ASSESSMENT OF THE QUALITY OF SECONDARY PRODUCTION FROM DIFFERENT AGRICULTURAL CROPS USED AS PRIMARY MATERIAL FOR DENSIFIED SOLID BIOFUELS

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Abstract

The quality of densified solid biofuels is directly influenced by the biomass characteristics used as feedstock. Under the conditions of the Republic of Moldova, the main source of raw material used in the production of briquettes and pellets is represented by agricultural residues and those from the food industry. For this reason, it is important to know the qualitative characteristics of these residues. The purpose of this study is to highlight the main qualitative parameters of agricultural residues used as energy sources specific for the Republic of Moldova. The issue of research refers to the estimation of the possibilities of using indigenous agricultural residues as a raw material for the production of densified solid biofuels with ENPlus 3 characteristics. The investigative methodology is based on a complex study, organized and realized in the Solid Biofuels Laboratory of the State Agrarian University of Moldova.
The paper presents the results of the research regarding the estimation of the calorific value, the moisture content, the ash content and the chemical analysis of the main agricultural residues from the agrarian sector depending on their origin and specificity, emphasizing on herbaceous, arboreal and vines residues.
The study showed that only about 10% of the residues from agricultural activities can be used directly to produce bio briquettes and pellets with qualitative indicators according to the requirements of ENPlus 3. It should be noted that practically, all agricultural and vineyard residues can be used as a raw material to the production of ENPlus certified densified solid biofuels, and herbaceous residues can only be used in mixtures with other types of vegetable biomass or require pre-treatment before densification, for example, by torrefaction.

Key words: agricultural residues, solid biofuels, calorific value, moisture content

The compliance with the requirements of the international standards EN Plus3 is one of the main factors which is directly affecting the economic and social aspects regarding the production of densified solid biofuels (DSBF).

For the beneficiaries the most important characteristics of biofuels are the calorific value and the ash and moisture content. When referring to the environment connected requirements the nitrogen, sulphur and chlorine content are the most severely regulated, as they favour the formation of acid rain and smog, have corrosive effects over metals and have a negative influence on the reliability of technological equipment (Marian Gr., 2016).

The above mentioned characteristics of the finite product depend on the properties of the raw material, which vary significantly according to its origin and source of origin.Vegetable biomass is the main component of raw material used for producing DSBF; the use of biomass is conditioned by a series of factors of which the quantity and quality potential in the biofuel production location is the most important one.

The Republic of Moldavia has a large agricultural potential; as a result, the main source for producing DSBF is represented by the secondary products obtained when from the growing of different crops. The agricultural secondary products are: straws from cereal crops, stems from maize and sunflower crops, tendrils from dormant pruning of vines, branches from orchard pruning etc. (Marian Gr., 2016).

The use of agricultural secondary products as raw materials for producing DSBF is a common practice in several countries, including Moldavia and Romania. Moreover, in the last decade, data referring to the quality of agricultural biomass used for the production of DSBF is available in both international papers (Alakangas E.A., 2016; Bentsen N. S. *et al*, 2014; Algieri A. *et al*, 2019) and national literature (Hăbăşescu I., Cerempei V., 2012; Marian Gr., 2016; Gudîma A., 2017; Pavlenco A., 2018).

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Based on the analysis of the specific papers we were able to establish that the results of the studies (especially the ones regarding the energy potential) vary significantly and are referring to specific types of biomass, according the climate areas taken into account.

The aim of the present study is the emphasize the most important quality parameters of the agricultural residues which are specific for the Republic of Moldavia, in order to evaluate the possibilities of using them for producing DSBF with the characteristics required by the international ENPlus 3 standards.

MATERIAL AND METHOD

The research was performed in the Laboratory for Solid Biofuels of the State Agricultural University of Moldavia. The main physical, chemical and energetic properties of different types of agricultural residues (herbaceous, but also from orchards and vineyards) were evaluated.

The calorific value was measured with the LAGET MS – 10A calorimetric bomb and the results were related to the content of dry substance. The high calorific value was measured and then the low calorific value at constant pressure was calculated using the specifications given by the SM EN ISO 18125:2017. The low calorific value was calculated based on the hydrogen, oxygen and nitrogen content, for the dry substance and for the moisture content of 10%.

The calorific value of the biomass with 10% moisture is important because this value of the humidity is recommended for the calculation of the available energy potential of biomass; it also represents the average humidity of biomass during processing. In the meantime, most of the agricultural secondary products are dried in the field down to a humidity of approx. 10%.

The moisture content was evaluated (dry basis) through weighting, according to the SM EN ISO 18134 1-3: 2017 standards series, which indicate the complete extraction of moisture form the tested material.

The ash content (dry basis) was evaluated according to the SM EN 18122:2017 standard, through slow calcination of the samples in the electric oven (LAC type LH 05/13) at 550 ^{c}o., for at least 6 hours.

The preparation of the samples was made according to the SM EN 14780:2017 standard. The biomass was grinded with the SM 100 mill and sieved with a 1 mm sieve. The chemical analysis was performed using the VarioMACRO cube CHNS&Cl elemental analyser. The detection and quantity analysis were performed using a thermal conductivity detector (TCD). The results were analysed using the dedicated software EAS, which enables the display, monitoring, recording and processing of data in order to obtain the characteristics of the chemical elements.

RESULTS AND DISCUSSION

The energy potential of biomass is given by the calorific value. The calorific value depends on the chemical composition and moisture and ash content. The results of the analytical phase are presented in Table 2 as the average value of five measurements; the standard error and confidence interval are also presented.

The chemical analysis of the samples provides important information regarding the carbon, hydrogen and oxygen content, which have a significant influence over the calorific value of the finite product. The nitrogen and sulphur content are also presented as they have negative effects over the quality of DSBF; *table 1* presents the requirements of the Unplugs standard referring to the nitrogen and sulphur content.

Table 1

Requirements of ENPlus 3 regarding the nitrogen and sulphur content

Chemical element	Quality class		
	A1	A2	A3
Nitrogen	≤ 0,3	≤ 0,5	≤ 1
Sulphur	≤ 0,04	≤ 0,05	≤ 0,05

Considering the data shown in *table 1* and *table 2* it was concluded that, taking into account the nitrogen and sulphur content, only the maize cobs perfectly comply with the requirements of ENPlus standards. The other herbaceous raw materials may be only used in mixtures containing other types of wooden biomass (orchard branches and vine tendrils), thus reaching the imposed nitrogen and sulphur content.

Ash is a ballast in DSBF and is regulated by Unplugs standards as follows:

Pellets – 0.7% for class A1; 1.2% for class A2 and 2% for class En-B.

Briquettes - 1% for class A1; 1.5% for class A2 and 3% for class B.

Taking these values into account and comparing them with the results presented in Table 2 it was concluded that highest amount of ash (11.8% ash) results from the combustion of sunflower stems and leaves, followed by wheat straws (5.7%) and maize stems (4.6% ash).

For the rest of the herbaceous raw materials the ash content after combustion was lower than 3%, thus corresponding to the requirements of class B for briquettes. As an exception, with less than 2% ash, cobs may be used for producing class En-B pellets.

Table 2

Physical and chemical properties of agricultural residues

Crop	Biomass type	Moisture content, %			Ash content, %				Calorific value, MJ/kg			Chemical analysis				
		$M_{r.av.}$	σ	CI	$A_{d.\ av.}$	$A_{av.\ M=10\%}$	σ	CI	$q_{v.gr.d}$	$q_{p.net.d.}$	$q_{p.net.m=10\%.}$	C	H	N	S	O
Herbaceous agricultural residues																
Autumn and spring wheat	straws	17.7	3.2	2.8	5.7	6.4	0.8	0.1	18.4	17.1	15.2	45.6	5.80	0.48	0.08	43,3
Autumn and spring rice	straws	24.3	5.9	5.2	2.4	2.7	0.1	9.2	18.5	17.2	15.3	47.1	5.70	0.46	0.09	44,3
Oat	straws	19.5	3.3	2.9	2.7	3.0	0.1	0.2	18.1	16.8	14.91	46.1	5.80	0.47	0.08	44,9
Maize	stems	37.8	6.4	5.6	4.6	5.2	0.2	0.2	17.9	16.7	14.8	47.5	5.50	0.62	0.09	41,7
	cobs	45.9	6.4	5.6	1.8	2.0	0.1	0.1	19.1	17.8	15.8	45.9	6.01	0.46	0.03	45,8
Sunflower	stems and leaves	45.0	10.5	9.2	11.8	13.1	0.2	0.2	16.9	15.8	14.0	42.5	5.10	1.11	0.11	39,8
Average		***31,7***			***4.8***	***5.4***			***18.2***	***16.9***	***15.0***	***45.8***	***5.7***	***0.6***	***0.08***	***43.3***
Orchard agricultural residues																
Apple trees	Pruning	25.4	2.8	2.5	1.0	1.2	0.2	0.3	20.3	19.0	16.8	46.5	5.98	0.28	0.03	46.1
Pear trees		40.5	3.1	2.7	1.7	1.9	0.3	0.4	20.7	19.6	17.4	45.4	5.37	0.28	0.03	47.2
Quince trees		26.0	2.3	2.0	1.7	1.9	0.0	0.0	20.1	18.8	16.7	46.4	6.10	0.25	0.02	45.5
Cherry trees		25.5	2.6	2.3	1.0	1.2	0.2	0.2	20.7	19.4	17.2	47.7	6.03	0.28	0.04	44.9
Sweet cherry trees		27.6	2.3	2.0	1.6	1.8	0.3	0.3	22.1	20.8	18.5	44.9	5.66	0.32	0.03	47.5
Apricot trees		24.3	1.4	1.3	0.9	1.0	0.1	0.1	20.8	19.5	17.3	45.7	6.02	0.29	0.03	47.1
Peach trees		25.4	1.5	1.3	1.4	1.5	0.2	0.3	21.4	20.0	17.8	44.3	6.11	0.28	0.03	47.9
Plum trees		34.8	1.9	1.7	0.8	0.8	0.5	0.6	21.4	20.1	17.8	45.2	6.08	0.30	0.03	47.6
Average		***28,7***			***1.3***	***1.4***			***20.9***	***19.6***	***17.4***	***45.8***	***5.9***	***0.3***	***0.03***	***46.7***
Vineyard agricultural residues, table grape varieties																
Moldova	pruning	36.3	2.0	1.8	2.5				20.7	19.4	17.2	46.4	5.96	0.34	0.03	44.8
Cardinal		37.3	1.7	1.5	2.4				20.3	19.1	16.9	46.4	5.83	0.44	0.03	44.9
Muscat of Hamburg		36.6	2.6	2.3	2.5				20.2	18.9	16.8	46.4	5.98	0.35	0.03	44.8
Early Muscat		35.6	2.7	2.4	2.6				20.3	19.0	16.9	46.4	5.84	0.37	0.03	44.8
Victoria		38.3	1.7	1.5	2.5				20.3	19.0	16.9	46.4	5.97	0.38	0.03	44.8
Chișmiș moldovenesc		37.9	1.3	1.2	2.8				20.2	18.9	16.8	46.4	5.92	0.34	0.03	44.5
Arcadia		38.1	1.4	1.2	2.8				20.2	18.9	16.8	46.4	5.93	0.39	0.03	44.5
Lora		37.3	1.6	1.4	2.7				20.3	19.1	16.9	46.4	5.82	0.38	0.03	44.7
Prezentabil		37.2	3.0	2.6	2.5				20.2	18.9	16.8	46.4	5.91	0.37	0.03	44.7
Tudor		36.6	3.0	2.6	2.6				20.2	18.9	16.8	46.4	5.92	0.35	0.03	44.7
Average		***37,1***			***2.6***				***20.3***	***19.0***	***16.9***	***46.4***	***5.9***	***0.4***	***0.03***	***44.7***
Vineyard agricultural residues, technical grape varieties																
Cabernet	Pruning	34.8	1.1	1.0	2.2				19.7	18.5	16.4	46.6	5.90	0.83	0.05	44.5
Sauvignon		34.9	1.6	1.4	2.1				19.6	18.4	16.3	46.6	5.80	0.81	0.04	44.6
Merlot		35.0	2.3	2.0	3.0				19.5	18.3	16.2	47.2	5.83	0.86	0.02	43.1
Pinot noir		33.8	1.5	1.3	2.7				19.6	18.3	16.3	47.1	5.81	0.81	0.02	43.5
Izabelgla		35.5	2.8	2.4	2.9				19.4	18.1	16.0	45.1	5.91	0.84	0.02	45.2
Traminer		34.5	2.2	1.9	2.5				19.7	18.4	16.3	46.4	5.85	0.83	0.05	44.4
Aligote		34.9	2.5	2.2	2.5				19.6	18.3	16.2	46.4	5.75	0.78	0.04	44.6
Chardonnay		34.6	2.7	2.4	2.5				19.7	18.5	16.4	46.4	5.85	0.77	0.04	44.5
Rcatsiteli		35.3	2.8	2.5	2.5				19.7	18.4	16.3	46.4	5.84	0.81	0.05	44.4
Savignon blanc		34.9	2.6	2.3	2.5				19.5	18.3	16.2	46.4	5.83	0.81	0.05	44.4
Muscat Ottonel		35.6	3.2	2.8	2.5				19.7	18.4	16.3	46.4	5.82	0.80	0.04	44.5
Media		***34,9***	***2.3***	***2.0***	***2.5***				***19.6***	***18.3***	***16.3***	***46.5***	***5.8***	***0.8***	***0.04***	***44.3***

Notations used in the table: $M_{r.av.}$ – The average moisture content at harvest; *σ* – Standard deviation; *CI* – Confidence interval; $A_{d.\ av.}$ – The average ash content; $A_{av.\ M=10\%}$ - The average ash content of biomass with 10 % moisture; $q_{v.gr.d}$ – High calorific value; $q_{p.net.d}$ – low calorific value at constant pressure (d.b.). $q_{p.net.m=10\%.}$ – low calorific value at 10% moisture.

The ash content was less than 1.7% for all the wooden residues which resulted from orchard pruning; the average ash content was 1.3%.

The vine residues produce the highest quantity of ash after combustion, with an average recorded value of 2.6% for ten table grape varieties and 2.5% for eleven technical grape varieties

It was concluded that, considerring the ash content criterion, all the orchard and vine residues may be used for producing DSBF in accordance with the ENPlus 3 requirements.

The lower calorific value (which, in our study, was calculated for a moisture content of 10% - $q_{p.net.m=10\%.}$) is an important characteristic which limits the use of certain types of biomass for producing ENPlus 3 certified DSBF.

Table 2 shows that the lowest calorific value was recorded for the herbaceous residues, with values between 14 MJ/kg for sunflower stems and leaves and 15.8 MJ/kg for maize cobs.

According to this criterion, all the types of orchard residues and vine residues from table grape varieties may be used for producing ENPlus briquettes and pellets; vine residues from technical grape varieties may be used as raw material for producing bio briquettes.

CONCLUSIONS

Based on the experimental results it was concluded that the herbaceous secondary products, with the exception of maize cobs, do not achieve the quality characteristics required by the ENPlus regulations; an in-depth analysis will indicate whether they are more useful for producing DSBF or as organic fertilizer. The analysis should take into account the technical, economic and social aspects, as well as the agricultural and environmental sustainability and durability.

Vine tendrils and orchard branches resulted from pruning may be used for producing ENPlus certified DSBF, when used in blends and mixtures.

Some herbaceous secondary products may be used in blends with the orchard and vine residues, but only after a laboratory analysis of the raw materials or of the final product; the analysis should also take into account the technical and economic aspects and the impact on the agricultural and environmental sustainability and durability.

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