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Article

Evaluation of Agricultural Residues as Organic Green Energy Source Based on Seabuckthorn, Blackberry, and Straw Blends

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Abstract: The use of biomass mixtures as a feedstock in the production of pellets requires optimization of the percentages of the components, since interactions occur during combustion between the components forming the blend (lignin, cellulose, and hemicellulose), affecting characteristics of pellets such as calorific value, ash content, fine fraction content, bulk density, and mechanical durability. Our study focuses on the assessment of the quality of pellets produced from biomass blends generated from pruning seabuckthorn and blackberry mixed with wheat straw. The results of literature data analysis and laboratory research show that wheat straw pellets exhibited the lowest calorific value (15.2 ± 0.2 MJ/Kg) and the highest ash content (5.7 ± 0.18%) while seabuckthorn and blackberry biomass pellets possessed significantly higher calorific value with low ash content. According to the maximization of the mixtures taken in the study, it was proved that the addition of up to 25% wheat straw remaining seabuckthorn biomass provides all the qualitative indicators specified by ENPlus 3 standards. The straw content can be increased up to 35% if 10–20% of blackberry biomass is added to the mixture. The production of pellets from biomass mixtures with an optimized composition, meeting the requirements of EN3Plus standards, will benefit the environment and the agricultural economy by replacing polluting fuels and making optimal use of straw and fruit tree pruning residues.

Keywords: agronomy; biomass blends; pellets; fruit bushes; seabuckthorn; blackberry; wheat straw

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1. Introduction

The agricultural sector is one of the pillars of the Moldovan and Romanian economy, resulting in a huge amount of residues that are often not valued at their fair value. One of the future directions of valorization of agricultural residues is their use as feedstock for the production of densified solid biofuels, the application for energy purposes being intensively studied in the literature, both worldwide [1–4] and in Moldova and Romania [5–10]. It is also known that only a part of agricultural residues can be used as feedstock for the production of densified solid biofuels with quality characteristics that meet the requirements of ENPlus 3 standards.

Research carried out in the Solid Biofuels Laboratory of the Agrarian State University of Moldova on the energy potential of agricultural residues specific to the Northern Zone of the Republic of Moldova has shown that only 9–10% of the total agricultural residues in this area ensure the quality parameters of the finished product in accordance with the requirements of classes A1 and A2 [11], the other residues being used as a filler in a mixture with other types of biomass [6,12]. Agricultural residues have a low calorific value per unit volume and are expensive to handle and transport, making densification challenging. Karkania et al. [13] highlighted the new market opportunity for the agricultural sector to replace coal and other polluting fuels with pellets from solid biomass blends. Other scientists [14] studied the combustion behavior of biomass pellets obtained from eucalyptus bark, mangosteen fruit peel, and papaya fruit peel using different binders. The highest calorific value (5068.60 ± 7.74 cal/g) was obtained when cashew nut shell liquid was used as a binder, but the unpleasant smoke and deposited tar has led researchers to not recommend the use of these pellets. Various blends of compost, wood chips, jatropha, and corn starch with the addition of exhaustion extinguishing powders (EEP) have also been used for pelletizing, the benefits being economic and environmental, but no results have been reported on the calorific value and ash content of these blended pellets [15]. A life cycle assessment (LCA) of the pellet/briquette production and bioethanol production processes from vine shoot waste indicated that the pellet/briquette process has a lower negative impact on the environment than bioethanol production [16]. Kizuka et al. [17] found that the wood pellets mixed with torrefied rice straw (WPTRS) could have the lower heating value (LHV) greater than of the wood pellets, provided that the torrefied rice straw (TRS) content is 10%. For higher precents of TRS, the ash content is very high and the LHV is less than that of the wood pellets. In addition, this study showed that the rice straw can be used in pellets only in small percentage and only if the torrefaction took place at a temperature of 280 °C. However, the torrefaction itself is energy and time consuming. A main direction for future research is the quality of mixed biomass pellets, as highlighted by Pradhan et al. [18] in their comprehensive review of biomass pellet production and use.

In Moldavia, one of the main agricultural crops, generating about 25% of the total volume of agricultural residues, is autumn and spring wheat. Our previous research, correlated with the literature, showed that wheat straw has a net calorific value, at 10% humidity, equal to 15.2 ± 0.2 MJ/kg and an ash content resulting from combustion equal to 5.7 ± 0.18% [7]. These considerations justify the use of wheat straw mixed with other types of plant biomass as feedstock for the production of densified solid biofuels. At the same time, biomass mixtures with a high straw content can cause problems because of the low fusibility temperature of the ash resulting from burning the straw [1].

The literature reports the possibility of using certain amounts of straw in a mixture with other types of plant biomass [19,20]. Thus, the study on the formation of raw material mixtures consisting of residues generated from pruning apple fruit trees and wheat straw in certain proportions showed that it can be recommended to use wheat straw as a component in the mixture in the manufacture of briquettes with EN Plus quality parameters in the following proportions: biobricks class A1 ENPlus—up to 10% straw; A2 ENPlus—up to 20% straw, and biobricks class B—up to 40% straw [21].

One of the ways of expanding the use of wheat straw as a raw material for the production of solid biofuels is the formation of mixtures with other types of plant biomass resulting from the technological links of as many agricultural crops with good development trends and prospects as possible. Among the crops with good development prospects are various species of fruit bushes, especially seabuckthorn and blackberry, which generate large volumes of plant residues that can be used as raw material for the production of BCSD [22].

Although there is substantial literature on the valorization of agricultural residues for energy purposes, the authors were unable to find data on the quantitative and qualitative estimation of biomass blends using seabuckthorn and blackberry residues mixed with wheat straw. Therefore, the aim of this paper is to present an exhaustive quantitative and qualitative characterization of biomass mixtures from the production chain of seabuckthorn and blackberry mixed with wheat straw from the point of view of its use as a raw material in the production of briquettes and pellets.

2. Material and Methods

2.1. Sampling and Sample Preparation for Biomass and Finished Product Testing

The biomass resulting from pruning seabuckthorn variety Cora, blackberry variety Black Satin, and wheat straw harvest 2021 served as the subject of the study.

The samples of seabuckthorn were taken from the experimental plantation of the company "Monsterax-GSG" Ltd. in the village of Pohrebea, Dubasari rayon, Republic of Moldova, a plantation established in 2014. Seabuckthorn biomass was taken from the pruning of seabuckthorn shrubs from the plantation of a peasant household in Trușeni village, municipality of Chișinău, Republic of Moldova, during March–April 2021.

Biomass sampling was carried out according to the requirements of SM EN ISO 18135:2017 [23], and sample preparation according to SM EN ISO 14780:2017 [24].

Pellets were produced from biomass mixtures, according to ENPLus 3 standard (Table 1) and the procedure given in Table 2, by using the mini pellet production line in the UASM Solid Biofuels Laboratory (made Kovonovak, type MGL 200, Kovo Novák, Czech Republic).

2.2. Methodologies Used for Biomass Characterisation

The formation of the biomass mixtures from which the pellets studied in this work were produced was carried out using the Box–Behnken polyfactor program shown in Table 1. The experimental design was such that the pellets produced from the biomass blends studied fell into the ISO ENPlus 3 classes. The experimental data were processed by applying the facilities of STATGRAPHICS 18 programs.

Table 1. Reference specifications for wood pellets according to ENPlus 3 standards (SM EN 17225: 2017).

Parameters	Unit	Class					
		ENplusA1	ENplusA2	En-B	I1	I2	I3
		For Commercial and Residential Applications			For Industrial Use		
Moisture, M	% in mass, as received, wet basis	M10 ≤ 10			M10 ≤ 10		
Ash, A_d	% in mass dry	A0.7 ≤ 0.7	A1.2 ≤ 1.2	A2.0 ≤ 2.0	A1.0 ≤ 1.0	A1.5 ≤ 1.5	A3.0 ≤ 3.0
Net calorific value, $q_{p,\, net,\, m\, =\, 10\%}$	MJ/kg or kWh/kg, as received	≥16.5 or ≥4.6			≥16.5 or ≥4.6		
Mechanical durability, DU	% in mass as received	DU97.5 ≥ 97.5 (DU98.0 ≥ 98.0 for D06)	DU97.5 ≥ 97.5	DU96.5 ≥ 96.5	97.5 ≤ DU ≤ 99.0	97.0 ≤ DU ≤ 99.0	96.5 ≤ DU ≤ 99.0
Fines, F (<3.15 mm)	% in mass, as received	F1.0 ≤ 1.0		F4.0 ≤ 4.0	F5.0 ≤ 5.0		F6.0 ≤ 6.0
Bulk density, BD	kg/m^3, as received	600 ≤ BD ≤ 750			BD600 ≥ 600		

Moisture content was determined according to the requirements of SM EN ISO 18134-3:2015 [25]. Biomass samples were dried.

Five samples selected in accordance with the requirements of SM EN ISO 14780:2017 [24] were shredded at SM 100 hammer mill and passed through a sieve with 1 mm mesh size. To avoid contact with the environment, the samples were placed inside a desiccator where they were kept until the tests were carried out.

Samples of 1 g mass were evenly distributed on the bottom of pre-heat-processed vials with lids at (105 ± 2) °C and kept in the desiccator until room temperature. After reaching ambient temperature, each vial was weighed together with the tested biomass content after being placed back into the oven and kept for at least 60 min at (105 ± 2) °C.

The operation was repeated until a constant mass was obtained (the difference between weighings should not exceed 1 mg. The amount of moisture in the studied samples was determined with the formula:

$$M_{ar} = \frac{(m_2 - m_3)}{(m_2 - m_1)}100,\ \% \tag{1}$$

where m_1 is the mass of the empty vial with cap, g; m_2 is the mass of the vial with cap and sample tested until dry, g; m_3 is the mass of the vial with cap and sample tested after dry, g.

The accuracy of the tests was determined by determining the standard deviation and confidence interval.

Ash content was determined according to the requirements of SM EN 18122:2017 by slow ashing of the samples in the LAC electric muffle furnace type LH 05/13 at 550 °C for at least 6 h.

The samples tested had a maximum particle size of 1 mm, which was ensured by sieving the biomass through a calibrated sieve with 1 mm mesh screen.

The samples were calcined by heating for 50 min to (250 ± 10) °C at a rate of +5 °C/min, holding at this temperature for 60 min and then heating to (550 ± 10) °C for 60 min and holding at this temperature for at least 120 min.

The ash content on a dry basis was calculated with the following equation:

$$A_d = \frac{(m_3 - m_1)}{(m_2 - m_1)} \cdot 100 \cdot \frac{100}{100 - W}, \% \tag{2}$$

where m_1 is the mass of the empty crucible, g; m_2 is the mass of the crucible plus mass of the test sample, g; m_3 is the mass of the crucible plus mass of ash, g; W is the moisture content of the test sample, %.

Volatile content was determined by burning (1 ± 0.1) g of analytical sample with particle size not more than 1 mm, prepared according to the requirements of MS EN ISO 14780:2017 [24]. The samples were kept in quartz glass crucibles with lid a muffle furnace, model LAC type LH 05/13 at 900 °C for 7 min ± 5 s. All analyses were repeated 5 times and the results were expressed in dry basis according to SM EN ISO 18123:2017 [26], using the following relation for calculation:

$$V_d = \left[\frac{100(m_2 - m_3)}{m_2 - m_1} - M_{ad}\right] \cdot \left[\frac{100}{100 - M_{ad}}\right] \tag{3}$$

where: m_1 is the mass of the empty vial with cap, g; m_2 is the mass of the vial with cap and test sample until dry, g; m_3 is the mass of the vial with cap and non-volatile residue after drying, g; M_{ad} is the moisture content of the test sample in % determined according to SM EN ISO 18134-3:2015 [25].

Energy capacity was estimated by determining the calorific value of the raw material and the finished product and by determining the energy potential and energy density of the biomass generated by the fruit bushes taken in the study.

The upper calorific value at constant volume was measured on the IKA C6000 isoperibolic calorimeter. The net calorific value on a dry basis and for a predetermined moisture content was determined for constant pressure conditions according to SM EN ISO 18125:2017 [27]. There were three replicates for each sample.

A chemical analysis was carried out to establish the lignin, cellulose, and hemicellulose content of the samples. The tests were carried out on the mixtures of lignocellulosic material in the form of sawdust. The samples were assessed for moisture content (Moisture determination by drying method using an analytical moisture balance TAPPI T 264 cm-07-Preparation of wood for chemical analysis), extracted using an ethanol–toluene mixture (1:2) on Soxhlet-type equipment (TAPPI T204 cm-17 Extractive Solvents from Wood and Cellulose, ASTM D1107-21-Standard Test Method for Ethanol-Toluene Solubility of Wood), and finally subjected to the following chemical analyses:

1. Determination of lignin content by the Klason–Komarov method using a 72% H_2SO_4 solution (ISO/DIS 21.436 Paste-determination of lignin content—acid hydrolysis method) (L, %);
2. Detection of hemicellulose content by rapid acid hydrolysis method using 4% H_2SO_4 solution in one step at 121 °C for 1 h (HC, %); [9];

The Klason method or 72% H_2SO_4 acid hydrolytic method is the most widely used method for the determination of lignin by wood chemistry analysts, being probably the simplest and generally the most reliable, despite its limitations. The samples are hydrolyzed with 72% sulfuric acid, then with dilute sulfuric acid, to hydrolyze and solubilize the polysaccharides; the insoluble residue is dried and weighed as lignin.

Procedure: The sample undergoes grinding to pass through a sieve of at least 20 mesh and subsequent solvent extraction before analysis.

Approximately 200 mg of sample is weighed to the nearest 0.1 mg into a small vial or beaker. Add one milliliter of 72% H_2SO_4 (conveniently determined by specific gravity) for each 100 mg of sample. The mixture is placed in a water bath at 30 ± 0.5° and is stirred frequently to ensure complete solution. After exactly 1 h, dilute and transfer quantitatively to a 125 mL Erlenmeyer flask, using 28 mL of water for every 1 mL of acid. Secondary hydrolysis is in an autoclave at 120 °C for 1 h. The hot solution is filtered through a tared fritted glass crucible and the Klason lignin residue is washed with hot water to remove the acid. The crucibles containing the samples are then dried to a constant temperature of 105 °C and weighed to the nearest 0.1 mg. Lignin is expressed as a percentage of the original sample.

Determination of hemicellulose content: The hemicellulose content of all materials was determined by the rapid one-step acid hydrolysis method which gives results comparable to the values determined by the conventional NREL method. The rapid quantification of hemicelluloses used 0.3 ± 0.01 g biomass (absolute dry weight) that was hydrolyzed in 87 mL of 4% sulfuric acid at 121 °C for 1 h. After one-step acid hydrolysis of the samples, the solid residues were collected by filtration, dried in a 105 °C oven, and weighed to calculate the respective efficiency by difference hemicellulose content.

3. Results

3.1. Experimental Plan for Optimizing the Constitution of the Studied Blends and the Results Obtained

Pellets, depending on their use, are classified into two categories: pellets for commercial and residential applications and pellets for industrial use. Table 1 shows the main characteristics of interest to the pellet user for these two categories of pellets.

Table 2 presents the experimental plan for optimizing the constitution of the studied blends and the results obtained. Levels of variation in the biomass content of seabuckthorn (0–70%), of blackberry biomass content (0–30%), the remaining wheat straw (from 0 to 100%) are also presented. Mixtures were determined in mass % and lignin, cellulose and hemicellulose contents were normalized to 100% (L% + C% + HC% = 100%) without extractives. Table 2 also presents the results of chemical analysis of the samples.

3.2. Results Regarding the Net Calorific Value at Humidity of 10% ($q_{p,net}$,M = 10%) Depending on the Percentage of Raw Material Constituents (Seabuckthorn Biomass + Blackberry + Straw)

After processing the experimental data, a graphical representation was obtained that expresses the dependence of the calorific value of the pellets on the content of the constituents of the raw material mixtures.

Using the graphs in Figure 1, we can establish all the proportions of the biomass components studied that ensure an established calorific value. For example, if we use 20% blackberry biomass, then, to obtain pellets with a calorific value equal to 16.5 MJ/kg, the biomass content of seabuckthorn must be 62% and the straw content no more than 18%.

Table 2. Experimental plan used to optimize the composition of biomass mixtures of seabuckthorn (Seabuckthorn), blackberry (Blackberry), and straw.

Sample No.	Influencing Factors					Response Factors								
	Coded Coordinates		Natural Coordinates, %			$q_{p,net,d.}$	$Q_{p,net,M = 10\%}$	A	F	DU	BD, (kg/m^3)	L	Ce	HC
	x_1	x_2	X_1	X_2	Straw	MJ/kg			(w-%)				%	
1	−1	0	0	15	85	17.25	15.29	4.68	2.67	97.843	548.8	21.27	45.19	33.54
2	−1	1	0	30	70	17.39	15.41	4.15	2.24	97.485	547.6	22.10	45.43	32.47
3	1	1	70	30	0	18.41	16.76	1.21	0.2	97.497	597.2	32.25	44.98	22.77
4	−1	−1	0	0	100	17.14	15.18	5.20	3.11	94.664	567.6	20.44	44.95	34.61
5	0	1	35	30	35	18.14	16.09	2.68	1.22	92.428	560	27.18	45.21	27.62
6	0	0	35	15	50	18.01	15.97	3.21	1.66	98.555	616.8	26.35	44.96	28.69
7	1	0	70	15	15	18.81	16.65	1.74	0.63	99.064	610	31.43	44.73	23.84
8	0	−1	35	0	65	17.89	15.86	3.73	2.09	99.203	618.4	25.52	44.72	29.76
9	1	−1	70	0	30	18.65	16.54	2.26	0.46	98.097	612	30.60	44.49	24.91

Legend: x_1—biomass content from seabuckthorn; x_2—biomass content from blackberries, X_1, X_2 – are x_1 and x_2, in wt. %; Straw—remaining straw, in %, Mixtures were established in mass %; $q_{p,net,d}$—net calorific value in dry base; $q_{p,net,M}$ = 10%, net calorific value at 10% of sample humidity; A—ash content; F—the content of the fine fraction; BD—bulk density; DU—mechanical durability; L—lignin content; Ce—cellulose content; HC—the content of hemicellulose.

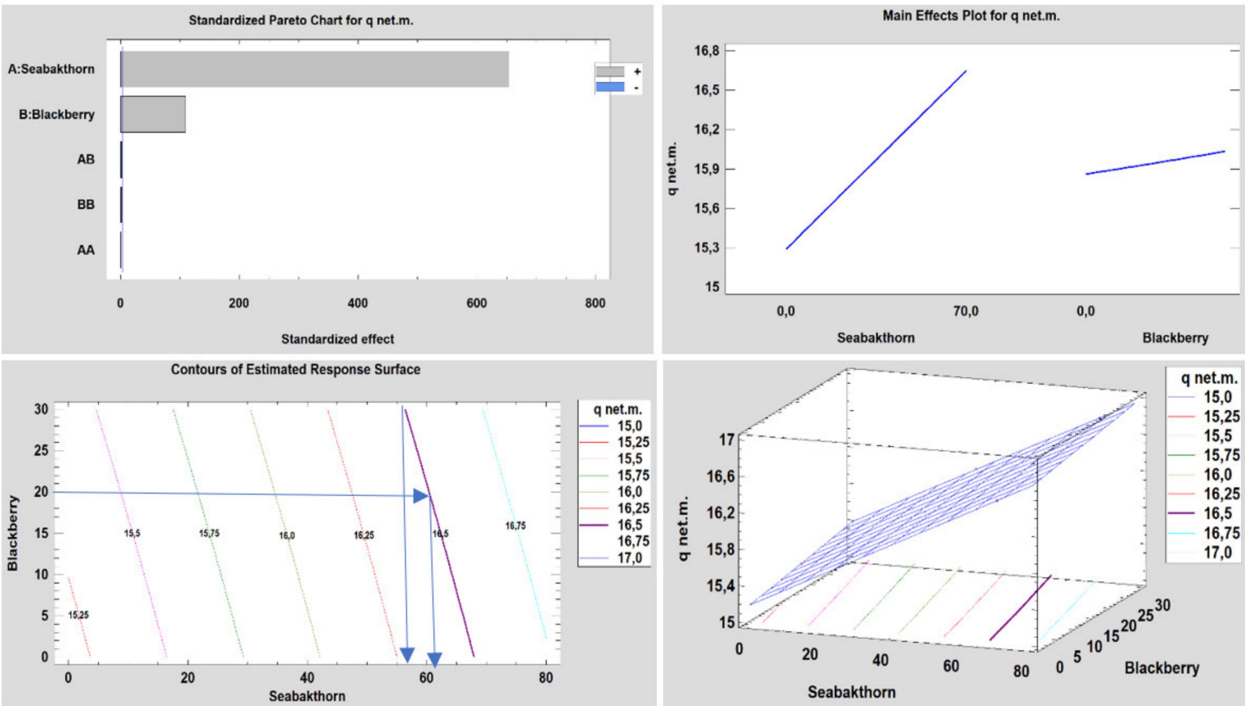

Figure 1. Graphical representation of the net calorific value at humidity of 10% ($q_{p,net,}$M = 10%) depending on the percentage of raw material constituents (seabuckthorn biomass + blackberry + straw).

3.3. Dependence of the Ash Content on the Percentage of the Raw Material Constituents

The second most important parameter, which limits the use of certain types of biomass as raw material in the production of densified solid biofuels, is the ash content. Figure 2 shows the amount of ash resulting from the burning of pellets produced from the mixtures studied.

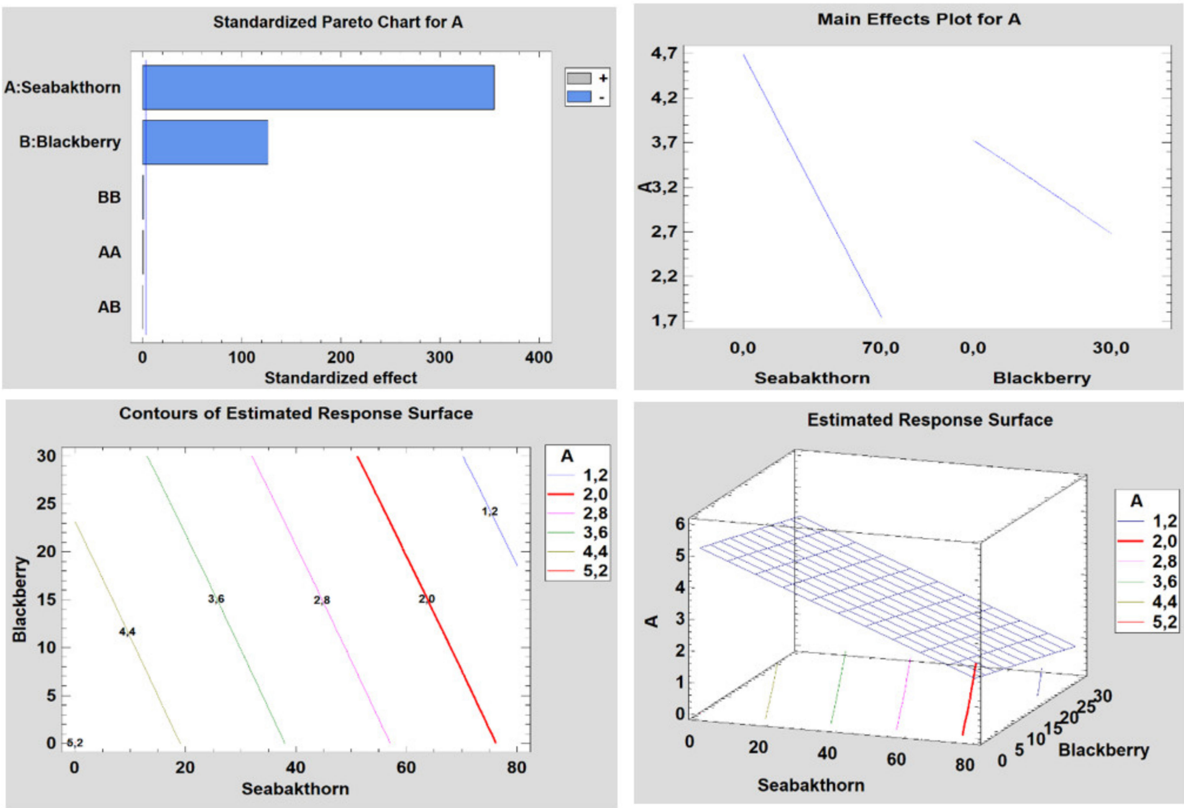

Figure 2. Graphical representation of the dependence of the ash content on the percentage of the raw material constituents (seabuckthorn biomass + blackberry + straw).

3.4. Dependence of the Content of Fine Fraction according to the Percentage of the Constituents of the Raw Material

The fine fraction content in the total mass of the pellets is limited by the ISO 17225-2 standard [11] and, as a rule, does not exceed 1% of the total mass of the pellets.

To characterize the calorific value of the pellets produced from the studied biomass mixtures, the net calorific value measured at constant pressure was used, which reflects more adequately the amount of heat released under real combustion conditions.

The results regarding the dependence of the content of fine fraction according to the percentage of the constituents of the raw material are presented in Figure 3.

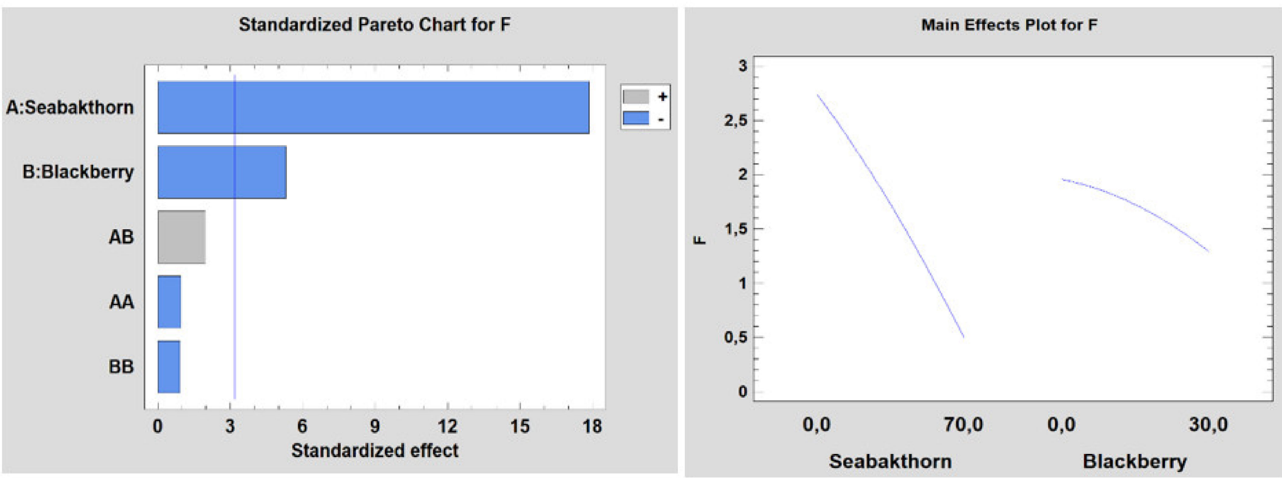

Figure 3. *Cont.*

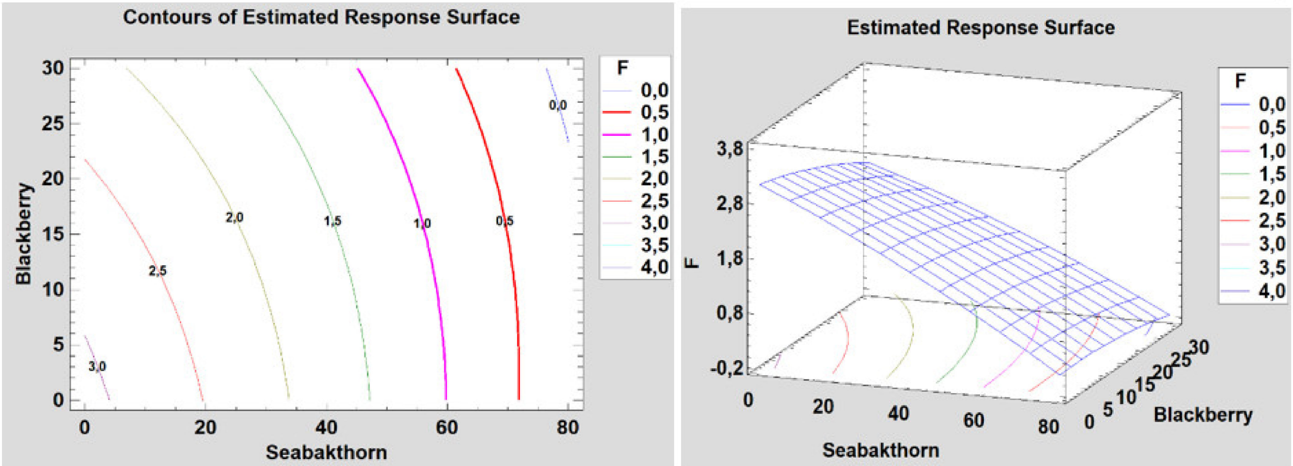

Figure 3. Graphic representation of the dependence of the content of fine fraction according to the percentage of the constituents of the raw material (seabuckthorn biomass + blackberry + straw).

3.5. Dependence of the Bulk Density of the Pellets according to the Percentage of the Constituents of the Raw Material

Our results, presented in Figure 4, show that seabuckthorn biomass increases the bulk density of the pellets, while the addition of blackberry plant residues, conversely, decreases it (see Main Effect Plots for BD, Figure 4). The lowest pellet bulk density was reported for pellets manufactured with 70% straw + 30% blackberry biomass. This value is even lower than for pellets made 100% from straw (see Table 2).

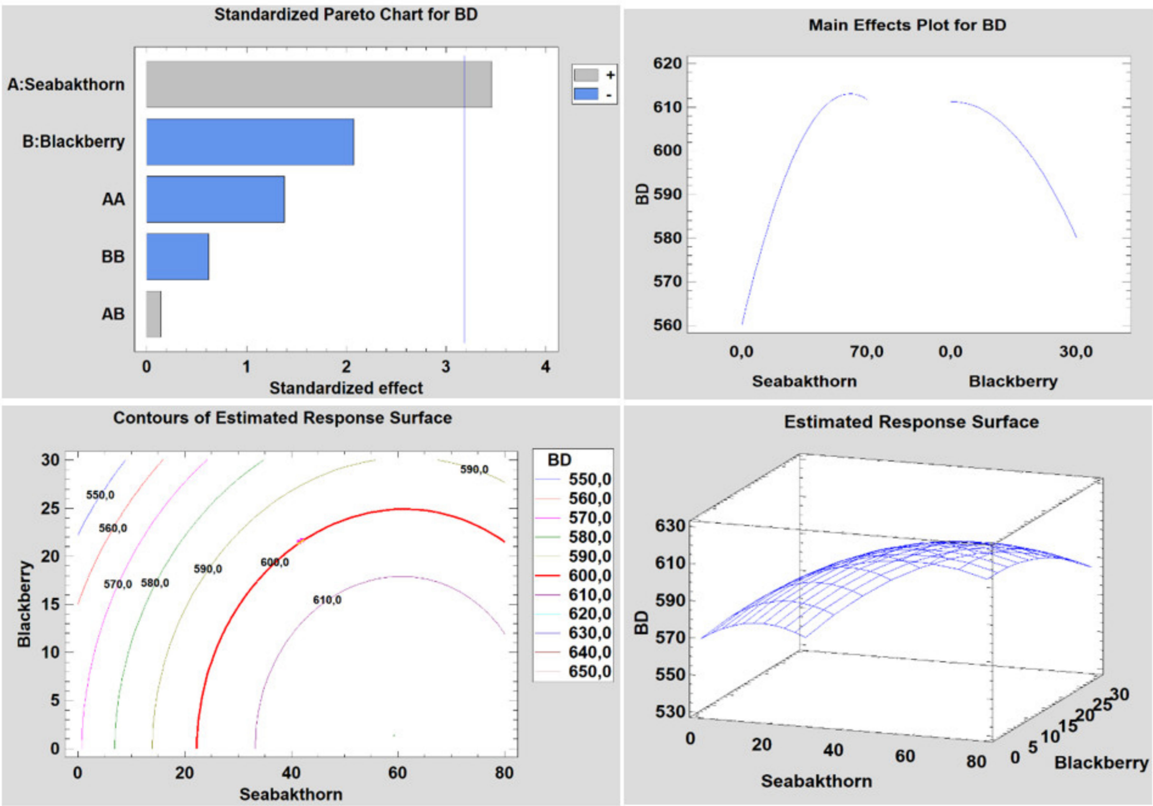

Figure 4. Graphical representation of the dependence of the bulk density of the pellets according to the percentage of the constituents of the raw material (seabuckthorn biomass + blackberry + straw).

3.6. Dependence of the Mechanical Durability of the Pellets according to the Percentage of the Constituents of the Raw Material

As a result of the statistical processing of the experimental data from Table 2, regression Equation (4) was obtained, which is visualized in Figure 5.

$$DU = 95.9261 + 0.0059 \cdot X_1 + 0.2631 \cdot X_2 + 0.0006 \cdot X_{12} - 0.0016 \cdot X_1 \cdot X_2 - 0.0086 \cdot X_{22} \quad (4)$$

These results are further discussed in Section 4.6.

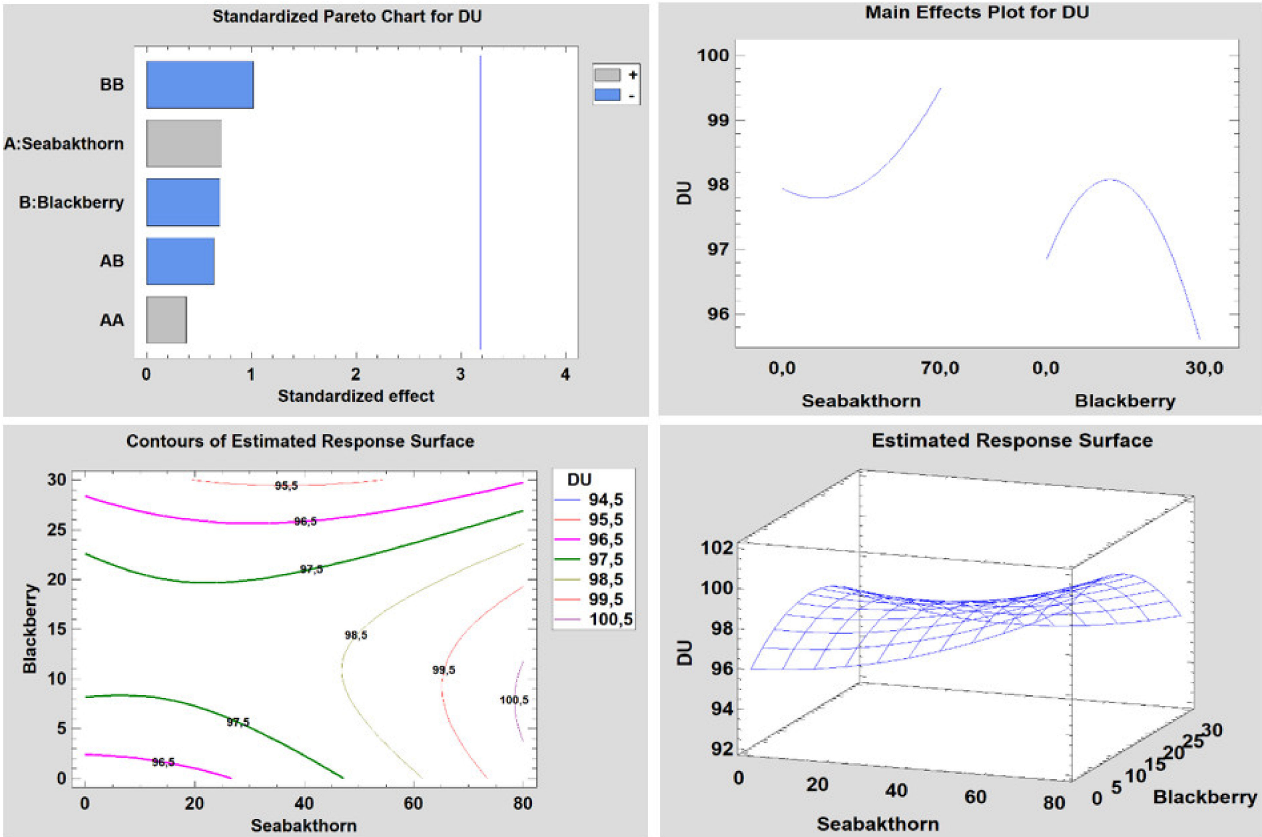

Figure 5. Graphical representation of the dependence of the mechanical durability of the pellets according to the percentage of the constituents of the raw material (seabuckthorn biomass + blackberry + straw).

4. Discussions

4.1. Use of Seabuckthorn, Blackberry, and Wheat Straw Plant Residues as Raw Material for Pellet Production

In the Republic of Moldova and Romania, the first industrial plantations of woody fruit bushes were established in the last two decades [28–30] and have developed rapidly due to a number of advantages, including: profitability of the business, insignificant initial investment, short payback period, fairly rapid production of the finished product, market demand, high nutritional and taste qualities, and wide range of use [29]. Among the fruit bushes which are increasingly growing rapidly in the Republic of Moldova and Romania, especially in the areas adjacent to the Prut River, are the blackberry and seabuckthorn.

The profitability of growing blackberry and seabuckthorn can also be increased by exploiting the residues generated by these crops by using them as feedstock for the production of densified solid biofuels.

Research carried out in the Solid Biofuels Laboratory of the Agrarian State University of Moldova shows that one hectare of seabuckthorn can generate about 2500 kg of plant residues with an energy potential of (37.61 ± 6.07) GJ [31]. A significant amount of biomass is also generated by blackberry and seabuckthorn, biomass that can be used as a feedstock for the production of densified solid biofuels, especially mixed with woody biomass [32].

One of the ways to improve the quality of pellets produced from agricultural residues mentioned above is to form blends that would ensure the requirements set out in the standards for pellet quality, e.g., the internationally accepted EN Plus 3 standard. This can be achieved by optimising the constitution of the raw material mixtures according to the requirements of the reference standards.

According to the results presented in Table 2, the calorific value of solid biofuels depends on the chemical composition of the lignocellulosic materials used to produce them. Among the main chemical components of wood, lignin and extractives have a major influence on the calorific value. As regards the calorific value of the chemical components of wood, the following values are mentioned: pure lignin (22.2 MJ/kg–28.5 MJ/kg) much higher than cellulose (16.5–17.3 MJ/kg) or hemicelluloses (13.9 MJ/kg). The highest values are for resins, which are at the level of 39.5 MJ/kg. In this context, it is important to know the chemical composition of wood waste in order to estimate the energy value of these solid biofuels.

From the analysis of the experimental data presented in Table 2, the following are found:

- Lignin percentages vary in a relatively wide range from 20.44% (mixture 4) to 32.25% (sample 7), increasing with the biomass content of seabuckthorn.
- The hemicellulose content of the wood and non-wood waste analyzed ranged from 22.77% (mixture 3) to 34.61% (mixture 4) being higher the higher the biomass content of wheat straw.
- The cellulose content varies within very narrow limits between biomass mixtures of different origins.

4.2. The Influence of the Composition of the Biomass Mixture on the Calorific Value of the Pellets

The main requirement of most interest to users of solid biofuels is the energy content measured in the heat of combustion stored in a unit of fuel used. The energy content is measured with the calorific value representing the number of units of heat released by the complete combustion of one unit of mass of fuel under the conditions prescribed by the standards. Knowing the calorific value is the initial step in establishing the composition of raw material mixtures used in the production of densified solid biofuels.

From the Parreto diagram, presented in Figure 1, it results that, within the limits established for the content of the components of the mixtures studied, seabuckthorn biomass has a much more significant effect than blackberry biomass. It can also be seen that the interaction between the two influencing factors is not significant.

The graph of the main effects shows that the biomass content of seabuckthorn affects the net calorific value much more sharply, having a sudden ascending character, while the content of blackberry biomass, within the studied limits, has a slow ascending character.

From the contour diagrams of the response surfaces, it can be established the composition of the biomass mixtures that ensure a calorific value equal to or greater than 16.5 MJ/kg—value required by ENPlus standards for both pellets for residential applications and for those classified for industrial use.

Thus, in the case of using only seabuckthorn biomass mixed with straw, the straw content may not exceed 32%. The blackberry biomass content can replace a certain part of the seabuckthorn biomass, but the effect of this substitution is not very accentuated. For example, the mixture of 30% blackberry biomass + 56% seabuckthorn biomass + 14% straw has the same effect as when we use 68% seabuckthorn and 32% straw.

4.3. Ash Content Resulting from the Burning of Pellets Produced from the Studied Biomass Mixtures

Analyzing the graphs of the main effects and the contours of the response surfaces (Figure 2), it is found that the seabuckthorn biomass strongly influences the ash content downwards. The same downward trend is followed in the case of blackberry biomass, except that the influence is less significant. As in the case of calorific value, the interaction between these two influencing factors (seabuckthorn biomass content and blackberry biomass content) is not significant.

For the production of pellets classified for residential applications of class En-B, the mixtures located to the right of line 2.0 are recommended, and for pellets of class ENplus A2, the mixtures located to the right of line 1.2.

For the production of pellets classified for industrial use class I3, mixtures located to the right of the line corresponding to the ash content of 3% are recommended, and for those of class I2, mixtures located to the right of the line corresponding to the ash content of 1.5% are recommended.

4.4. Influence of the Composition of the Biomass Mixture on the Fine Fraction Content of the Pellets

Fine fractions are particles of organic or inorganic origin with a size less than or equal to 3.15 mm detached from the pellets themselves or which have not been incorporated into the base fuel. Fine fractions can occur both in the manufacturing process of densified biofuels and during handling and transportation.

The analysis of the experimental data shows that, with the increase of the content of seabuckthorn and blackberry biomass, the content of fine fraction decreases, bearing a sudden descending character in the case of seabuckthorn biomass and slower descending for blackberry biomass (see Figure 3).

It can be deduced that, in order to ensure the requirements of the ISO 17225-2 standard regarding the content of fine fractions in the pellet mass, it is necessary to limit the content of straw which can be up to 40% by volume depending on the percentage of seabuckthorn and blackberry biomass. The higher the straw content in the mixture, the more organic and inorganic particles smaller than 3.15 mm are present. The content of the constituents for the formation of the biomass mixtures of white seabuckthorn + blackberry + straw, which ensure a fine fraction content of less than 1%, can be established using the contours of the response surfaces in Figure 3 (the area to the right of the line 1.0).

4.5. Influence of Biomass Mixture Composition on Pellet Bulk Density

According to the ISO 17828 standard, the bulk density of pellets is a parameter used to estimate the quality of pellets based on volume, which together with the net calorific value determines the energy density.

It is known that straw pellets have a low bulk density due to the low percentage of lignin, they have a high content of ash and fine fraction [33,34], which is why several options for improving these indicators are being sought. The use of biomass mixtures, which have a higher lignin content, is one of these options.

The too large volume of the pellets makes it difficult to transport the pellets over long distances, requires larger spaces for storage. A smaller volume, i.e., higher bulk density, on the one hand, represents a higher energy per unit volume of fuel, and, on the other hand, worsens the combustion process of thermal plants. For these reasons, the ENPlus norms regulate both the lower and the upper value of the bulk density for pellets, limiting it to the range of 600–750 kg/m^3.

The results presented in Figure 4 emphasize that, compared to blackberry plant residues, seabuckthorn biomass increases the bulk density of pellets (see Main Effects Plots for BD, Figure 4), whereas blackberry residues decrease it. The lowest pellet bulk density was reported for pellets made from 70% straw plus 30% blackberry biomass. The value is even lower than that for pellets made from 100% straw (see Table 2).

Based on the findings from the experiments on the influence of the percentage of the constituents of the raw material mixtures studied in this paper, it can be concluded that blackberry residues reduce the bulk density of straw-based pellets and are not recommended to be used as an additive in mixtures with straw. Moreover, following the graphs of the response surface accounts in Figure 4, it is highlighted that the addition of at least

24% of seabuckthorn biomass ensures a pellet density of at least 600 kg/m3, i.e., it meets the requirements of the EN Plus norms.

4.6. Influence of Biomass Mixture Composition on Mechanical Durability of Pellets

Mechanical durability is one of the essential properties regulated by the EN Plus norms and is a measure of pellet friability. Durability is very important for handling, storage and fueling of pellet plants [35]. Durability is influenced by a number of factors such as moisture content, particle size, technological densification factors, and, last but not least, the chemical composition of the raw material [36,37].

Analyzing the results of the dependence of the durability of the pellets according to the percentage of the constituents of the studied mixtures (Figure 5), it can be asserted that the seabuckthorn biomass positively influences the durability of the pellets with a slow upward trend, while the addition of blackberry biomass initially increases durability after decreasing it quite suddenly.

From the graph of the contours of the response surfaces (Figure 5) it can be concluded that, in order to ensure a mechanical durability of the pellets of at least 97.5%, produced from the biomass mixtures studied in this work, we need to add at least 30% seabuckthorn biomass and at most 20% blackberry biomass, and the rest can be wheat straw biomass.

5. Conclusions

This study was developed to expand the sources of plant biomass spread in the areas adjacent to the Prut River in Romania and the Republic of Moldova for the production of densified solid biofuels in the form of pellets with characteristics conforming to ENPlus 3 requirements. Considering the results obtained in this study and correlated with those from the literature, it was demonstrated that the formation of raw material mixtures for the production of pellets based on the plant biomass generated from the cultivation of the fruiting bushes of seabuckthorn and blackberry allows the inclusion, as a filler, of wheat straw. This process permits the use of lower quality biomass, biomass present in fairly large quantities in Romania and the Republic of Moldova, in the supply chains to produce pellets with quality characteristics conforming to EN Plus 3 requirements.

The chemical composition of wood waste varies from mixture to mixture, depending on the percentage of biomass of different origins found in this waste. Thus, the mixtures with a high content of seabuckthorn biomass led not only to the biofuels with the highest lignin content, but also to those with the highest calorific value (mixtures 3, 7, and 9 from Table 2). In all cases where the percentage of wheat straw biomass is high, considerably higher values are recorded for hemicelluloses, the component with the lowest calorific value among the structural components of the biomass, and implicitly the determined calorific values were lower.

It has been shown that the most limiting characteristics of the amount of straw added to feedstock mixtures are the calorific value and ash content of the pellets. Namely, these characteristics limit the use of straw to 25% in biomass mixtures based on seabuckthorn. This percentage of straw can be increased up to 35% if at least 10% of blackberry biomass is added to the mixture, but the amount of blackberry biomass must not exceed 20%, as in this case the requirement for mechanical durability is not met of pellets.

For producers of solid biofuels in the form of pellets, the use of biomass mixtures resulting from the pruning of fruit bushes mixed with straw with the following constitution can be recommended:

1. At least 75% seabuckthorn biomass, the rest wheat straw;
2. At least 70% seabuckthorn biomass + (10–20)% blackberry biomass, the rest straw.
3. At most 20% blackberry biomass, the rest seabuckthorn biomass.

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