace or increase, due to corrosion, the rate of wear of metal boiler elements [14,70]. Hence, fuels with a low ash content are favored, but in the case of the 20 wt.% rye bran addition to plum stones, pellets were obtained with an average ash content of 1.5 wt.%, which is still a very low value.

Rye bran contains around four times the amount of ash that plum stones do. This indicates that rye bran has a higher amount of mineral salts, which could have been natural ashes chemically linked to the carbon structure or as so-called foreign ashes, that can be considered as mineral soil particles, that were absorbed by the plant while its state of vegetation or transferred to the biomass during harvesting and transport [71].

Another parameter, which is notably different in the tested feedstocks, is the nitrogen content. During combustion, the elemental nitrogen contained in the fuel is fully converted into nitrogen and nitrous oxides (i.e., NO_x) [72]. NO_x emissions originating from combustion have detrimental effects on the environment. Various mechanisms have been recognized that can lead to the formation of significant amounts of nitrogen oxides [73] during the combustion of solid fuels. These mechanisms include either the binding of molecular nitrogen contained in the oxidizing agent (air) or the oxidation of organic nitrogen chemically contained in the fuel. In the case of fuels with low nitrogen content, nitrous oxide is formed as a result of oxidation of N₂ originally contained in the air dosed for combustion processes [74,75]. For fuels having high contents of organically bound nitrogen, oxidation of fuel-related nitrogen is the dominant source of nitrogen oxides. Only a minor amount of nitrogen is included in the ash.

An increase in the content of rye bran from 10 to 20 wt.% in a mixture with plum stones causes a slight decrease in the lower heating value by ca. 0.35% from 20.41 to 20.06 MJ·kg⁻¹. It results from the fact that the calorific value of plum stones is ca. 3.5 MJ·kg⁻¹ higher than of rye bran (as measured). In another research, a decrease in the pellet LHV was also obtained when rye bran was added to cherry stones [76]. Moreover, it was noticed that the HHV value calculated according to the Milne formula is more accurate for plum stones than for rye bran; thus, the numerical method can be used more successfully in the case of materials with higher calorific value.

3.2. Pressure Agglomeration Tests

Figure 3 presents the influence of the rotational speed of the matrix and rye bran content on the density of produced pellets.

$$\rho = 981.53 - 6.60rb_{\%} - 0.65m_{rs} + 0.11rb_{\%}^2 \left[\text{kg}\cdot\text{m}^{-3} \right] \quad (4)$$

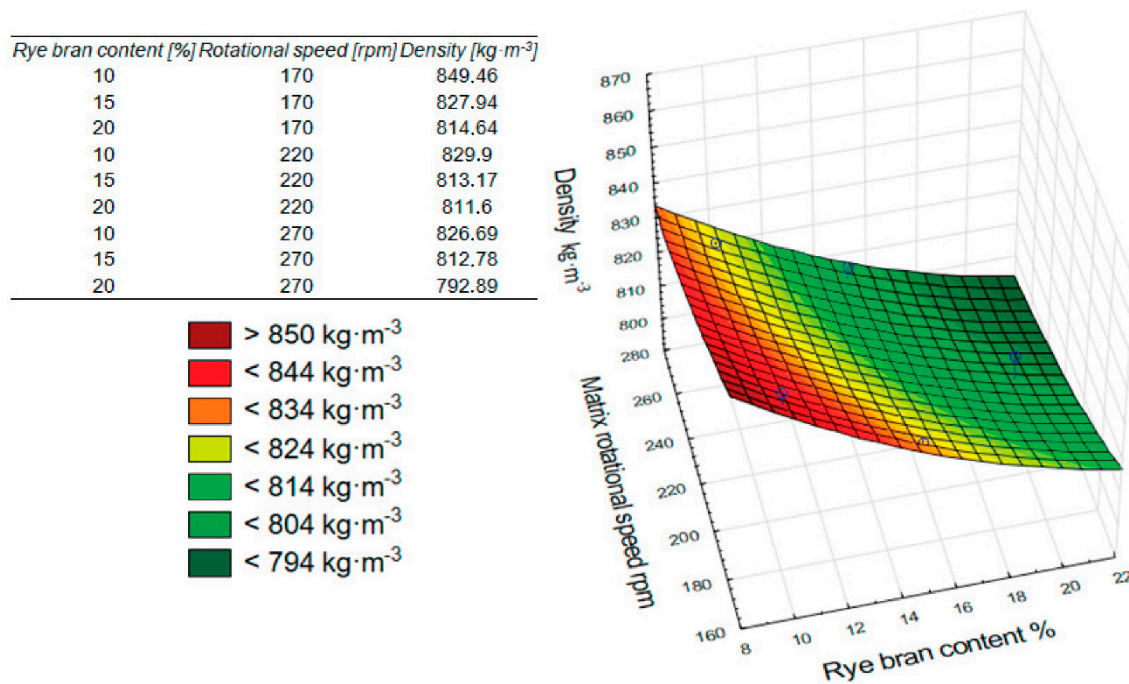


Figure 3. The impact of rye bran content and rotational speed of the matrix on the density of pellets.

The unit density, bulk density, and low calorific value of pellets define the amount of energy possible to recover from a certain volume of a fuel [77]. Therefore, it is highly important to optimize the material and processing factors of granulation for obtaining a high-density product (i.e., pellet). An increase in the content of rye bran from 10 to 20 wt.% in the feedstock mixture with comminuted plum stones caused a pronounced decrease in the physical densities of the produced pellets (Figure 3), from 849.46 to 792.89 $\text{kg} \cdot \text{m}^{-3}$. The highest density was obtained as 849.46 $\text{kg} \cdot \text{m}^{-3}$, with pellets produced at a matrix rotational speed of 170 rpm; however, such pellets did not show the best strength properties (Figure 4). It was found that the density of pellets decreased with the increase of bran content; however, their kinetic durability increased. The high density of pellets obtained with a low addition of rye bran is also due to the differences in bulk density of the original feedstock, i.e., pure plum stone and rye bran pellets had average densities of 423.4 and 279.85 $\text{kg} \cdot \text{m}^{-3}$, respectively. It should be noted that plum-stone pressure agglomeration tests without the addition of rye bran were also carried out; however, the obtained kinetic durability values were not satisfactory (below 50%).

$$P_x = 61.30 + 3.57rb_{\%} - 0.22m_{rs} + 0.04rb_{\%}^2 - 0.01rb_{\%}m_{rs} \quad [\%] \quad (5)$$

Kinetic durability is defined as the abrasion resistance of pellets and, according to European standards, should not be lower than 97.5% for industrial wood pellets [78] or above 92% for agro-pellets sold for fuel purposes. The increase in rye bran content in the mixture with ground plum stones caused an increase in the kinetic durability of the obtained pellets at all tested rotational speeds of the granulator matrix (Figure 4). For example, at 170 rpm, an increase in rye bran content from 10 wt.% to 20 wt.% resulted in an increase in kinetic durability from 61.6% to 87.8%. Rye bran contains arabinoxylans, which form high-viscosity solutions in water, thus increasing the agglomeration susceptibility of the mixture, and thus enabling the obtainment of pellets with higher kinetic durability [79].

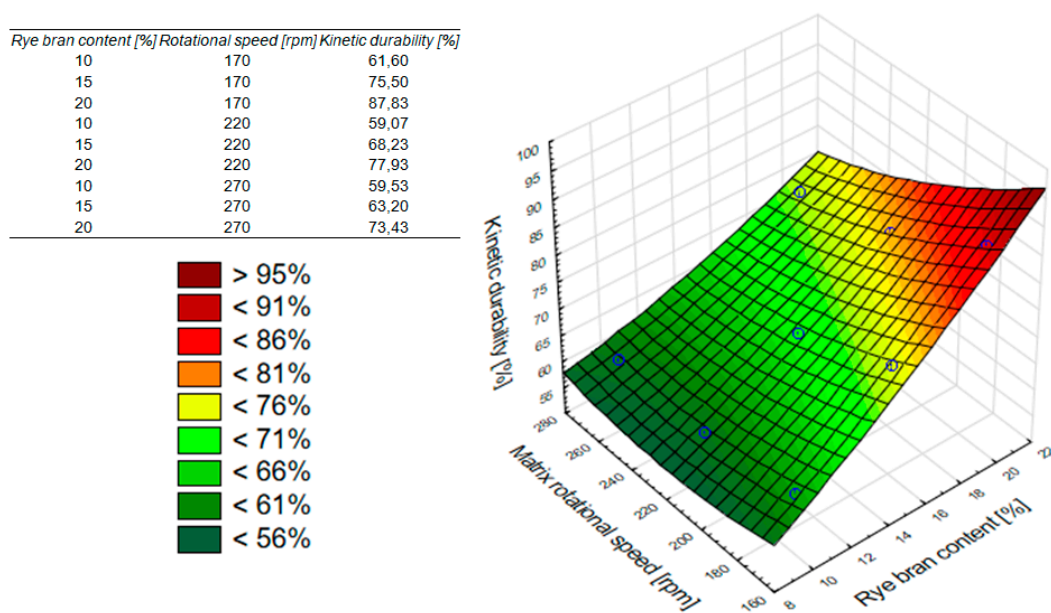


Figure 4. The impact of rye bran and rotational speed of the matrix on the kinetic durability of plum stones pellets.

Lowering the pellet production costs directly influences the energy cost. Therefore, a very important issue in pellet production is the energy consumption of the pelletizer, especially in small-scale pellet production plants where the effect of economy-of-scale might be observed [80]. Depending on the agglomerated material properties, the addition of a binder might affect the power demand of the granulator in both ways, by causing a decrease or increase in the power consumption. An increase in the amount of rye bran from 10 wt.% to 20 wt.% in the produced pellets resulted in a slight effect on increasing the power demand of the granulator from 1.65 to 1.81 kW with a rye bran content of 10 wt.% and at a matrix speed of 170 rpm (Figure 5). An increase in the rotational speed of the matrix and in the amount of rye bran added caused an increase in the energy consumption of the device from 1.65 to 2.21 kW. As a result of increasing the addition of rye bran (lowering the fat content in the mixture), the friction resistance of the agglomerated material against the elements of the working system increases. This has an impact on increasing unit agglomeration pressures, and thus on increasing the process energy consumption. However, on the other hand, increasing the friction in the matrix increases the energy demand and results in faster wear of the granulator working elements [81]. The production of durable pellets is strongly correlated with high energy consumption [80,81]; therefore, for each material, optimization tests of the pressure agglomeration process should be carried out separately, to obtain the highest quality pellets with the lowest possible energy consumption. Moreover, it should be emphasized that waste of biological origin (e.g., sawdust, scales, and stones) is used for the production of fuel pellets, and the overriding goal of the process is their management and chemical energy recovery [82,83].

$$N_g = 3.608 + 0.0034rb\% - 0.0221m_{rs} - 2e^{-5}rb\%m_{rs}E + 6e^{-5}m_{rs}^2 \quad [\text{kW}] \quad (6)$$

| Rye bran content [%] | Rotational speed [rpm] | Power demand [kW] |
|----------------------|------------------------|-------------------|
| 10 | 170 | 1,65 |
| 15 | 170 | 1,73 |
| 20 | 170 | 1,81 |
| 10 | 220 | 1,68 |
| 15 | 220 | 1,77 |
| 20 | 220 | 1,89 |
| 10 | 270 | 2,07 |
| 15 | 270 | 2,11 |
| 20 | 270 | 2,21 |

| | |
|--|---------|
| | > 2,3 |
| | < 2,225 |
| | < 2,125 |
| | < 2,025 |
| | < 1,925 |
| | < 1,825 |
| | < 1,725 |
| | < 1,625 |

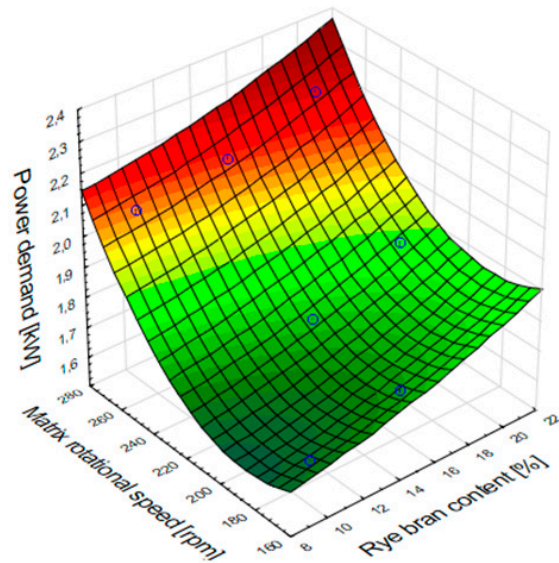


Figure 5. Influence of rye bran and rotational speed of the matrix on the granulator demand for power during the production of plum stones pellets.

3.3. Combustion Tests

Pellets, produced at a rotational speed of 170 rpm and with the highest obtained kinetic durability (80 wt.% plum stones and 20 wt.% rye bran), were used for the combustion tests. Preliminary tests showed that pellets containing 10 and 15 wt.% rye bran, due to their low kinetic durability, were crumbled in the automatic screw feeding system of the boiler, causing operational problems; hence, these samples were not considered for the experimentation. Figure 5 presents the results of flue gas composition obtained during the combustion of plum stone pellets containing 20 wt.% of rye bran and also the original plum stones in the form leaving the processing plant (a.r.) (see Figure 2a). The bars in Figure 6 define the minimum and maximum obtained value of flue gas emissions.

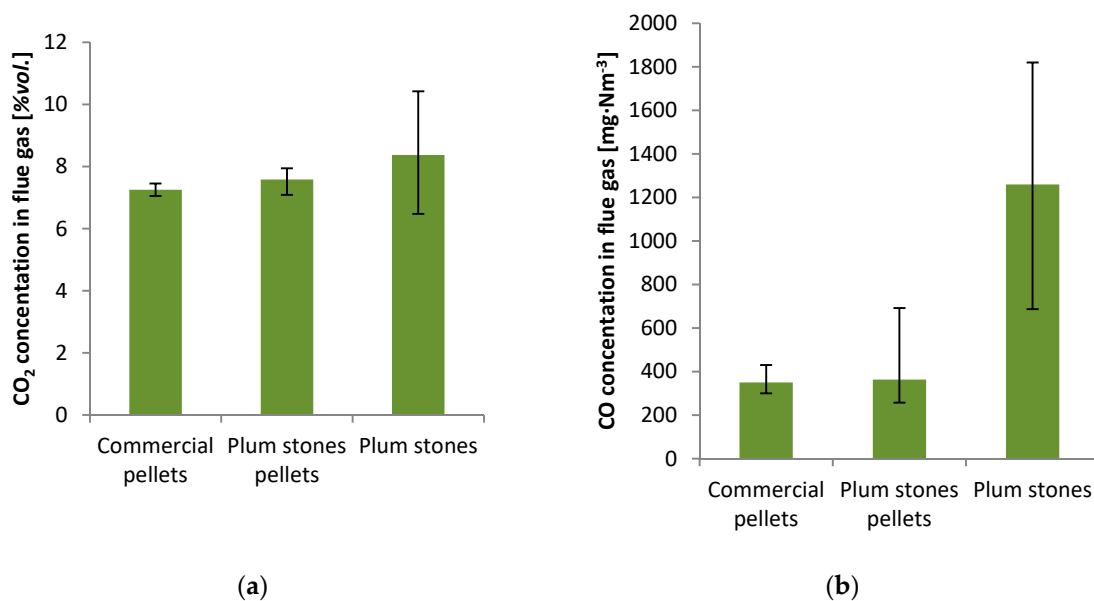


Figure 6. Cont.

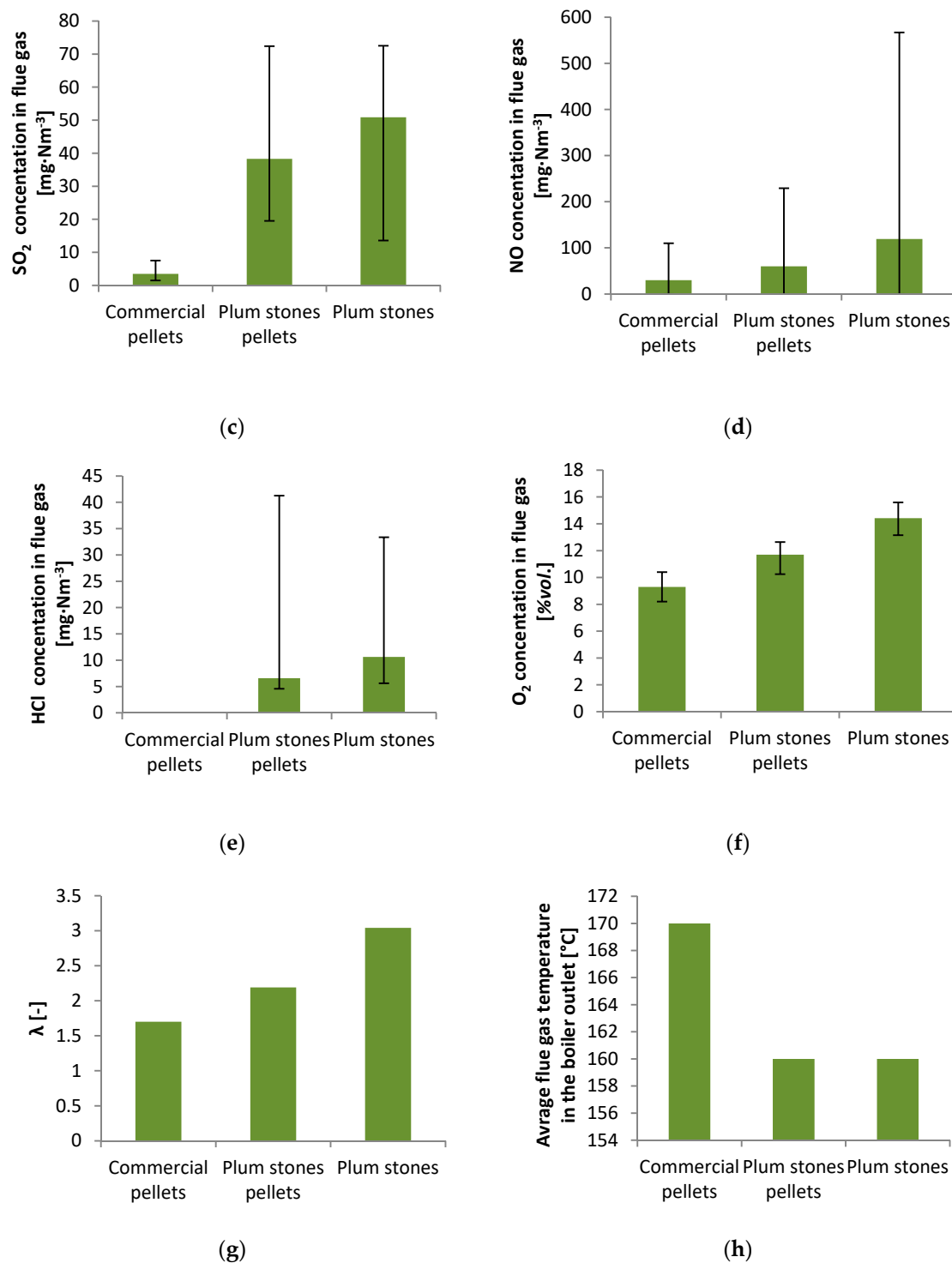


Figure 6. Conditions of combustion of commercial wood pellets, plum stone pellets containing 20 wt.% of rye bran, and plum stones without any pretreatment: (a) CO₂ emissions; (b) CO emissions; (c) SO₂ emissions; (d) NO emissions; (e) HCl emissions; (f) actual O₂ concentration in the flue gas; (g) excess air factor λ ; (h) average flue gas temperature in the boiler outlet.

In Figure 6h, the actual average content of oxygen in the exhaust gas is shown, according to which the excess air factor, λ , was determined. The difference between the value of λ for fuels pellets and combusted whole plum stones is easily visible, which confirms that these pellets are advantageous to be utilized in low power boilers with a retort grate. Szyszlak-Bargłowicz et al. [84] and Menghini et al. [85] claim that the most important parameter affecting the emission and efficiency of a boiler installation

is the excess air. Excess air is needed to ensure sufficient mixing of fuel and air for a complete and effective combustion (Figure 6a,b,f–h).

The λ depends on the fuel and the installation in which it is combusted, and, for instance, in the case of waste of biomass origin, it can range in values of up to 2–2.5 [86]. The emissions of NO_x , CO, dust and organic pollutants are strictly dependent on the combustion technology used, technical conditions of the process implementation, combustion technique, and physical and chemical properties of the fuel [68,87,88]. This is confirmed by Oleniacz [89], stating that the type of waste introduced into the installation has a significant impact on the type and amount of air pollutants arising from the combustion process. The best economic and ecological effect is obtained by using boilers equipped with automatic fuel–air ratio control systems, where λ is 1.02–1.03 [90].

Particular attention is paid to the CO content in the exhaust gas as an indicator of the increased content of hydrocarbons, soot, furans, and dioxins [91]. The Ecodesign EU directive determinates the maximum CO contribution in the flue gas for boilers with a heating capacity <0.5 MW and automatic fuel feeding, at the maximum amounts of $500 \text{ mg}\cdot\text{m}^{-3}$, which is also a requirement of the norm [92] for Class 5 boilers. The above condition was met when using plum pellets as a fuel (Figure 6b). Burning whole plum stones resulted in more than twice exceeding the applicable CO emission standard. Higher air excess coefficient, λ , and high carbon monoxide emission point to difficult air–fuel contact while the combustion process of the whole plum stones.

Incomplete combustion of biomass (partial oxidation of hydrocarbons contained in biomass) can lead to emissions of pollutants such as carbon monoxide, hydrocarbons, polycyclic aromatic hydrocarbons, tars, and soot [72,93]. Effective reduction of these pollutants can be achieved through an optimized combustion process, which consists of the selection of the excess air ratio, primary air flow rate, appropriate mixing of air and exhaust gas during post-combustion, a correspondingly high concentration of oxygen above the fuel bed, the time the fuel stays in the combustion chamber, and combustion temperature [94].

Wielgosiński et al. [95] noticed that, due to an increase in the temperature and decrease of air flow while combustion was taking place, a decrease in NO emissions was observed. As reported by the authors, this may be a result of modifications in the synthesis of NO under these conditions. This phenomenon was also confirmed in this research, while combustion of the whole stones and pellets, where the temperature of pellet combustion was higher than stones and the observed NO emission was lower (Figure 6d).

Obernberger et al. [68], based on the research of Miller and Bowman [96] and Fenimore [97], states that the so-called “thermal” nitrogen oxides are formed as a result of the reaction of nitrogen with oxygen radicals at temperatures above $1300 \text{ }^\circ\text{C}$, and their quantity increases with increasing temperature. The authors also specify “instant” nitrogen oxides that form at temperatures above $1300 \text{ }^\circ\text{C}$ with low oxygen content and in the presence of hydrocarbons. Due to the relatively low combustion temperatures of solid biofuels (around $800\text{--}1200 \text{ }^\circ\text{C}$), the “thermal” and “immediate” NO_x formation is of only minor importance.

As a part of this study, with the use of a K thermocouple, the furnace temperature was investigated while the combustion of plum stone pellets and it reached approximately $740 \text{ }^\circ\text{C}$. Therefore, it is concluded that the Zeldowicz’s reaction does not occur. Considering the high λ coefficient, the so-called processes, i.e., prompt NO—where in a rich mix N_2 and hydrocarbons combust, are not taking place [96]. In the investigated biomass combustion circumstances, the primary source of nitrogen oxides is nitrogen included in the fuel (temperatures under $1300 \text{ }^\circ\text{C}$). Nitrogen oxides formed from the oxidation of nitrogen contained in the fuel (during a number of elementary stages of chemical reactions) are generally the most important mechanism in biomass combustion units. NO_x emissions increase as the nitrogen content in the fuel increases. In addition, air supply, furnace geometry, combustion temperature, and type of combustion technology used are the main variables affecting the NO_x formation [68,73,98].

Sulfur contained in biomass, during combustion, is oxidized mainly to sulfur (IV) SO_2 oxide (and in small amounts also to sulfur (VI) SO_3 oxide) and forms alkali and sulfates [68]. As Zając et al. [99] report, SO_x emissions from wood biomass combustion are usually not significant. Low emission values were also observed in the case of plum stone granulate combustion with the addition of rye bran (Figure 6c). This is due to the small amount of sulfur contained in these waste materials. However, it should be noted that, also in the case of SO_x emissions, a more favorable (lower) value was obtained for pellets than whole stones.

Chlorine is included in the biomass, while most of the combustion processes is released in the form of hydrogen chloride HCl [100], which can further react with other exhaust components promoting the formation of dioxins [64]. Due to the subsequent cooling of the flue gas, outside the combustion chamber, a large part of the chlorine condenses as salts on the surfaces of the heat exchanger or on fly ash particles in the flue gas, causing high-temperature chloride corrosion of boiler plant components [101]. It should be noted that the melting point of potassium and sodium chlorides is high, but their eutectics with other metal chlorides have a much lower melting point. Therefore, in boilers in which biomass containing chlorine, heavy metals, and alkalis is combusted, the risk of corrosion occurs already at $250\text{ }^\circ\text{C}$ [102]. In the case of analyzed waste, further research should be conducted in this phase.

In the combustion experiments, the hydrogen chloride content was higher during the combustion of whole plum stones than from plum stones–rye bran pellets (Figure 6e). According to Liu et al. [103], high chlorine content in biomass fuels is highly undesirable, despite the fact that it can also cause some advantages, promoting the oxidation of mercury, and consequently facilitate its capture and regulation. This phenomenon occurs at temperatures below $427\text{ }^\circ\text{C}$; at higher temperatures, the importance of chlorine in the binding of mercury is marginal [104].

4. Conclusions

In the search for the most favorable parameters of the agglomeration process (due to the minimization of energy consumption in the process), it should be assumed that the obtained pellets should have adequate durability (it should be characterized by a specific kinetic strength), e.g., due to transport, storage, and be characterized by optimized density.

Being an agri-food waste, plum stones are feedstock with high calorific value and lower contents of nitrogen, sulfur, and chlorine. These properties make plum stones cleaner and alternative solid fuels for combustion. When they are pelletized without any additives, pellets with low kinetic durability are obtained, mainly due to the higher fat contents (ca. 4.2 wt.%) of plum stones. The use of a binder, such as rye bran, during the pelletization of plum stones has the effect of increasing the kinetic durability of produced pellets, while slightly decreasing their low heating value (LHV). An increase in rye bran content from 10 to 20 wt.% resulted in a reduction in the LHV by approximately $0.3\text{ MJ}\cdot\text{kg}^{-1}$, while the increase in the kinetic durability was up to 30%. Accordingly, the pellets with the addition of 20 wt.% rye bran were evaluated as the highest-quality product among the tested based on their kinetic durability and unit density.

A fundamental environmental stage of waste utilization in the processes of direct combustion is their emissivity. Through the combustion of pellets produced from the mixture of plum stones and rye bran (80 wt.% and 20 wt.%, respectively), in comparison to virgin plum stones, reductions in the emissions were observed, i.e., more than two times for carbon monoxide (while maintaining the same flow and thermal conditions of the boiler installation). Besides, in comparison to whole plum stones, reduced emissions of sulfur dioxide (24% lower value for pellets), nitric oxide (32% lower), and hydrogen chloride (40% lower) were obtained. The calculated excess air coefficient, λ , indicates a beneficial increase in the contact area between the combustible particles and the oxidizing agent (air) with combustion pellets, rather than using the whole plum stones as a fuel. In addition, it should be noted that pellets made from plum stones mixed with a 20 wt.% content of rye bran meet the emission requirements of the Ecodesign Directive.

Hence, the results of the presented study can motivate future investigators to use the plum stones for producing alternative biofuels that can be applied for heat and/or electricity production, either in domestic installation or in industrial energy plants. Moreover, energy processing of plum stones is decreasing the agri-food waste amount, and in the form of pellets, due to low emission factors and high calorific value, it can be considered as a valuable substitute for fossil fuels.

5. Patents

The presented research has been applied for a patent of a novel biofuel from plum stones and rye bran:

Jadwisieńczyk, K.; Choszcz, D.; Obidziński, S.; Dołżyńska, M.; Kowczyk-Sadowy, M. Fuel granulate from fruit waste and grain residues. Patent application no. P. 434557, dated 07/03/2020. Patent Office of the Republic of Poland, 2020.

Author Contributions: Conceptualization, M.D.; methodology, M.D. and S.O.; software, M.D. and S.O.; validation, M.D.; formal analysis, M.D. and G.Y.; investigation, M.D. and S.O.; resources, M.D., S.O., and J.P.; data curation, M.D.; writing—original draft preparation, M.D.; writing—review and editing, G.Y.; visualization, M.D.; supervision, S.O. and J.P.; project administration, S.O.; funding acquisition, S.O. All authors have read and agreed to the published version of the manuscript.

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Nomenclature

| Symbol | Description |
|-----------|--|
| LHV | lower heating value ($\text{MJ}\cdot\text{kg}^{-1}$) |
| HHV | higher heating value ($\text{MJ}\cdot\text{kg}^{-1}$) |
| w | moisture content (wt.%) |
| Z_{s1} | the actual chemical content in the exhaust gas ($\%, \text{mg}\cdot\text{Nm}^{-3}$) |
| Z_{s2} | content of the chemical compounds in the exhaust gas for a given oxygen content ($\%, \text{mg}\cdot\text{Nm}^{-3}$) |
| O_2' | set value of the oxygen content in the exhaust (%) |
| O_2'' | actual oxygen content in the exhaust gas (%) |
| λ | excess air factor (-) |
| $rb\%$ | rye bran content (%) |
| m_{rs} | matrix rotational speed (rpm) |
| ρ | pellet's density ($\text{kg}\cdot\text{m}^{-3}$) |
| P_x | pellet's kinetic durability (%) |
| N_g | granulator's power demand (kW) |
| wt.% | weight percent |
| vol.% | volume percent |
| a.r. | as received |
| d.b. | dry basis |
| n.d. | not determined |

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