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Yu. V. Maksimuk, V. N. Kursevich, A. S. Korsakova, M. V. Antonava, V. S. Krouk

Research Institute for Physical Chemical Problems of the Belarusian State University, Minsk, Belarus

HEATING VALUE OF AGRICULTURAL BIOMASS: THE BASIC VALUE AND INTERVALS FOR CERTAIN TYPES

Abstract. Higher heating value (HHV) on a dry and ash free basis (daf) is a convenient platform for comparing the energy content in various types of agricultural biomass. HHV and ash content for 90 samples of straw, seed, husk, meal, its waste, etc. were experimentally determined. HHV_{daf} for 80 samples from different regions were calculated by the literature data. The basic value of HHV_{daf} agricultural biomass at 19.6 MJ kg^{-1} was recommended for verifying data on solid biofuels. The intervals of variation of HHV_{daf} for sugar beet pulp, straw, meal, flax shives and sunflower husk are established. The deviations from the base value of HHV_{daf} and from intervals of variation of HHV_{daf} for certain types of agricultural biomass are discussed.

Keywords: higher heating value, agricultural biomass, straw, sugar beet pulp, flax shives, sunflower husk

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Ю. В. Максимук, В. Н. Курсевич, А. С. Корсакова, М. В. Антонова, В. С. Крук

Научно-исследовательский институт физико-химических проблем БГУ, Минск, Беларусь

ТЕПЛОТА СГОРАНИЯ СЕЛЬСКОХОЗЯЙСТВЕННОЙ БИОМАССЫ: БАЗОВОЕ ЗНАЧЕНИЕ И ИНТЕРВАЛЫ ДЛЯ ОТДЕЛЬНЫХ ВИДОВ

Аннотация. Высшая теплота сгорания (ВТС) в пересчете на сухое и обеззольное состояние (daf) является удобной платформой для сравнения энергоемкости различных видов сельскохозяйственной биомассы. Экспериментально определены ВТС и зольность для 90 образцов соломы, семян, лузги, шрота и т.д. На основании литературных данных рассчитаны значения $ВТС_{daf}$ для 80 образцов из разных регионов. Предложено базовое значение $ВТС_{daf}$ сельскохозяйственной биомассы равное 19,6 МДж кг$^{-1}$ для верификации данных по твердому биотопливу. Установлены интервалы варьирования $ВТС_{daf}$ для свекловичного жома, соломы, шрота, льнокостры и лузги подсолнечника. Обсуждены отклонения $ВТС_{daf}$ от базового значения и интервалов варьирования для отдельных видов сельскохозяйственной биомассы.

Ключевые слова: высшая теплота сгорания, сельскохозяйственная биомасса, солома, жом сахарной свеклы, льнокостра, лузга подсолнечника

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Introduction. The use of agricultural residues as solid biofuel is one of the trends to curb climate change, as well as the final stage of comprehensive waste recycling. Heating value is the main consumer characteristic of fuel, which is necessary to assess the efficiency of boilers, mutual calculations for supplies, etc. At the same time, higher heating value (HHV) is a fundamental characteristic of organic matter, which reflects the amount of internal energy. Its value is determined by the bonding energies of the structural components that make up the substance. Water is an integral, but non-combustible component, so the HHV for biomass is most often presented on a dry basis (HHV_d). For 1000 samples of plant biomass [1], HHV_d values are in the range 5.7 (14.8 to 20.5) MJ kg^{-1}, and equal, on average, to 18.1 ± 1.4 MJ kg^{-1}. Conversion of HHV_d to dry and ash free basis (daf) taking into account ash content on a dry basis (A_d) [1] results in HHV_{daf} values, which are in the narrower interval 3.3 (17.9 to 21.2) MJ kg^{-1}, and equal, on average, to 19.9 ± 0.7 MJ kg^{-1}. The 1.7-fold narrowing of the interval HHV_{daf} compared to HHV_d indicates a tendency for HHV_{daf} values to be constant across biomass species. It is logical to assume that the interval HHV_{daf} will be even narrower for the same biomass species.

The external trigger for this study was the work [2], which compiled HHV values for wheat straw from Mexico, Canada, and Turkey in the interval 5.4 (14.9 to 20.3) MJ kg^{-1}. Such a wide interval creates a false impression of a significant difference in HHV for the same biomass species in different regions.

In fact, this is explained by the fact that the values of HHV refer to different bases. Analysis of references shows that the value (in MJ kg^{-1}) 14.86 is obtained on a wet basis (w) [2], the value 17.00 on a dry basis (d) [3], the value 18.55 on an extractive free, dry and ash-free basis (ef, daf) [4]; and the value 20.3 is an error [5].

Literature HHV data is given for different parts of plants belonging to different crops and grown in different regions: Canada [5], Greece [6], Spain [7], Cuba [8], Portugal [9], China [10] and others. In many papers [6–8, 11–13], HHV values are presented without a basis, which is a problem when comparing data and creates a risk of their erroneous interpretation. For example, in [7] for 100 samples HHV values are given probably as HHV_w. This is confirmed by the very low value of HHV = 15.16 MJ kg^{-1} for wood chips, which, taking into account moisture content (W) of 25.6 %, gives the typical wood HHV_d value = 20.38 MJ kg^{-1}. However, is this true for all samples? For example, the similarly calculated HHV_d value equals to 20.04 MJ kg^{-1} for oats bran no longer looks "typical". The source of uncertainties may be the authors' use of different experimental and/or data presentation techniques. For example, in [10] for 784 crop straw samples the HHV values "on a dry basis" obtained by drying at 45 °C according to ASTM E 1757 and W values "on a dry basis" obtained by drying at 103 °C according to ASTM E 871 are presented. For comparison, we present two data sets for samples from [10]. Based on the literature values of W, A_d, HHV_w or HHV_d using ISO 16993, the HHV_{daf} values were calculated and represented in Table 1. Their values vary in the following intervals (in MJ kg^{-1}): 2.1 (18.16 to 20.28) for wheat straw; 2.7 (16.85 to 19.55) for straw rice; 2.7 (17.81 to 20.51) for straw rye, rape, barley, mustard, flax. Such wide intervals and, accordingly, high error (5.5–14.8 %) of average HHV_{daf} values for the same type of biomass (in this case, straw) cannot be considered acceptable.

T a b l e 1. **Calculated higher heating values on dry and ash free basis (HHV_{daf}, MJ kg^{-1}) for the literature agricultural biomass**

Sample	Origin	*W*, %	A_d, %	HHV_w	HHV_d	Ref.	HHV_{daf}
Wheat straw	South Asian region	8.45	4.99		17.25	[14]	18.16
	Turkey		8.0		16.80	[15]	18.26
	mainland China		9.24		16.65	[10]	18.35
		5.36	9.78	16.65	17.59		19.50
	n.d.		7.70		17.355	[16]	18.80
			6.40		18.905		20.20
		8.87	6.90		17.988	[17]	19.32
	Baja California, Mexico	5.58	17.04	14.86	15.74	[2]	18.97
	India	6.40	12.59		(16.63)	[11]	19.03
	California, USA		8.90		17.51	[18], [19]	19.22
	USA		6		18.44	[20]	19.73
			7.02		17.94	[21]	19.29
	Denmark	7.9	5.8		18.4	[22]	19.4
	Dnipro region, Ukraine	10.06	7.1			[23]	19.568
		10.83	3.2				19.968
	Tomsk region, Russia		6.35		18.50	[24]	19.75
			8.55		18.55	[25]	20.28
	Spain	7.7	5.3	(17.344)	18.79	[7]	19.84
Rye straw		8.7	3.2	(17.113)	18.74		19.36
Spelt straw	n.d.		7.1		18.7	[1]	19.79
Rice straw	South Asian region	6.96	20.02		13.48	[14]	16.85
	Mainland China		12.21		15.50	[10]	17.65
		4.04	12.72	15.50	16.15		18.62
	n.d.	8.10	20.38		14.85	[17]	18.65
	California, USA		13.42		16.28	[18]	18.80
			24.36		14.56		19.25
	USA		18.67		15.09	[21]	18.55
	Japan	9.41	14.21		16.30	[26]	19.00

The end of the table 1

Sample	Origin	W, %	A_d, %	HHV_w	HHV_d	Ref.	HHV_{daf}
	Cambodia		16.11		16.40	[27]	19.55
corn straw	South Asian region	8.78	5.95		17.08	[14]	18.16
	Novosibirsk region, Russia		8.52		16.65	[25]	18.20
			7.18		18.14	[24]	19.54
	mainland China	4.22	7.00		17.00	[10]	18.28
			7.31	17.00	17.75		19.15
	n.d.	7.44	7.65		17.68	[28]	19.14
barley straw	Canada	6.9	10.52	(15.7)	16.86	[5]	18.85
	California, USA		10.30		17.31	[18]	19.30
	Novosibirsk region, Russia		8.85		17.87	[24]	19.61
	Spain	9.8	6.1	(17.369)	19.26	[7]	20.51
rape stalk	mainland China		6.64		16.63	[10]	17.81
		4.61	6.96	16.63	17.43		18.74
mustard straw	India	6.86	14.98		(16.12)	[11]	18.96
rape straw	n.d.	8.68	4.65		18.34	[28]	19.23
rapeseed straw			6.7		18.4	[1]	19.72
	Czech Republic	9.37	4.98	16.71	18.44	[29]	19.61
rape straw pellets		8.03	4.57	17.36	18.88		19.93
oat straw	Poland	12.5	(9.2)		(17.6)	[30]	19.38
	Novosibirsk region, Russia		10.21		17.87	[24]	19.90
flax straw	Canada	7.9	3.26	17.00	18.46	[5]	19.08
	n.d.		3.5		19.1	[1]	19.79
wheat husk	India	5.98	12.1		(16.42)	[11]	18.68
wheat bran	Spain	9	3.5	(17.370)	19.09	[7]	19.78
rice husk/hulls	South Asian region	7.88	14.02		15.45	[14]	18.27
	India	4.65	9.29		16.93	[11]	18.66
	n.d.	8.47	21.24		14.693	[17]	18.66
		8.48	18.64		15.29		18.79
	Brasil	6.89	13.43	16.50	16.50	[31]	19.06
	Krasnodar Region, Russia		21.91		15.33	[25]	19.63
			17.82		16.20	[24]	19.71
	USA		17.86		16.14	[18]	19.65
			20.26		15.84	[21]	19.86
	Spain	7.27	13.7	(15.899)	17.15	[7]	19.87
buckwheat husk	Novosibirsk region, Russia		2.05		19.87	[24]	20.29
sunflower husk	Zaporizhzhya region, Ukraine	9.45	3.8			[23]	21.169
	Krasnodar Region, Russia		2.92		25.73	[24]	26.50
corncobs	Turkey		1.00		17.00	[15], [16]	17.17
	n.d.		1.10		18.795	[16]	19.00
	California		1.36		18.77	[16], [18]	19.03
	Novosibirsk region, Russia		4.86		18.10	[24]	19.03
	Spain	7	2.4	(17.692)	19.02	[7]	19.49
	South Asian region	11.74	10.67		18.36	[14]	20.55
rye cereals	Spain	10.76	1.8	(16.141)	18.09	[7]	18.42
wheat grain		10.3	2.8	(16.325)	18.20		18.72
barley grain		9.9	3	(16.519)	18.33		18.90
oat grain	Poland	10.7	(2.5)		(19.4)	[30]	19.90
flax shive	Novosibirsk region, Russia		3.01		19.75	[24]	20.36
			6.84		19.65	[25]	21.09
olive stone	Spain	11	1.4	(17.884)	20.09	[7]	20.38
	Andalusia, Spain		0.77		20.46	[32]	20.62
olea wastes	northern Portugal		4.0		(21.09)	[9]	21.97
olive pits	California, USA		3.16		21.39	[18]	22.09
beetroot pellets	Spain	12.5	9	(15.095)	17.25	[7]	18.96

In parentheses are the values for which Ref. is not given the basis; n.d. no date.

The aim of this work is to establish the basic value and intervals of HHV_{daf} for agricultural biomass, which can be used to verify data on solid biofuels. The use of such an approach for agricultural biomass seems most appropriate, since it is characterized by high values of A_d and, accordingly, a wide interval of variation of HHV_d. It is reasonable to estimate the basic value on the basis of a critical review of the literature and experimental studies for certain types of agricultural biomass.

Another important indicator of the quality of solid biofuel is the ash content (A), which, in contrast to HHV, depends on the experimental conditions. Thus, A is determined for solid biofuel according to ISO 18122 at (550 ± 10) °C, for biomass according to ASTM E 1755 at (575 ± 25) °C, for wood according to ASTM D 1102 from 580 to 600 °C. Therefore, a related task of the work was to determine A_d for agricultural biomass at different temperatures and evaluate its effect on the HHV_{daf} value.

Materials and methods. Initial samples were taken from industrial batches of agricultural biomass from Belarus, Ukraine and Russia, mainly used as solid biofuel. Laboratory experiments were carried out for general analysis samples with the particle sizes of no more than 1.0 mm prepared according to ISO 14780. The measurements of HHV_w and A_w were carried out in parallel with the measurements of W according to ISO 18122. W was determined by drying 1–2 g of the sample at (105 ± 2) °C in the aluminum cylindrical container of 70 cm^3 to a constant weight for at least 3 h (ISO 18134-3). A_w was determined by baking of ~1 g of preliminarily carbonized sample at 550 °C for 120 min in porcelain crucibles (ISO 18122). The hot crucibles were kept in the air for 5 minutes after being removed from the oven, then placed in the desiccator and weighed after 15 min. In W determining the drying oven SNOL 24/200 (AB UMEGA, Lithuania) was used, in the case A the muffle furnace MIMP-3P (LLC MIUS, Russia) was applied. The accuracy of temperature maintenance in the test chambers was no worse than ±2 °C. Three parallel determinations were made during the measurements, with the maximum difference between the determinations not exceeding 0.2 %. HHV_w was determined according to ISO 18125 using the bomb isoperibolic calorimeter BIC 100 (CJSC BMC, Belarus) with the water jacket [33]. Calibration of the calorimeter was carried out with benzoic acid K-3 (certified reference material from VNIIM, St. Petersburg) which has a certified value of the specific energy of combustion equal to 26.454±0.005 MJ kg^{-1}, when weighing in the air [34]. General analysis samples weighing of 1.0–1.2 g were obtained with an accuracy of 0.1 mg with a DV215CD balance (Ohaus, USA) and burned as air-pressed pellets in heat-resistant stainless steel crucible. Copper wire of 0.5 mm diameter was used as a fuse. The initial pressure of oxygen in the calorimeter bomb was 3 MPa. The repeatability of the measurement results averaged 0.05, with a maximum discrepancy not exceeding 0.10 MJ kg^{-1}.

Results and Discussion. Experimental values of HHV_w, A_w have been recalculated to HHV_d, A_d and HHV_{daf} according to ISO 16993 (Table 2). The literature and experimental HHV_{daf} values for selected groups of agricultural biomass are combined in Fig. 1, except for the minimum value for straw rice. The results of the ash content determination tests are presented in Table 3. The values of A_d obtained at 600 °C are lower than those at 550 °C, but the difference between them does not exceed the ISO 18122 repeatability limit.

Prerequisites for the existence of the basic value of HHV for plants. The plant is an organomineral nanocomposite, the main organic part of which is a lignin-carbohydrate matrix. This matrix is considered from the standpoint of physical chemistry as a quasi-equilibrium, thermodynamically limited ordered system of biopolymers: cellulose, hemicelluloses and lignin [35], which are “soaked” with extractives. The composition, structure, and ratio of matrix components and extractives in plants vary depending on the species, habitat, environmental conditions, and stage of development. However, a comparative analysis of the HHV and biomass composition diagrams [1, 10] indicates that the variability of plant HHV is much lower than the diversity and variability of its constituents. Plant growth and development processes are characterized by a dynamic equilibrium in which the content of some components changes at the expense of others, while HHV remains almost constant. That is, a plant substance is considered “as a thermodynamically self-organizing nanobiocomposite system” [35], in which the main changing parameter is entropy. The existence of such a system allows us to propose a unified value of HHV_{daf} for the plant kingdom. The variation of this value is ±10 %, and for certain types of biomass, for example, for hardwood or softwood, ±5 % [36]. The constancy of HHV_{daf} means that variation in plant components has an energy limit, which is probably regulated during evolution. On the other hand, the lability of HHV_{daf} is the energetic basis of the biodiversity generation mechanism to ensure survival

T a b l e 2. **Ash content (A, %) and higher heating value (HHV, MJ kg^{-1}) of the studied samples**

Sample	Origin	n	A_d	ΔA_d	HHV_d	ΔHHV_d	HHV_{daf}	ΔHHV_{daf}
Rape straw	Minsk region, Belarus	2	5.85	5.8–5.9	18.40	18.1–18.7	19.54	19.2–19.9
Rape straw pellets		5	6.01	4.0–8.4	18.61	18.3–18.9	19.80	19.6–20.0
	Gomel region, Belarus	3	6.60	2.7–8.8	18.40	17.8–19.2	19.70	19.5–19.8
	Brest region, Belarus	2	4.52	4.4–4.7	18.78	18.7–18.9	19.66	19.6–19.8
	Grodno region, Belarus	2	4.13	3.7–4.6	18.97	18.9–19.0	19.79	19.7–19.9
Rape straw pellets (with additives)		5	5.08	3.5–7.7	19.73	18.8–20.5	20.78	20.4–21.3
Wheat straw	Minsk region, Belarus	1	9.55		17.72		19.60	
Wheat straw pellets		1	5.24		18.69		19.73	
Triticale straw		1	6.82		18.21		19.54	
Triticale straw pellets		1	3.63		18.98		19.69	
Rye straw pellets	Mogilev region, Belarus	3	5.68	4.2–8.3	18.63	18.2–18.9	19.75	19.7–19.8
Corn straw	Krasnodar region, Russia	1	4.51		18.35		19.21	
Oat husk	Belarus	1	2.81		19.07		19.63	
Rice husk pellets	n.d.	1	18.67		16.13		19.84	
Buckwheat husk pellets	Belarus	3	2.82	1.6–4.1	19.46	19.2–19.7	20.02	20.0–20.1
Soybean husk pellets	Kursk region, Russia	1	3.14		19.50		20.13	
Rye seeds	Minsk region, Belarus	1	1.81		18.42		18.76	
Small barley seeds		1	2.84		18.53		19.08	
Grain hulling waste		1	3.66		18.42		19.12	
Grain wastes from malting production	Belsolod JSC, Belarus	2	2.46	3.9–4.9	18.00	17.9–18.1	18.83	18.8–18.9
Malt polishing waste		1	5.73		18.53		19.66	
Malt sprouts		1	6.95		18.99		20.41	
Grain processing waste / pellets	bakery plants / elevators, Belarus	7	11.54	5.9–19.6	17.65	16.1–18.9	19.95	19.9–20.1
Grain waste / sawdust pellets		2	7.03	4.5–9.6	19.03	18.7–19.4	20.47	20.3–20.7
Rapeseed oil cake	Minsk region, Belarus	1	3.92		30.21		31.44	
Rapeseed spring		1			28.39		29.53	

Rapeseed meal spring		1	7.02		20.47		22.02	
Rapeseed winter		1			29.29		30.51	
Rapeseed meal winter		1	7.67		19.44		21.06	
Rapeseed meal		1	7.53		19.61		21.21	
Soybean meal	Lviv region, Ukraine	1	5.47		19.92		21.08	
Sunflower meal	Vinnytsia region, Ukraine	1	5.86		19.79		21.00	
Sunflower husk / pellets	Ukraine	3	4.52	3.1–7.1	20.03	19.5–20.3	20.98	20.9–21.0
Sunflower husk	Vitebsk oil extraction plant, Belarus	5	2.97	2.6–3.5	20.81	20.6–21.0	21.51	21.2–21.8
Sunflower husk pellets		1	5.99		20.54		21.85	
Sunflower husk oilseed	Nikolaev region, Ukraine	1	5.98		21.55		22.93	
Flax shive / sunflower husk (50 %)	Orsha linin mills, Belarus	1	5.29		20.34		21.48	
Flax shive / sunflower husk (30 %)		1	4.46		20.19		21.13	
Flax shives spinning waste / briquettes		3	8.48	7.1–10.9	20.77	20.0–21.9	22.69	22.0–23.7
Flax shives		1	2.03		19.56		19.97	
	Pruzhany flax mill, Belarus	1	1.85		20.35		20.74	
	Slonim flax mill, Belarus	1	13.85		17.21		19.98	
Flax shives briquettes	Postavy flax plant, Belarus	1	1.97		20.01		20.42	
Flax shives pellets	Grogno/Vitebsk region, Belarus	6	6.56	2.7–19.9	19.23	16.7–20.3	20.59	19.7–20.9
	Orsha boiler-house, Belarus	1	3.89		20.27		21.09	
Sugar beet pulp pellets	Gorodeya / Skidel sugar factory, Belarus	6	3.61	3.2–4.2	17.79	17.6–18.1	18.40	18.2–18.8
Olive stone shells	n.d.	2	0.67	0.6–0.7	20.34	20.3–20.4	20.48	20.5–20.5

n.d. no date. n number of samples, Δ the interval from minimum to maximum values.

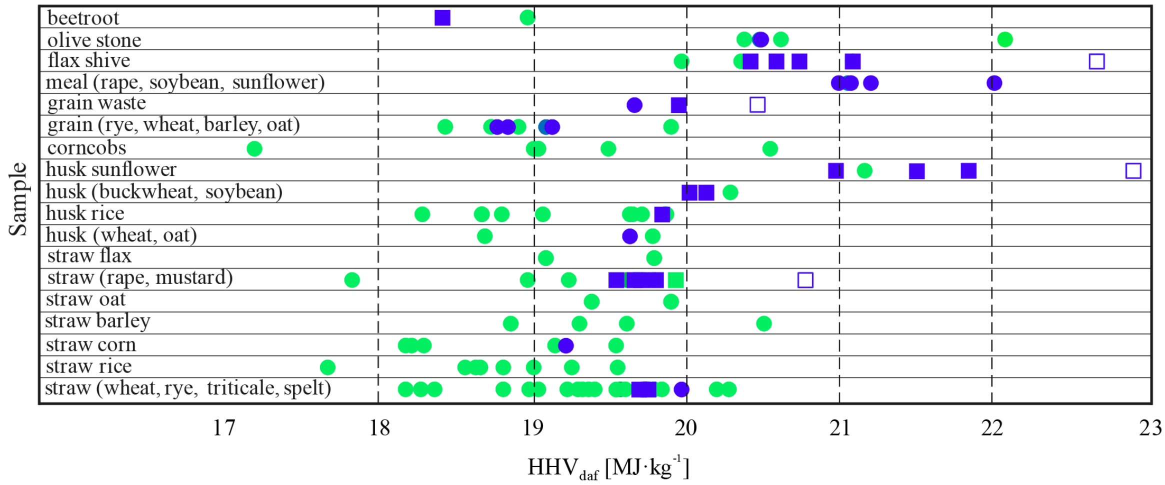

Fig. 1. Higher heating value on dry and ash free basis. Experimental data (●), (■) pellets/ briquettes, (□) with additives. Literature data (●), (■) pellets

Table 3. **Ash content on dry basis (A_d, %)**

Sample	550 °C, 4 h	600 °C, 4 h	Difference	Repeatability limit ISO 18122
Flax shives	5.88 (0.11)	5.32 (0.20)	–0.56	0.56
	3.44 (0.03)	3.34 (0.03)	–0.10	0.34
Rape straw	7.38 (0.09)	6.82 (0.12)	–0.56	0.71
Wheat straw	9.56 (0.09)	9.29 (0.01)	–0.27	0.94
Sugar beet pulp	3.81 (0.07)	3.52 (0.17)	–0.29	0.37

In parentheses are the repeatability values.

and/or adaptation in changing environmental conditions. The highest variability of HHV_{daf} is observed for individual plant parts: bark, leaves, fruits (seeds, shells), through which communication with the environment is translated. The smallest variation in HHV_{daf} accounts for the largest part of the plant, i.e. the trunk or stem.

The values of HHV_{daf} for agricultural biomass, short rotation forestry, hardwood and softwood, calculated according to [37] are (19.46 ± 1.12), (20.13 ± 0.80), (20.16 ± 0.56) and (20.53 ± 0.80) MJ kg^{-1}, respectively. It can be seen that in the series agricultural biomass – short rotation forestry – hardwood the value of HHV_{daf} increased by 0.7 MJ kg^{-1}, which is due to the accumulation of carbon during the life of the plant. The high variability of the average value (20.1 ± 1.7) MJ kg^{-1} confirms that it is impossible to establish the basic value of HHV_{daf} for all types of biomass with an error of less than ±8 %.

Galhano dos Santos et al. [38] proposed a hierarchical cluster analysis based on the ultimate data (C, H, O, N, S), which then used to estimate the HHV of a sample according to its position within the cluster. The samples are grouped in clusters in terms of their "similarity". In the present work, we will take as the basis the HHV_{daf}, the value of which for agricultural biomass will be estimated in different ways.

The basic value of HHV_{daf} for agricultural biomass. The HHV_{daf} value = (19.46 ± 1.12) MJ kg^{-1} for 23 agricultural biomass calculated from [37] data correlates with the similar value (19.7 ± 2.0) MJ kg^{-1} for 128 agricultural wastes of northern Portugal calculated from [9].

The HHV_{daf} value is a free term in the equations from Table 4. For different types of biomass, HHV_{daf} values vary between 2.1 (18.96 to 21.04) MJ kg^{-1}, which is, on average, (19.88 ± 0.60) MJ kg^{-1}.

The aim of the work was to calculate HHV_{daf} as the sum of HHV_{daf} of the main components of biomass, taking into account their percentage content. For this purpose there were used HHV_{daf} (in MJ kg^{-1}) for cellulose (17.36), hemicelluloses (17.54) and lignin (25.0) [43] taking into account their content, normalized to 100 % [44]. Thus, for 115 samples of 53 species of herbaceous and agricultural biomass containing (in %) 46.1 of cellulose, 30.2 of hemicelluloses and 23.7 of lignin [44], the calculated average $HHV_{ef,daf}$ value was 19.23 MJ kg^{-1}. The calculated $HHV_{ef,daf}$ values for straw of most crops are the same (in MJ kg^{-1}): barley straw (19.08), oat

Table 4. **Equations for higher heating value calculation on dry basis (HHV_d, MJ kg^{-1})**

$HHV_d = HHV_{daf} - aA_d$	R^2	Sample	Ref.
$HHV_d = 18.960 - 0.22527A_d$	0.88	Rice straw and wheat straw	[39]
$HHV_d = 19.24 - 0.22A_d$	0.58	Biomass	[40]
$HHV_d = 19.246 - 0.196A_d$	0.89	Field crops (straws)	[18]
$HHV_d = 19.914 - 0.2324A_d$	0.63	Biomass	[41]
$HHV_d = 20.067 - 0.234A_d$	0.73	All biomass	[18]
$HHV_d = 20.086 - 0.261A_d$	0.91	Greenhouse crop	[42]
$HHV_d = 21.042 - 0.282A_d$	0.71	Food and fibre processing wastes	[18]

straw (19.10), rape straw (19.09), rye straw (18.99), triticale straw (19.00), wheat straw (19.13), corn stovers (19.13) coincide with the experimental value (19.03) for rape straw [43]. The lowest (18.57) and the highest (20.13) $HHV_{ef,daf}$ values were obtained for rice straw and legume straw, respectively. This is due to the lowest (14.9 %) and highest (35.3 %) lignin content, on the one hand, and the highest A and lowest extractives content, on the other hand, respectively. Most importantly, the average value of $HHV_{ef,daf}$ for straw of 19.19 MJ kg^{-1} is the same as the average value for herbaceous and agricultural biomass of 19.23 MJ kg^{-1}. Adding to which the contribution of extractives 0.38 MJ kg^{-1} taken from [43] gives HHV_{daf} = 19.6 MJ kg^{-1}.

The average value of HHV_{daf} for agricultural biomass samples from Fig. 1, except for samples with additives, is (19.58 ± 0.91) MJ kg^{-1}. The frequency histogram HHV_{daf} for the same samples indicates that 11% of them are between 18.15 and 18.65 MJ kg^{-1}, and 82 % are between 18.65 and 20.61 MJ kg^{-1} (Fig. 2, above). This asymmetry in the probability density of the distribution is especially noticeable for straw samples (Fig. 2, below), which is related to the prevalence of "underestimated" values of HHV_{daf} in the literature and "overestimated" values of HHV_{daf} for pellets.

This analysis allows us to take the basic value HHV_{daf} for agricultural biomass equal to (19.6 ± 0.6) MJ kg^{-1}. The maximum error of the experimental determination of HHV_{daf} is ±0.3 MJ kg^{-1}. It is calculated based on the reproducibility limit from ISO 18125 for HHV_d, equal to 0.4 MJ kg^{-1} and the reproducibility limit from ISO 18122 for A_d, equal to 2.0 at A_d = 10 %.

The basic value is the average HHV_{daf} value for all agricultural biomass species or the plant as a whole. At the same time, individual species of agricultural biomass or plant parts have HHV_{daf} that differ from the basic value and are conveniently represented as intervals of variation of HHV_{daf}. Differences are due to a change in the ratio of components in the lignin-carbohydrate matrix or in the extract during crop processing. Thus, HHV_{daf} is reduced by the mono-, di and polysaccharides such as fructose, sucrose, glucose, cellulose, starch, pectin, but is increased by lignin, proteins, oils, resin acid, terpens and et al. For example, from the flax straw with HHV_{daf} = 19.8 MJ kg^{-1} [1], the flax fiber (richer in cellulose) with HHV_{daf} = 17.8 MJ kg^{-1} is separated and the flax shive (richer in lignin) with HHV_{daf} = 20.5 MJ kg^{-1} is remained.

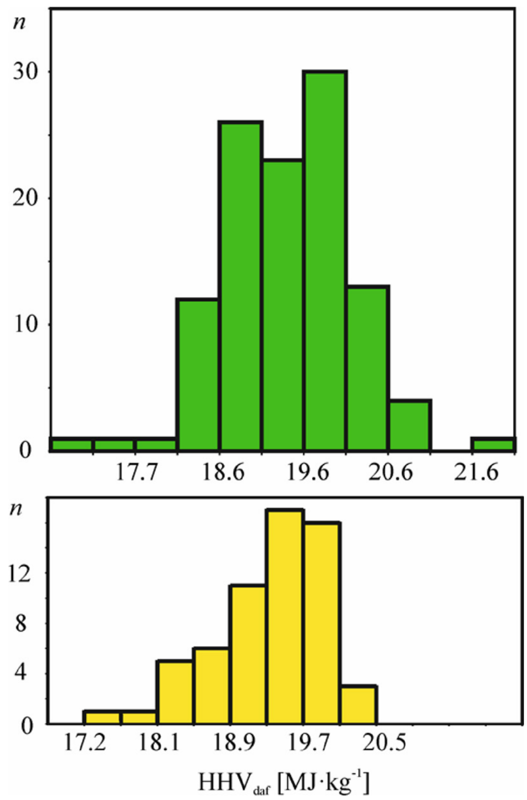

Fig. 2. Higher heating value on dry and ash-free basis. Histogram for samples (n = 112) of agricultural biomass (higher) and for samples (n = 60) of straw (below)

***HHV_{daf}* *variation for certain types of agricultural biomass*.** In practice, the value of HHV_{daf} is a benchmark for identifying and verifying data on solid biofuels from agricultural biomass. For a more accurate estimation, the HHV_{daf} intervals for certain types of agro-residues should be established.

The literature values of HHV_{daf} for straw vary in the wide range 3.7 (16.85 to 20.55) MJ kg^{-1} (Table 1) and average (19.13 ± 0.72) MJ kg^{-1}. Experimental values for straw rape, wheat, rye, corn, triticale from Belarus vary in the narrow range 0.7 (19.21 to 19.90) MJ kg^{-1} (Table 2) and average (19.47 ± 0.35) MJ kg^{-1}. The proposed range of HHV_{daf} variation for straw is from 19 to 20 MJ kg^{-1}. The HHV_{daf} values for straw (rape, wheat, triticale) pellets are 0.13–0.20 MJ kg^{-1} higher than for straw (rape, wheat, triticale), respectively (Table 2). A similar difference (0.19 MJ kg^{-1}) can be traced from the literature data for rapeseed straw and rape straw pellets (Table 1). The higher values of HHV_{daf} for pellets are due to "light" carbonization (carbon content increased by 0.2–0.5 %) of raw materials in the process of pelletizing. The HHV_{daf} values for the 12 straw rape pellets (Table 2) vary within a narrow range of 19.5 to 20.0 MJ kg^{-1}. Going beyond the upper limit of the HHV_{daf} interval for 5 similar samples 20.4–21.3 MJ kg^{-1} indicates that they contain rapeseed oil cake with HHV_{daf} = 31.4 MJ kg^{-1}.

The HHV_{daf} = 18.40 MJ kg^{-1} for sugar beet pulp pellets derived from waste sugar production is lower than the basic value due to the high content (up to 50 %) of pectins having a low HHV_d = 13.73 MJ kg^{-1} [20] or HHV_{daf} = 14.9–16.3 MJ kg^{-1} [46]. Rye seed (18.76) and small barley seed (19.12), as well as grains of other cereals, have HHV_{daf} values at the lower limit of the basic value range, which is associated with high (over 50 %) content in the endosperm of seeds of starch with HHV_{daf} = 17.1–17.3 MJ kg^{-1} [46]. The values of HHV_{daf} (in MJ kg^{-1}) for grain hulling waste (19.12), oat husk (19.63) and mail polishing waste (19.66), rice husk pellets (19.84) correspond to the basic value. The slight increase in HHV_{daf} for buckwheat husk pellets (20.02) and soybean pellets (20.12) is explained by pelletizing of husks with higher lignin content (buckwheat) with HHV_d = 25.0 MJ kg^{-1} [43] or proteins (soybean) with HHV_d =24.1 MJ kg^{-1} [46], respectively. The overestimated HHV_{daf} values for malt sprouts (20.41 MJ kg^{-1}) are explained by the high (over 30 %) protein content. Even higher HHV_{daf} values of 21.0–22.0 MJ kg^{-1} are observed for meals (rape, soybean, sunflower), which, with a similar protein content, contain significantly less mono- and disaccharides compared to sprouts. Abnormally high HHV_{daf} values for rapeseed spring (29.53) and rapeseed winter (30.51) are directly proportional to their oil content of 41.64 and 48.32 %, respectively, having HHV_{daf} = 39.59 MJ kg^{-1} [45].

Flax shives are the residue after separation of low-energy cellulose fibers, which has an increased lignin content and corresponding values of HHV_{daf} = 20.0–21.1 MJ kg^{-1} (Tables 1, 2) exceeding the upper limit of the basic value. Adding 50% sunflower husk to flax shives increases the HHV_{daf} value to 21.5 MJ kg^{-1}. Values above 22.0 MJ kg^{-1} for industrial flax shive spinning waste indicate the ingress of oiling agents used in the spinning machines into the flax shives.

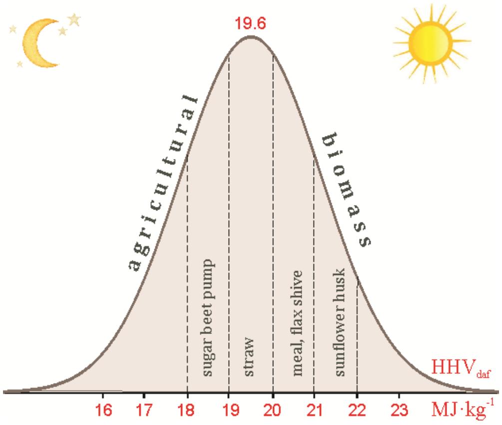

Fig. 3. Higher heating value on dry and ash-free basis. The basic value and intervals for certain types

The sunflower husk is characterized by abnormally high HHV_{daf} values from 21.2 to 21.9 MJ kg^{-1}, which is explained by the presence of wax. A further increase in HHV_{daf} to 22.9 MJ kg^{-1} is explained by the residual content of sunflower oil in the husk. And the value of HHV_{daf} = 26.5 MJ kg^{-1} [24] from Table 1 means that it is not sunflower husk but sunflower cake.

Conclusions. The concept of a unified value of HHV_{daf} for plants was proposed. It is substantiated to take the average value HHV_{daf} = 19.6 MJ kg^{-1} for agricultural biomass as a baseline for identifying or verifying data on solid biofuel. The intervals of HHV_{daf} variation (in MJ kg^{-1}) from 18 to 19 for sugar beet pulp, from 19 to 20 for straw (wheat, rye, corn, barley, rape, oat, flax), from 20 to 21 for meal (rape, soybean, sunflower) and flax shives, from 21 to 22 for sunflower husk, were established (Fig. 3).

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Information about the authors

Maksimuk Yury V. – Ph. D. (Chemistry), Associate Professor, Leading Researcher. Research Institute for Physical Chemical Problems of the Belarusian State University, (14, Leningradskaya Str, 220006, Minsk, Republic of Belarus). E-mail: maksimuk@bsu.by

Kursevich Vera N. – Researcher. Research Institute for Physical Chemical Problems of the Belarusian State University (14, Leningradskaya Str, 220006, Minsk, Republic of Belarus). E-mail: kursevich@bsu.by

Korsakova Alina S. – Junior Researcher. Research Institute for Physical Chemical Problems of the Belarusian State University (14, Leningradskaya Str, 220006, Minsk, Republic of Belarus). E-mail: a.korsakova@mail.ru

Antonova Maria V. – Ph. D. (Biology), Senior Researcher. Research Institute for Physical Chemical Problems of the Belarusian State University (14, Leningradskaya Str, 220006, Minsk, Republic of Belarus). E-mail: mariantonova@gmail.com

Krouk Vladimir S. – Ph. D. (Chemistry), Researcher. Research Institute for Physical Chemical Problems of the Belarusian State University, (14, Leningradskaya Str, 220006, Minsk, Republic of Belarus). E-mail: krouk@bsu.by

Информация об авторах

Максимук Юрий Владимирович – канд. хим. наук, доцент, вед. науч. сотрудник. НИИ физико-химических проблем БГУ (ул. Ленинградская, 14, 220006, Минск, Республика Беларусь). E-mail: maksimuk@bsu.by

Курсевич Вера Николаевна – науч. сотрудник. НИИ физико-химических проблем БГУ (ул. Ленинградская, 14, 220006, Минск, Республика Беларусь). E-mail: krouk@bsu.by

Корсакова Алина Сергеевна – мл. науч. сотрудник. НИИ физико-химических проблем БГУ (ул. Ленинградская, 14, 220006, Минск, Республика Беларусь). E-mail: a.korsakova96@mail.ru

Антонова Мария Викторовна – канд. биол. наук, ст. науч. сотрудник. НИИ физико-химических проблем БГУ (ул. Ленинградская, 14, 220006, Минск, Республика Беларусь). E-mail: mariantonova@gmail.com

Крук Владимир Сергеевич – канд. хим. наук, науч. сотрудник. НИИ физико-химических проблем БГУ (ул. Ленинградская, 14, 220006, Минск, Республика Беларусь). E-mail: krouk@bsu.by