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CALORIFIC VALUE OF PELLETS PRODUCED FROM RAW MATERIAL COLLECTED FROM BOTH SIDES OF THE RIVER PRUT

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Abstract. The production of pellets has recently experienced a sudden upward trend worldwide, including the Republic of Moldova and Romania, especially due to the energy crisis caused by the war in Ukraine and rapid depletion of fossil energy sources. The widespread use of pellets has several reasons: it is an eco-friendly fuel, it allows the automation of the combustion process, and it can be easily produced in any region that has enough raw materials. The calorific value of pellets is the main characteristic feature that determines their price and is used in combustion engineering to find out the thermal efficiency of combustion plants. This paper synthesizes the results regarding the calorific value of the pellets produced from different types of plant biomass specific to the Republic of Moldova and the counties adjacent to the river Prut in Romania. The research has been carried out within the Solid Biofuels Laboratory, SAUM using standard methods of testing densified solid biofuels. The experimental results obtained in this study showed that the pellets produced from arboriculture residues, residues generated from vine pruning, table varieties, as well as those produced from sunflower seed husk have a calorific value equal to or greater than 16.5 MJ/kg, i.e., they meet ENPlus 3 requirements.

Keywords: wood pellet, calorific value, biomass, agricultural residues, energy crops, biomass conditioning, combustion.

Rezumat. Producerea de peleți în lume, inclusiv în Republica Moldova și în România cunoaște un trend brusc ascendent în ultimii ani, în special în condițiile crizei energetice cauzate de războiul din Ucraina și epuizarea galopantă a surselor fosile de energie. Folosirea pe larg al peletilor are mai multe motivații dintre care faptul că este un combustibil non ofensiv

mediului, permite automatizarea procesului de combustie, este accesibil pentru producere în orice zonă unde există suficientă materie primă. Valoarea calorifică a peleișilor este principala caracteristică care determină prețurile peleișilor și care este folosită în ingineria arderii pentru stabilirea randamentului termic al instalațiilor de combustie. Această lucrare prezintă o sinteză a rezultatelor referitoare la valoarea calorifică a peleișilor produși din diferite tipuri de biomasă vegetală specifică Republicii Moldova și județelor adiacente râului Prut din România. Cercetările au fost efectuate în cadrul Laboratorului de Biocombustibili Solizi, UASM cu folosirea metodelor standard de testare a biocombustibililor solizi densificați. Rezultatele experimentale obținute în acest studiu au arătat că peleișii produse din reziduuri de arboricultură, reziduuri generate de tăierea viței-de-vie, soiuri de masă, precum și cele produse din coajă de semințe de floarea soarelui au o putere calorică egală sau mai mare de 16,5 MJ/kg, adică îndeplinesc cerințele ENPlus 3.

Cuvinte cheie: *peleiși de lemn, valoare calorifică, biomasă, reziduuri agricole, culturi energetice, condiționare biomasă, peletizare, combustie.*

1. Introduction

This paper presents the qualitative study on determining the calorific value of the pellets produced from different types of plant biomass produced from agricultural crops and energy crop species that have achieved a more pronounced spread in agricultural households located on both banks of the river Prut, both in the Republic of Moldova and Romania.

Pellets are solid biofuels produced from plant biomass with or without additives, dehydrated and compressed to at least twice the energy density of the biomass in the chopped form with a random length of 5-40 mm and a diameter of up to 25 mm with irregular ends [1].

The demand for biomass energy, including in the form of pellets, is experiencing a rapid rise especially due to the energy crisis and increased prices of fossil fuels, mainly gas and coal. The increased consumption of pellets has led to the diversification of indigenous raw material sources recording characteristics meeting the international standard requirements. As the result, biomass from agricultural residues, wood co-products and energy crops, along with their combination, represents the most important source of raw materials used in the production of pellets in the areas adjacent to the river Prut both in the Republic of Moldova and Romania.

Qualitative assessment of pellets produced from the biomass specific to certain regions, correlated with the search for solutions for the efficient use of local energy resources, is crucial nowadays, thus contributing to the continuous development of the densified solid biofuels production with characteristics meeting the requirements of international standards.

The use of indigenous plant biomass as a raw material for pellets' production contributes to reduce the dependence of the energy sector on fossil fuels, concomitantly representing a stimulus for creating employment opportunities in rural areas [2-5].

Since the production of pellets consumes more energy than the production of split wood, wood chips or straw bales, the real benefits of pellets can be obtained when their quality characteristics correlate with the requirements of the international standards stated by the standard ISO 17225- 2 [1].

The quality of pellets depends on a number of factors that are grouped into two categories: the quality of raw material and the conditioning and pelletizing variables [3, 6].

The quality of raw material, used in the production of pellets, depends on the biomass origin, the way it is dried, the content of impurities, the collection period, the storage period, the particle sizes, etc. [6-8].

A series of procedures are used to ensure the quality of raw material, including the formation of mixtures from different biomass types with complementary characteristics, the use of different organic additives, the thermochemical treatment of biomass and finished product, etc.

Conditioning of raw material and palletization itself involve ensuring all the requirements related to the conditioning of the raw material before it is processed (moisture content, purity and biomass granulation) and the technological palletization methods (compression pressure, temperature of granule formation, roller speed), constructive parameters of the pelletizing matrix (diameter and length of the channels, the gap between the rollers and the matrix), etc.

Therefore, the purpose of this research is to fill the information gap regarding the energy potential of pellets produced from biomass specific to the regions on both banks of the river Prut by presenting a clear understanding of their calorific value.

In order to achieve the proposed goal a series of pellets, produced from different biomass types have been analysed from the point of view of their energy potential. The studies have been carried out using standard methods, applied in the field of qualitative assessment of densified solid biofuels.

2. Materials and Methods

Sampling. The biomass has been collected from various agricultural farms in the Republic of Moldova and from the counties of Iasi, Botosani, Vaslui and Galati in Romania. There have been used 56 samples of pellets produced from the biomass of distinct species of agricultural residues and energy crops. The biomass has been collected in different harvest periods and conditioned directly in the field or under the drying room conditions of the Solid Biofuels Laboratory of the State Agrarian University of Moldova. The conditioning directly in the field has been carried out only for some types of arboreal species residues by their natural drying at the edge of the field during summer and some biomass types generated from energy crops and coarse woody debris by shredding directly in the field using Murena portable shredder (see figure 1).



Figure 1. Coarse shredding of *Miscanthus* biomass using Murena shredder attached to the MT 8E2 tractor.

Energy crop samples have been collected manually (see figure 2).



Figure 2. Miscanthus sample collection.

The experimental samples have been collected in accordance with the requirements of standard ISO 18135 [9], and the preparation of the samples has been carried out in accordance with standard ISO 14780 [10]. The pellets have been produced at the mini pelletizing line within the SAUM Solid Biofuels Laboratory.

Establishing the calorific value of pellets. The gross calorific value has been measured at constant volume using the IKA C6000 isoperibolic calorimeter. Measurements and calculations have been performed according to the standard EN ISO 18125 [11] (see figure 3). Five replicates have been used during this experiment, based on which the standard deviation has been determined.



Figure 3. Determining the gross calorific value by IKA C6000 isoperibolic calorimeter in the Solid Biofuels Laboratory, SAUM.

Pellet samples, before being tested, had been crushed in a Retsch SM 100 hammer mill. Sample weighing has been done using the analytical scales AS 220/C/2, RADVAG (see Figure 4). All samples used to determine the calorific value have been dehydrated by drying in the German Memmert UNBU oven. The oven is equipped with a control system and stable temperature maintenance within the limits established by the standard and with a ventilation system of the precinct depending on the granulation of the samples used for testing. The net calorific value has been determined for dehydrated pellets, i.e., on a dry basis and for the pellets with a moisture content equal to 10% using the following formulas:

$$q_{p,net,d} = q_{v,gr,d} - 212,2 \times w(H)_d - 0,8 \times [w(O)_d + w(N)_d], \quad (1)$$

$$q_{p,net,m} = q_{p,net,d} \times (1 - 0,01M) - 24,43 \times M, \quad (2)$$

where:

$q_{(p,net,d)}$ is net calorific value at constant pressure of the dry (moisture-free) fuel, J/g.

$q_{p,net,m}$ is net calorific value at constant pressure of the biofuel with moisture content M , J/g.

$q_{v,gr,d}$ is gross calorific value at constant volume of the biofuel of the dry (moisture-free) fuel (dry basis, in the dry matter), J/g.

$w(H)_d$; $w(O)_d$; $w(N)_d$ are, respectively, the hydrogen, oxygen and nitrogen content, in percentage by mass of the moisture-free biofuel, %.

3. Essential information regarding the calorific value of pellets and its role in the qualitative assessment of pellets for residential and industrial use

The main qualitative characteristic of the pellets that mostly interests the beneficiaries is the calorific value, i.e., the burning power. Historically, the calorific value is used in thermal and combustion engineering to calculate thermal efficiency of power plants and represents the amount of energy released as heat when a unit of mass of fuel burns completely and perfectly and the flue gases cool down to 25 °C. Thus, the higher the calorific value of the pellets, the more energy we get per unit of mass. This is the main reason why the calorific value determines the price of pellets.



Figure 4. Pellet crushing and sample dosing by weighing.

The calorific value of pellets is generally expressed using several values. Thus, quality certificates, as a rule, include the gross and net calorific values on a dry basis and at the reception moisture level. Studies often specify the net calorific value at a moisture content equal to 10%, the maximum value recommended by the ENPlus 3 standards.

Gross calorific value or higher thermal value, also includes the heat obtained from the transformation phases of condensation and solidification, being determined by returning all combustion products to the reference temperature (25 °C). In other words, when the quality of pellets is assessed by means of the gross calorific value, it is also taken into account the heat released by the water vapour produced in the combustion process and transformed into a liquid.

The gross calorific value for both solid and liquid fuels is measured at constant volume, and it is measured at constant pressure for gaseous fuels.

The gross calorific value of pellets at constant volume represents the absolute value of the specific combustion energy, in joules, for a unit of mass of the pellets burned in an oxygen environment in a calorimeter bomb under special conditions. Combustion products usually consist of solid ash, gaseous oxygen, nitrogen, carbon dioxide, sulfur dioxide, liquid water (in balance with its vapor) saturated with carbon dioxide under bomb reaction conditions, all at reference temperature (25 °C) [9].

The net calorific value is determined by subtracting the amount of heat produced as a result of vaporization phase transformations from the gross calorific value. In this case, the energy consumed for water vaporization is not considered as heat-producing energy. Thus, the net calorific value assumes that the vaporization heat is latent and is not recovered in the pellet combustion process.

The net calorific value can be calculated for constant volume or pressure conditions. Standard ISO 18125 recommends using the net calorific value as operative heat for constant pressure conditions, i.e. atmospheric pressure.

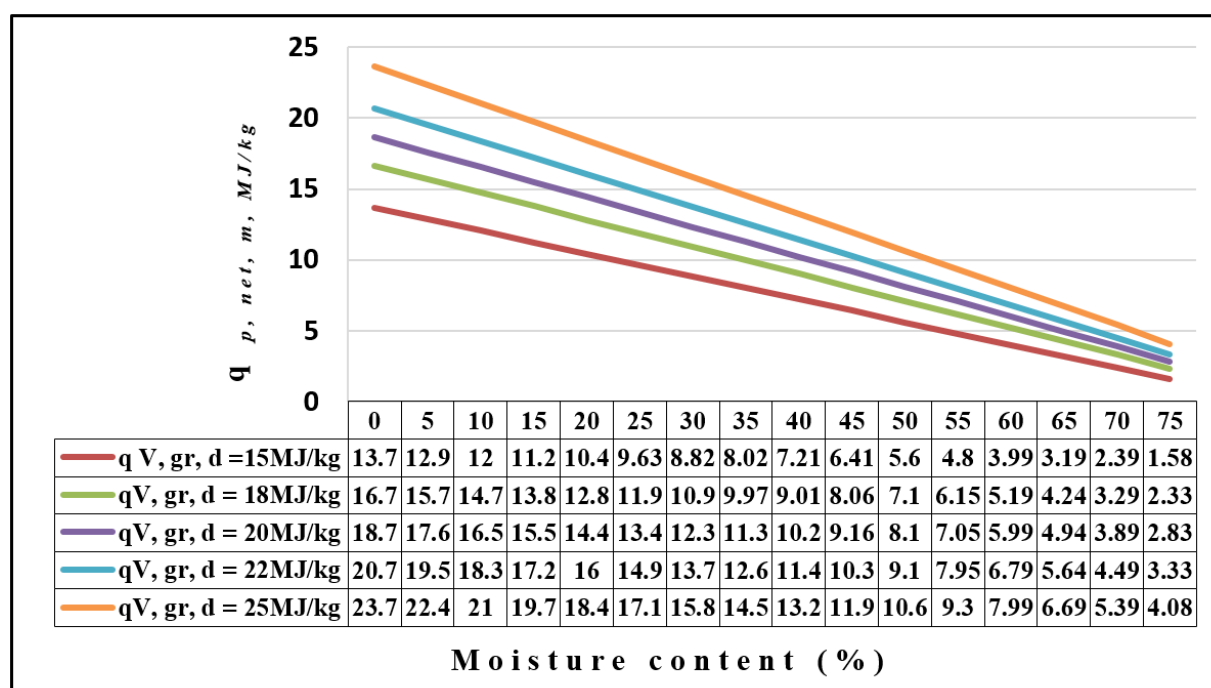


Figure 5. Dependence of net calorific values of pellets on the moisture content. Data are presented for the following conditions: $H = 6.2\%$, $N = 0.5\%$, $S = 0.05\%$, $O = 42\%$.

This value is calculated by subtracting the losses of latent vaporization heat associated with the pellet moisture and the water content formed during combustion from the gross calorific value (see formulas 1 and 2 in section 2).

The net calorific value at reception represents a specific feature meeting the ENPlus requirements, as it expresses the real amount of heat obtained from the complete and perfect combustion of a pellet unit without the evidence of vaporization heat, i.e., the amount of heat obtained from the combustion of pellets in thermal power plants used nowadays for residential and industrial purposes. According to standard ISO 17225-2 [2], the net calorific value at reception of pellets for all ENPlus property classes both for residential and industrial uses should not be less than 16.5 MJ/kg.

It should be noted that the net calorific value is greatly influenced by the moisture content of pellets. This can be seen in Figure 5, which shows the dynamics of the net calorific value depending on the moisture content for pellets with different gross calorific values on a dry basis. It is also mentioned that the percentages in which the moisture content is expressed refer to the mass participation. Thus, the pellets include 0.1 kg of water per kg of fuel at a moisture content of 10%.

The second factor that greatly influences the calorific value of pellets is the quality of the raw material. This aspect is studied in the following chapter.

4. Results and Discussion

As mentioned above, the calorific value of pellets is greatly influenced by the raw material from which they are made. Organic substances such as cellulose, hemicellulose and lignin vary quite significantly depending on the type of plant biomass and on the plant parts from which they are taken [5, 10].

Table 1 presents the net calorific value of the pellets produced from various types of plant biomass collected from different regions in the Republic of Moldova and the counties of Iasi, Botosani, Vaslui and Galait, Romania. The calorific value is provided for a moisture content equal to 10%. The data represent the average \pm standard deviation determined for 5 parallel measurements carried out in the same laboratory by the same operator for the same analysed samples.

It is known that agricultural residues represent the most accessible source for pellet production both in the Republic of Moldova and Romania [3, 13 - 17]. However, not all agricultural residues can be used directly as raw material, because some of their characteristics do not meet the requirements of the international standards, especially the calorific value.

The results presented in this paper show that the pellets produced from biomass derived from herbaceous agricultural residues have a net calorific value at 10% moisture lower than 16.5 MJ/kg (except those produced from sunflower seed husk). At the same time, tree biomass pellets have a much higher calorific value, varying within the limits of (16.76 ± 0.22) MJ/kg for the pellets produced from quince residues and 18.40 ± 0.18 for the ones produced from cherry residues. Pellets produced from vine residues, sampled table varieties, both in the Republic of Moldova and Romania also have recorded a calorific value within the limits stipulated by the ENPlus3 requirements. The burning power of pellets produced from technical varieties of vine residues, is somewhat lower; their calorific value is close to the one recommended by the ENPlus 3 standards.

The residues generated from sea buckthorn bushes have good prospects to be used as a raw material for the production of pellets; their calorific value is (16.62 ± 0.15) MJ/kg. The pellets produced from the residues of blackberry and blackcurrant bushes marked values lower than 16.5 MJ/kg, so this biomass can only be used in combination with other types of biomass with higher calorific values, for example residues of fruit bushes.

An important source of raw material for the production of pellets is the one generated by energy crops. A vast variety of energy crops requires more thorough research regarding the possibility of using the biomass resulting from their cultivation as a raw material for the production of densified solid biofuels.

This study focuses on determining the calorific value of pellets produced from plant biomass generated from several species of energy crops with a real perspective of use as raw material under the conditions of the Republic of Moldova and the counties in Romania adjacent to the river Prut.

The analysis of values of the measured parameters of pellets produced from energy crops biomass, presented in Table 1, made it possible to determine the difference in the net calorific value at 10% moisture of 1.84 MJ/kg between the pellets with the highest calorific value (produced from energy willow with $q_{p, net, m=10\%} = 17.45 \pm 0.17$ MJ/kg) and those with the lowest calorific value (produced from the reed sampled from the Danube delta with $q_{p, net, m=10\%} = 15.61 \pm 0.23$ MJ/kg).

The results presented above show that the energy willow biomass can be recommended to be used as a raw material in the production of solid densified biofuels from the point of view of the energy potential.

Table 1

Calorific value of pellets produced from biomass collected in the regions adjacent to the river Prut

Raw material used	Biomass type	$q_{v, gr, d}$	$q_{p, net, d}$	$q_{p, net, m=10\%}$
		MJ/kg		
Sunflower seed husk	Seed husk	20.24 ± 0.19	18.91 ± 0.19	16.78 ± 0.17
Winter and spring wheat	Straw	18.48 ± 0.18	17.15 ± 0.18	15.19 ± 0.16
Winter and spring barley	Straw	18.47 ± 0.22	17.14 ± 0.22	15.18 ± 0.21
Oats	Straw	18.31 ± 0.17	17.04 ± 0.17	15.09 ± 0.16
Corn stalks	Stalks	17.92 ± 0.22	16.72 ± 0.21	14.80 ± 0.19
Sunflower stalks and leaves	Stalks and leaves	16.59 ± 0.31	15.47 ± 0.31	13.68 ± 0.28
Average		18.34	17.07	15.12
Apricots	Cuttings	20.81 ± 0.24	19.50 ± 0.24	17.31 ± 0.21
Sweet cherries		22.06 ± 0.19	20.71 ± 0.19	18.40 ± 0.18
Quinces		20.22 ± 0.24	18.89 ± 0.24	16.76 ± 0.22
Apples		20.26 ± 0.33	18.94 ± 0.33	16.80 ± 0.31
Pears		20.72 ± 0.21	19.39 ± 0.21	17.21 ± 0.20
Peaches and nectarines		21.40 ± 0.19	20.07 ± 0.19	17.82 ± 0.18
Plums		21.40 ± 0.18	20.08 ± 0.19	17.82 ± 0.18
Cherries		20.81 ± 0.19	19.46 ± 0.19	17.27 ± 0.18
Average		20.96	19.63	17.42
Alb de Suruceni	Cuttings	20.19 ± 0.22	18.84 ± 0.22	16.71 ± 0.21
Apiren roz		20.19 ± 0.21	18.84 ± 0.21	16.71 ± 0.20

Continuation Table 1

Cardinal		20.44 ± 0.24	19.09 ± 0.24	16.94 ± 0.22
Chismis moldovenesc		20.13 ± 0.20	18.78 ± 0.20	16.44 ± 0.19
Codreanca (Blac Magic)		20.39 ± 0.26	19.04 ± 0.26	16.89 ± 0.24
Italia		20.22 ± 0.23	18.87 ± 0.23	16.74 ± 0.22
Moldova		20.29 ± 0.24	18.94 ± 0.24	16.80 ± 0.23
Muscat de Hamburg		20.19 ± 0.22	18.84 ± 0.22	16.71 ± 0.21
Muscat timpuriu		20.21 ± 0.19	18.86 ± 0.19	16.73 ± 0.19
Prezentabil		20.30 ± 0.28	18.95 ± 0.28	16.81 ± 0.26
Average		20.25	18.90	16.75
Chasselas Baneasa		19.99 ± 0.14	18.64 ± 0.14	16.53 ± 0.13
Coarna alba		20.12 ± 0.13	18.77 ± 0.13	16.65 ± 0.11
Coarna neagra		20.00 ± 0.14	18.65 ± 0.14	16.54 ± 0.14
Gelu		20.00 ± 0.16	18.65 ± 0.16	16.54 ± 0.15
Greaca	Cuttings	19.99 ± 0.15	18.64 ± 0.15	16.53 ± 0.14
Otilia		19.99 ± 0.14	18.64 ± 0.14	16.53 ± 0.12
Roz Romanesc		20.10 ± 0.16	18.75 ± 0.16	16.63 ± 0.15
Select		19.99 ± 0.14	18.64 ± 0.14	16.53 ± 0.14
Victoria		20.00 ± 0.15	18.65 ± 0.15	16.54 ± 0.12
Average		19.14	17.90	15.87
Aligote		19.66 ± 0.14	18.31 ± 0.14	16.24 ± 0.13
Cabernet		20.00 ± 0.16	18.65 ± 0.16	16.54 ± 0.15
Chardonnay		19.87 ± 0.14	18.52 ± 0.14	16.43 ± 0.13
Feteasca alba		19.72 ± 0.21	18.38 ± 0.21	16.29 ± 0.19
Izabela		19.40 ± 0.14	18.05 ± 0.14	16.00 ± 0.13
Merlot		19.54 ± 0.13	18.19 ± 0.13	16.13 ± 0.12
Muscat Ottonel		19.67 ± 0.15	18.32 ± 0.15	16.24 ± 0.14
Pinot noir	Cuttings	19.90 ± 0.16	18.55 ± 0.16	16.45 ± 0.15
Rara neagra		19.97 ± 0.14	18.62 ± 0.14	16.51 ± 0.13
Rcatsiteli		20.01 ± 0.12	18.66 ± 0.12	16.55 ± 0.12
Saperavi		19.88 ± 0.13	18.54 ± 0.13	16.44 ± 0.12
Sauvignon		19.43 ± 0.14	18.08 ± 0.14	16.03 ± 0.13
Savinion blanc		19.53 ± 0.15	18.18 ± 0.15	16.12 ± 0.14
Traminer		19.32 ± 0.16	17.97 ± 0.16	15.93 ± 0.15
Average		19.71	18.36	16.28
Sea buckthorn		20.00 ± 0.16	18.73 ± 0.16	16.62 ± 0.15
Blackberry	Cuttings	18.54 ± 0.26	17.30 ± 0.26	15.32 ± 0.24
Blackcurrant		18.73 ± 0.28	17.39 ± 0.28	15.40 ± 0.26
Average		19.09	17.81	15.78
Miscanthus giganteus		19.87 ± 0.13	18.57 ± 0.13	16.47 ± 0.12
Silphium		19.00 ± 0.12	17.68 ± 0.12	15.66 ± 0.11
Sakhalin buckwheat		19.27 ± 0.28	17.96 ± 0.28	15.92 ± 0.26
Energy willow	Cuttings	20.99 ± 0.18	19.66 ± 0.18	17.45 ± 0.17
Energy poplar		19.40 ± 0.21	18.11 ± 0.21	16.06 ± 0.19
Reed from the Danube Delta		18.84 ± 0.26	17.62 ± 0.26	15.61 ± 0.23
Average		19.56	18.27	16.19

Miscanthus giganteus pellets produced from the biomass harvested in 2022 showed good burning power indices ($q_{p, net, m=10\%} = 16.47 \pm 0.12$ MJ/kg). These data correlate with the results presented by us before regarding the calorific value of the Miscanthus biomass

collected in the experimental fields of the Alexandru Ciubotaru National Botanical Garden (Institute) from the Republic of Moldova in 2020 and 2021 [18].

Basically, the net calorific value of the pellets produced from *Miscanthus giganteus* complies with the values required for all quality classes of ENPlus certified pellets. These findings show that *Miscanthus giganteus* is a promising industrial crop to be used as a feedstock in the production of densified solid biofuels.

To support the recorded findings, it can be added that this crop can be cultivated on marginal agricultural areas and has an impressive productivity - of about 15 ... 20 t/ha [19, 20]. At the same time, it is known that *Miscanthus* inflorescences do not provide nectar or pollen, so it is recommended to provide measures in order to increase biodiversity in *Miscanthus* growing regions. Co-cultivation of honey plants with high energy potential would be a perfect solution for this purpose.

The studies carried out at Alexandru Ciubotaru National Botanical Garden (Institute) in the experimental sector of the Vegetal Resources Laboratory, highlighted the following plants with high melliferous potential: phacelia (*Phacelia tanacetifolia* Benth., *Hydrophyllaceae* R. Br. family); alfalfa, clover (*Medicago sativa* L., *Trifolium* sp., *Fabaceae* Lindl. family); sylvia, sunflower and Jerusalem artichoke (*Silphium perfoliatum* L., *Helianthus annuus* L., *H. tuberosus* L., *Asteraceae* Bercht. & J. Presl family), etc. [21].

5. Conclusions

Based on the research carried out in this study, it can be concluded that the pellets produced from plant biomass generated from agricultural residues and a series of energy crops have a sufficient burning power to be used for residential and industrial purposes. The biomass generated from tree residues, sunflower seed husks and vine residues, table varieties ensure the production of pellets with a calorific value equal to or greater than 16.5 MJ/kg, i.e., are in compliance with the ENPlus 3 requirements. Other types of biomass studied in this research from the point of view of their calorific value, can be used in mixtures along with other types of biomass.

Thus, the average calorific value of the pellets produced from arboreal agricultural residues is 17.42 MJ/kg, the highest calorific value being recorded by the pellets produced from cherry arboreal residues (18.4±0.18) MJ/kg. The average calorific value of the pellets produced from agricultural vine residues is 16.75 MJ/kg, the best results being recorded by the pellets produced from Cardinal vine variety residues (16.94±0.22) MJ/kg. The calorific value of the pellets produced from sunflower husk is (16.78±0.171) MJ/kg.

Data presented in this study can be used both by producers of densified solid biofuels and specialists that deal with the development and design of technologies for the production of pellets from plant biomass.

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Conflicts of Interest: The authors declare that they have no conflict of interest.

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