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PREDICTION OF HIGHER HEATING VALUE OF RAW MATERIALS AND BIOCHAR

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Abstract. One of the most essential characteristics of biochar (charcoal) is its higher heating value. The higher heating value for the dry ashless state of 35 samples of raw vegetable materials and charcoal was determined to establish the dependencies between the quality of the raw material and the produced biochar samples. Biochar production was carried out using modernized equipment under the patented technology. Mathematical and graphical dependencies of the experimental and calculated higher heating values for the vegetable raw materials to produce pyrolysis gas and charcoal were established. The results indicate the acceptability of the established dependencies and allow the conclusion about the possibility of predicting the higher calorific properties of plant raw materials and charcoal. The obtained data have considerable practical significance. The use of the results proposed by the authors will significantly improve the biowaste processing process in industry and increase the share of the circular economy.

Keywords: biomass, charcoal, higher heating value, mathematical dependencies, proximate and ultimate analysis.

1. Introduction

Non-conventional and renewable energy sources (NCRES) are common for modern energy. Using NCRES contributes to solving not only the issues of effective energy supply but also many environmental, economic, and social problems. NCRES are also one of the advantages of the global low-carbon development policy and a means of preventing the increase in carbon dioxide (CO_2) emissions into the environment and avoiding the consequences of the greenhouse effect. The New Energy Strategy (NES) of Ukraine until 2035 "Security, Energy Efficiency, Competitiveness" envisages a wider use and increase of all types of renewable energy in the total primary energy supply, which in the future will lead to a decrease in environmental pollution and help ensure guaranteeing energy independence and secure in the short- and medium-term perspective. Cabinet of Ministers of Ukraine according to the NES program, renewable energy is planned to increase to 12 % of the total primary energy supply (TPES) and at least 25 % by 2035 (including all hydro-generating and thermal energy)[1, 2].

Currently, organic raw materials (biomass) rank fourth in importance among energy sources in the world; their consumption is approximately 14 % of the total consumption of primary energy carriers in the world (in developing countries, it is more than 30 %, sometimes up to 50–80 %). In developed European countries, the share of biomass in the total consumption of primary energy carriers is much smaller and amounts to slightly more than 3 %. Combustion of wood waste in modern developed equipment belongs to environmentally acceptable methods of using industrial waste. According to Plachkova *et al*.[3], in Ukraine, the annual volume of wood harvested is 10308.7 thousand m^3, of which 7300 thousand m^3 (4391.5 thousand tons) are unused and can be taken for heat production. That is why modern energy problems can be solved with the rational use of all available fuel and energy sources, among which wood biomass has a prominent place. This is indicated by Rahimi *et al*.[4].

When wood is burned, the amount of CO_2 that was removed during photosynthesis is released. Using biomass, compared to, for example, coal, for direct energy production creates less pressure on the environment and is more ecological. According to Roni *et al*.,[5] combustion of biomass produces about 0.2 % sulfur and from 3 % to 5 % ash, compared to 2–3 % and 10–15 % for coal, the rest is

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mainly carbon dioxide. In addition, biomass ash can be returned to the soil, which ensures a closed cycle of biogenic elements. In terms of carbon dioxide, biomass is practically neutral, that is, during the growth period, plants take solar energy, water, and carbon dioxide, produce oxygen, and form carbon during photosynthesis; the process is reversed during combustion: oxygen is taken, and heat, water, and carbon dioxide are produced. When 1 kg of dry biomass (wood) is formed, 1.83 kg of CO_2 is taken, and the same amount is produced during its decomposition (oxidation and combustion). The same model is seen for CO_2 when considering oil, coal, and gas, but rebalancing CO_2 takes several million years. Therefore, wood is an environmentally friendly energy carrier.

On the other hand, it is undesirable to use wood for burning due to the need to preserve forests. Therefore, the search for new sources as ecologically "clean" as wood is extremely relevant. One of the alternatives is biochar obtained from various types of waste. Considering this, numerous studies, as publications by Funke and Ziegler[6], Zhang *et al.*[7], Pambudi *et al.*[8], Su *et al.*[9] and Ngambia[10], are very relevant. Also, this information can be useful for obtaining pyrolysis gas, charcoal, and torrefied biomass according to Wang *et al.*[11], Khan *et al.*[12], Gan *et al.*[13], and Ni *et al.*[14].

The researchers Durango Padilla *et al.*[15], Daba and Hailegiorgis[16] studied the possibility of replacing coal used in blast furnaces with biochar obtained from agricultural waste. In this study, the researchers examined biomass and coal and investigated the effect of pyrolysis temperature on combustion parameters and physicochemical properties of biochar. The results of these studies showed that the registered materials can be potential sources of raw materials for the production of biochar. However, the quality and properties of the obtained products depend on the nature of the raw materials and pyrolysis conditions.

One of the effective ways to improve solid biofuel is through torrefaction. To predict the torrefied biomass properties as a result of torrefaction using biomass characteristics and torrefaction conditions as input variables, in addition to experimental studies, various forecasting and analysis methods are widely used (Zhang *et al.*[7], Pambudi *et al.*[8], Su *et al.*[9], Daba and Hailegiorgis[16], Kaya[17]). So, Pambudi *et al.*[8] used statistical analysis to investigate the effect of both inert and oxidizing conditions on the biochar properties obtained by torrefaction of used coffee grounds. The effect of temperature and residence time during torrefaction was also considered. The fuel analyses, such as torrefaction index, high heating value, thermosgravimetric analysis, hygroscopicity, proximate characteristics, and Fourier-transform infrared spectroscopy, were conducted. Su *et al.*[9] proposed six machine learning models developed by the authors to predict the biochar characteristics during the dry torrefaction of lignocellulosic biomass, using biomass characteristics and torrefaction conditions as input variables. The authors also developed software to accurately determine the element, yield, and higher heating value of biochar. The results allow a deeper knowledge of the main aspects, factors, and their interaction affecting the torrefaction process and biochar properties. Wang *et al.*[18] proposed a new idea to optimize the directional preparation process of biochar. The authors used extreme gradient boosting regression and an artificial neural network for prediction based on biomass characteristics and pyrolysis conditions. Also, empirical correlations were used for comparison. The PySimpleGUI library was used to develop a program for predicting the higher heating value of biochar.

Charcoal also has a wide range of applications and is important for many industries. Pyshyev *et al.*[19] analyzed in detail the use of charcoal for various industries. There was a discussion of the influence of the raw material nature (wood or agricultural waste), its characteristics (size, physical properties, chemical composition), and the carbonation temperature, heating rate, oxygen level, and pressure on the yield and quality of charcoal. The charcoal production technologies (Lambiotte, DPC, Carbonex) were analyzed.

Kaya *et al.*[17] and Hu *et al.*[20] presented a statistical analysis of the dependence between indicators of proximate and ultimate analyses, as well as the higher heating values of 362 samples of vegetable raw materials for producing pyrolysis gas, charcoal, and torrefied biomass. It was established that the carbon and oxygen content are the most considerable and related biomass parameters. The linearity of the carbon content dependence on the oxygen content, with the coefficient of determination $R^2 = 0.898$, as well as the quadratic dependence of the atomic ratio of carbon to oxygen (C/O) on the carbon content, with the coefficients $R^2 = 0.946$ and $R^2 = 0.965$, respectively, are demonstrated. Mathematical and graphical dependencies have been developed that make it possible with high accuracy (R^2>0.849) to predict higher heating values of vegetable raw materials based on the data of its ultimate analysis, namely: by the content of carbon (1), oxygen (2) and the atomic ratio of carbon to oxygen (3):

$$HHV = 0.0066 \cdot (\mathrm{C}^{\mathrm{daf}})^2 - 0.3549 \cdot \mathrm{C}^{\mathrm{daf}} + 21.124 \quad (1)$$

$$HHV = 0.0055 \cdot (O_d^{daf})^2 - 0.569 \cdot O_d^{daf} + 42.294 \quad (2)$$

$$HHV = -0.3215 \cdot \left(\frac{\mathrm{C}}{\mathrm{O}}\right)^2 + 5.2847 \cdot \left(\frac{\mathrm{C}}{\mathrm{O}}\right) + 12.53 \quad (3)$$

where HHV is the higher heating value on a dry ashless state, MJ/kg; C^{daf} and O_d^{daf} is the content of carbon and oxygen, respectively, in the dry ashless state, %; $\frac{\mathrm{C}}{\mathrm{O}}$ is an atomic ratio.

In addition, the authors Hu *et al.* [20], Malik *et al.*[21] presented a statistical analysis of the dependence between indicators of proximate and ultimate analyses, and also the higher heating values of 73 charcoal samples. The authors established that the indicators of carbon and oxygen content are most similar in the charcoal organic mass ($R^2 = 0.987$). The dependence of the atomic ratios (C/H and C/O) on the carbon and oxygen content has a graded nature, as well as the dependence of the higher heating value on these ratios. The prediction of the higher heating value of vegetable raw materials with the highest accuracy can be done by the determination of the volatile matter (Eq. (4), $R^2 = 0.8002$) and non-volatile carbon (Eq. (5), $R^2 = 0.8002$), or based on the carbon content (Eq. (6), $R^2 = 0.6928$), oxygen (Eq. (7), $R^2 = 0.7081$), atomic ratios of carbon to oxygen (Eq. (8), $R^2 = 0.6358$) and carbon to hydrogen (Eq. (9), $R^2 = 0.4886$) in charcoal.

$$HHV = -0.1777 \cdot V^{daf} + 35.609 \quad (4)$$

$$HHV = 0.1777 \cdot FC^{daf} + 17.836 \quad (5)$$

$$HHV = 0.2676 \cdot C^{daf} + 8.6568 \quad (6)$$

$$HHV = -0.3051 \cdot O_d^{daf} + 34.888 \quad (7)$$

$$\text{HHV} = 24.451 \cdot \left(\frac{C}{O}\right)^{0.0963} \quad (8)$$

$$HHV = 27.265 \cdot \left(\frac{C}{H}\right)^{0.1244} \quad (9)$$

where V^{daf} is a volatile matter on a dry ashless state; %; FC^{daf} is a non-volatile carbon to a dry ashless state, %; $\frac{C}{H}$ is an atomic ratio.

The development of mathematical dependencies that make it possible to predict the higher heating values for carbon materials (coal, coke) was also carried out in other works, such as Kambo and Dutta[22], Reza *et al.*[23], and Libra[24].

So, one of the most important indicators of biochar is its heat of combustion. Prediction of this indicator based on the raw material characteristics makes it possible to effectively manage biochar production processes and ensure the competitiveness of the obtained products. However, most of the obtained results (including the authors of this manuscript) were carried out using several types of raw materials in laboratory conditions. Therefore, the purpose of the research is to verify previously developed regression equations by the authors of this manuscript for determining the higher heating value on a dry ashless state of vegetable raw materials and charcoal using various types of raw materials and obtaining biochar at a modern industrial unit.

2. Materials and Methods

2.1. Materials

35 samples of vegetable raw material were used (unprocessed wood, processed wood, straw, grass and plants, husks, shells, pits, seaweed, and waste from the olive industry). Data of proximate (W^a, A^d, S^d_t, V^{daf}, FC^{daf}), ultimate (C^{daf}, H^{daf}, N^{daf}, O^{daf}_d), and calorimetric (HHV) analyses of vegetable raw materials are given in Table 1.

Table 1. Data of technical and elemental analyses of vegetable raw material samples

No.	*Origin of raw materials*	W^a, wt. %	A^d, wt. %	V^{daf}, wt. %	FC^{daf}, wt. %	C^{daf}, wt. %	H^{daf}, wt. %	N^{daf}, wt. %	S^{daf}, wt. %	O_d^{daf}, wt. %	***HHV***, MJ/kg
1	2	3	4	5	6	7	8	9	10	11	12
1	Shells	2.2	5.0	72.5	26.2	43.44	5.11	1.04	0.12	50.29	17.33
2	Straw	1.7	4.2	76.2	22.9	64.28	4.08	0.49	0.31	30.84	24.75
3	Unprocessed wood	1.8	4.3	89.1	10.5	46.26	6.13	0.98	0.24	46.39	18.44
4	Seaweed	1.4	3.1	82.1	17.4	48.33	9.22	1.26	0.16	41.03	20.10
5	Husks	1.6	5.4	92.6	7.1	52.31	6.47	0.55	0.06	40.61	21.15
6	Processed wood	2.6	2.1	87.2	12.6	68.98	5.93	0.22	0.24	24.63	29.24
7	Olive waste	3.0	1.4	72.1	27.6	78.12	11.24	0.37	0.28	9.99	34.08
8	Pits	2.1	1.8	72.3	27.2	54.66	5.12	2.08	0.33	37.81	21.71
9	Plants	1.5	1.3	80.5	19.3	48.9	6.27	1.39	0.59	42.85	19.64
10	Grass	1.2	4.9	84.6	14.7	73.11	4.86	0.62	0.14	21.27	30.05
11	Processed wood	1.1	3.0	84.5	15.1	51.52	9.10	1.06	0.27	38.05	21.92
12	Unprocessed wood	2.6	3.4	85.7	13.8	54.1	5.61	0.44	0.40	39.45	21.53

Continuation of **Table 1**

1	2	3	4	5	6	7	8	9	10	11	12
13	Husks	2.4	6.8	75.3	23.1	43.73	5.23	0.56	0.29	50.19	17.36
14	Seaweed	2.2	2.5	72.2	27.2	48.28	5.88	1.14	0.23	44.47	19.25
15	Straw	2.8	2.3	75.2	24.2	43.79	4.41	0.27	0.06	51.47	17.34
16	Pits	2.0	2.2	76.5	23.0	58.91	7.24	2.18	0.76	30.91	25.23
17	Shells	2.3	4.7	90.1	9.5	46.73	6.84	0.19	0.53	45.71	18.65
18	Plants	1.3	8.2	91.6	7.8	49.00	5.23	0.85	0.39	44.53	19.33
19	Grass	1.7	4.3	81.4	17.9	55.77	6.41	0.93	0.62	36.27	22.83
20	Olive waste	1.0	5.1	84.0	15.2	61.86	5.29	1.74	0.22	30.89	25.02
21	Unprocessed wood	1.7	2.9	90.8	9.0	44.58	5.22	0.25	0.34	49.61	17.62
22	Straw	1.6	3.6	81.1	18.2	50.78	4.74	0.87	0.18	43.43	19.84
23	Seaweed	1.4	3.6	92.8	6.9	49.6	6.13	0.64	0.29	43.34	19.81
24	Processed wood	1.0	2.1	80.5	19.1	43.72	8.11	1.21	0.26	46.7	17.47
25	Pits	3.0	3.4	83.2	16.3	49.56	5.15	2.05	0.45	42.79	19.67
26	Plants	2.5	5.5	74.7	24.0	49.00	7.73	0.38	0.41	42.48	19.96
27	Grass	2.1	5.4	83.5	15.7	52.69	5.01	0.98	0.08	41.24	20.70
28	Husks	1.0	6.3	90.8	8.6	46.13	6.95	0.31	0.20	46.41	18.41
29	Shells	1.8	7.2	91.4	8.1	69.95	4.87	1.06	0.37	23.75	28.46
30	Olive waste	1.0	2.8	79.8	19.6	49.21	7.02	0.51	0.26	43.00	19.88
31	Unprocessed wood	1.1	2.7	82.0	17.5	70.18	6.29	0.54	0.36	22.63	30.45
32	Processed wood	1.9	4.4	94.6	5.3	54.45	4.81	0.83	0.17	39.74	21.28
33	Straw	1.0	2.7	88.4	11.3	49.96	6.17	1.08	0.33	42.46	20.04
34	Pits	0.9	3.7	89.0	10.6	47.79	4.77	0.88	0.07	46.49	18.77
35	Grass	0.9	3.0	82.8	16.7	60.9	4.39	1.23	0.11	33.37	23.70
Average		1.8	3.9	83.2	16.3	53.73	6.09	0.89	0.29	39.00	22.03

2.2. Biochar production

The biochar was produced using bio-raw materials and waste at the continuous industrial installation of Greenpower LLC[25]. The installation is patented in Ukraine, Indonesia, Turkey, and the Philippines. The installation productivity is up to 50 tons/month.

The continuous industrial installation (Fig. 1) for the thermal processing of vegetable raw materials consists of a furnace body with a hopper in the upper part for loading raw materials into the working chamber, located in the central part of the furnace body. Stabilizing hopper to process raw materials located in the lower part of the furnace body. The working chamber of the furnace contains two vertical channels for the heat carrier and one vertical channel for the raw material, connected by the movement of heat carrier flow and made with the possibility to do the counter-current movement of the raw material and the heat carrier. At the same time, one wall of each heat carrier channel is the wall of the raw materials channel.

2.3. Analysis methods

The parameters of the quality of vegetable raw materials and biochar were established by the following documents of National Standard: CEN/TS 14774:2004 Methods for the Determination of Moisture Content: Oven Dry Method for moisture content (W^a); CEN/TS 14775:2004 Solid Biofuels: Method for the Determination of Ash Content for ash content (A^d); CEN/TS 15148:2005 Solid Biofuels: Determination of the Content of Volatile Matter for the yield of volatile matter (V^{daf}); CEN/TS 15104:2005 Solid Biofuels: Determination of Total Content of Carbon, Hydrogen, and Nitrogen. Instrumental Methods for the carbon (C^{daf}), hydrogen (H^{daf}), and nitrogen (N^{daf}) contents; CEN 15289:2006 Solid Biofuels: Determination of Total Content of Sulfur and Chlorine for the sulfur content; and CEN/TS 14918:2005 Solid Biofuels: Method for the Determination of Calorific Value for the gross calorific value (*HHV*).

Using the formula (10), the oxygen content (O^{daf}) was found

$$O^{daf} = 100 - C^{daf} - H^{daf} - V^{daf} - S^{daf}. \quad (10)$$

Although the oxygen content value is calculated, its significance for the formation of the higher heating value of plant material can be compared only with the carbon content, since its concentration can be almost 50 % or even more.

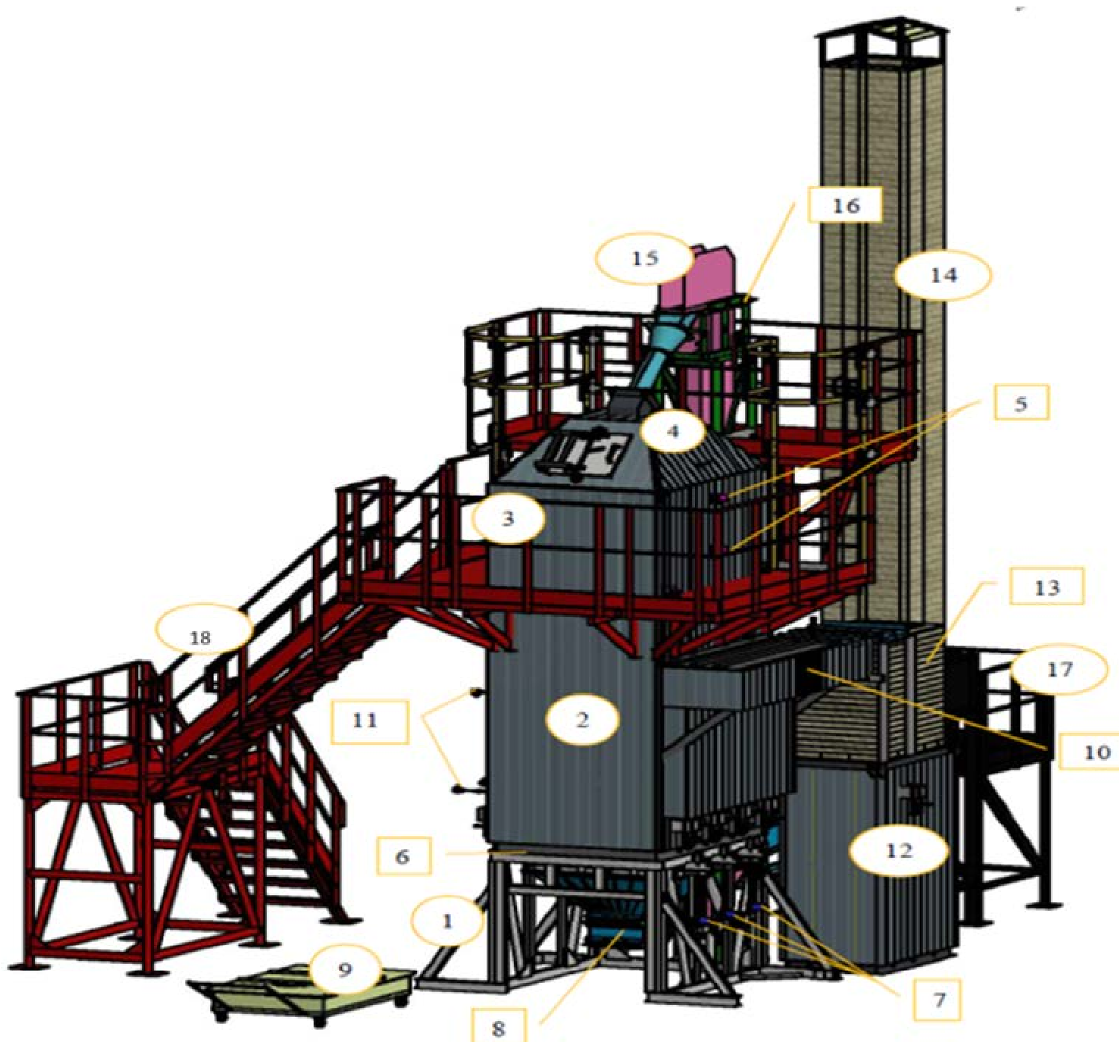

Fig. 1. Continuous industrial installation for thermal processing of plant raw materials:
1 – furnace base; 2 – furnace chamber; 3 – loading hopper; 4 – loading hopper hatch;
5 – level sensors; 6 – power supply device; 7 – power supply drive; 8 – stabilizing hopper;
9 – cart; 10 – the channel of the used heat carrier with a temperature sensor;
11 – temperature sensors of raw material channels; 12 – the lower part of the afterburner;
13 – the upper part of the afterburner; 14 – smoke pipe; 15 – noria; 16 – noria farm;
17 – storage hopper; 18 – stairs and service areas

3. Results and discussion

Table 2 presents the data of proximate, ultimate, and calorimetric analyses of charcoal samples obtained at the continuous-action installation from vegetable raw material samples, the quality indicators of which are listed in Table 1.

Figs. 2–4 show graphical dependencies of the experimental and calculated higher heating values of vegetable raw materials on C^{daf}, O_d^{daf}, and C/O content, respectively. Figs. 5–7 show the graphic dependencies between the experimental and calculated higher heating values of vegetable raw materials according to Eqs. (1–3), respectively.

Figs. 8–13 show the dependencies of the experimental and calculated higher heating values of the obtained charcoal on its V^{daf}, FC^{daf}, C^{daf}, O_d^{daf}, C/O and C/H content. Graphical dependencies between the experimental and calculated higher heating values of charcoal according to Eqs. (4–9) are presented in Figs. 14–19.

Table 3 presents the obtained mathematical dependencies of the experimental higher heating values of vegetable raw materials ((11)–(13)) and charcoal ((14)–(19)) on the calculated values and their statistical evaluation.

Table 2. Data of proximate, ultimate and calorimetric analysis of charcoal samples

No	W^a, %	A^d, %	V^{daf}, %	FC^{daf}, %	C^{daf}, %	H^{daf}, %	N^{daf}, %	S^{daf}, %	O_d^{daf}, %	***HHV***, MJ/kg
1	2.2	8.0	41.5	53.9	63.14	4.08	2.02	0.31	30.45	28.91
2	1.7	8.1	37.4	57.6	76.28	5.08	1.04	0.66	16.94	29.41
3	1.8	7.1	37.0	58.6	76.26	5.17	0.44	0.49	17.64	29.33
4	1.4	7.1	36.8	58.7	87.56	2.98	0.82	0.99	7.65	29.11
5	1.6	9.2	29.8	63.8	88.40	4.16	1.15	0.14	6.15	31.01
6	2.6	7.4	25.7	68.9	88.97	0.93	0.22	0.25	9.63	32.47
7	3.0	7.9	20.4	73.3	91.55	1.89	0.78	0.28	5.50	33.16
8	2.1	6.1	42.6	54.0	64.50	5.12	1.81	0.51	28.06	27.76
9	1.5	6.7	41.6	54.5	68.10	3.26	0.91	0.92	26.81	28.08
10	1.2	7.6	42.9	52.8	72.62	4.21	1.38	0.13	21.66	28.09
11	1.1	5.6	44.2	52.7	74.68	3.10	0.78	0.34	21.1	27.18
12	2.6	5.1	44.7	52.5	69.7	4.51	1.82	0.61	23.36	27.31
13	2.4	7.6	42.7	53.1	73.18	5.23	0.38	0.32	20.89	28.24
14	2.2	7.8	43.1	52.5	71.17	5.64	2.04	0.29	20.86	27.70
15	2.8	9.5	35.8	58.2	87.62	4.41	0.52	0.78	6.67	28.77
16	2.0	7.5	36.8	58.5	86.34	5.50	1.28	0.87	6.01	28.41
17	2.3	8.0	37.2	57.8	85.78	3.81	0.41	0.80	9.20	28.90
18	1.3	7.6	36.1	59.1	86.20	4.22	0.51	0.57	8.50	30.04
19	1.7	8.5	38.5	56.3	86.84	5.45	1.27	0.99	5.45	28.06
20	1.0	8.6	31.2	62.9	87.56	5.21	1.17	0.24	5.82	31.04
21	1.7	8.6	29.7	64.3	87.55	4.20	0.23	0.44	7.58	31.19
22	1.6	9.1	30.1	63.6	88.38	2.17	0.98	0.53	7.94	29.45
23	1.4	10.1	31.9	61.3	87.52	4.31	1.21	0.31	6.65	30.02
24	1.0	8.6	31.0	63.1	87.50	3.36	0.90	0.28	7.96	29.15
25	3.0	7.7	31.2	63.5	87.50	5.15	0.36	0.60	6.39	29.79
26	2.5	8.3	31.4	63.0	87.71	2.74	1.10	0.44	8.01	29.10
27	2.1	8.7	30.5	63.5	86.92	5.01	1.23	0.38	6.46	29.72
28	1.0	8.7	26.6	67.1	89.33	3.11	2.11	0.33	5.12	31.09
29	1.8	9.8	26.5	66.4	89.06	4.22	1.04	0.67	5.01	30.70
30	1.0	11.5	30.1	61.9	87.96	5.02	1.01	0.43	5.58	29.15
31	1.1	7.0	19.8	74.6	90.16	1.78	0.54	0.36	7.16	32.78
32	1.9	8.9	20.5	72.4	90.35	1.80	0.37	0.27	7.21	32.83
33	1.2	7.5	37.6	57.8	88.6	2.34	0.81	0.19	8.06	29.11
34	2.1	8.5	34.7	59.9	75.9	3.48	0.98	0.54	19.1	29.62
35	1.6	5.9	31.5	64.5	80.8	5.11	1.12	0.49	12.48	30.20
Average	1.8	8.0	36.9	55.4	82.6	3.94	0.99	0.48	12.09	29.62

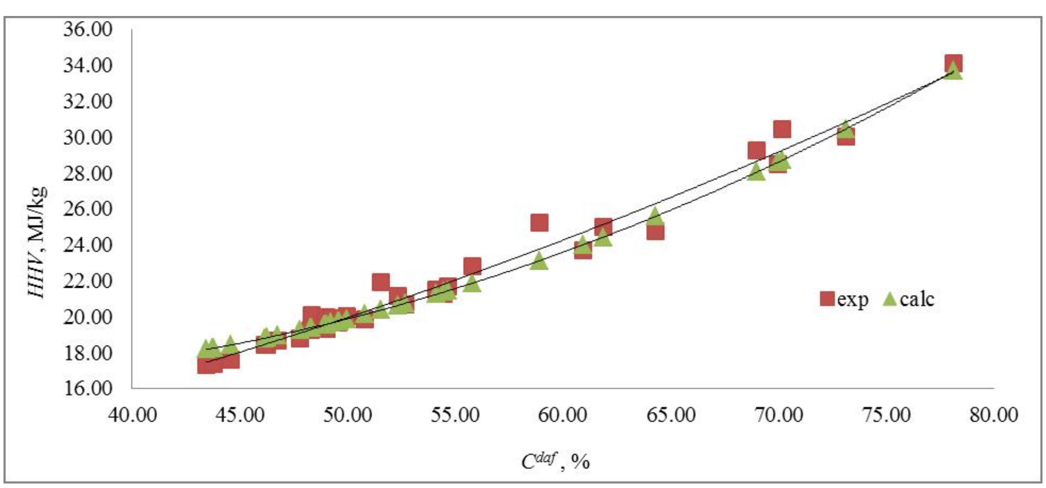

Fig. 2. Dependence between *HHV* and C^{daf}

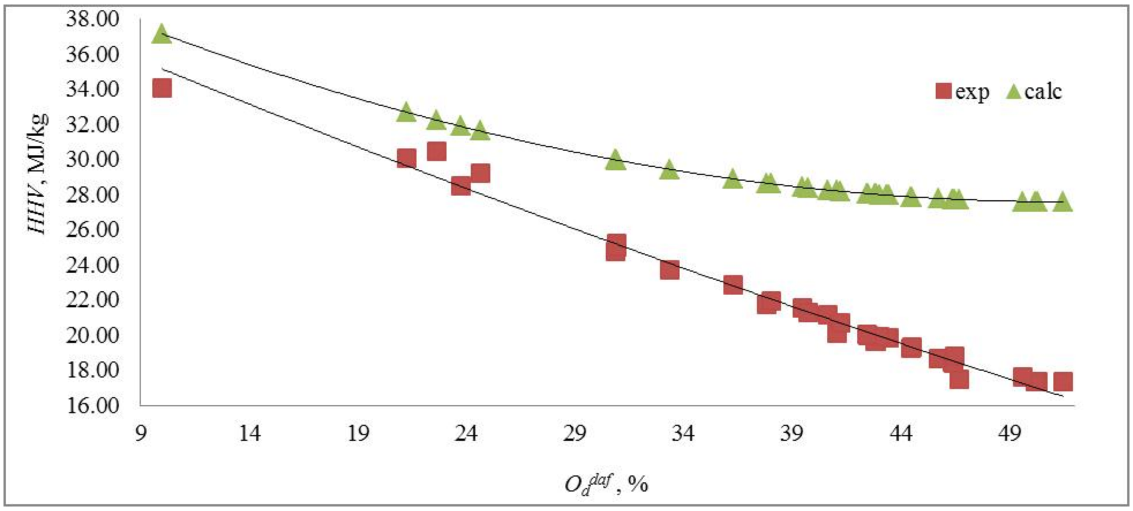

Fig. 3. Dependence between *HHV* and O_d^{daf}

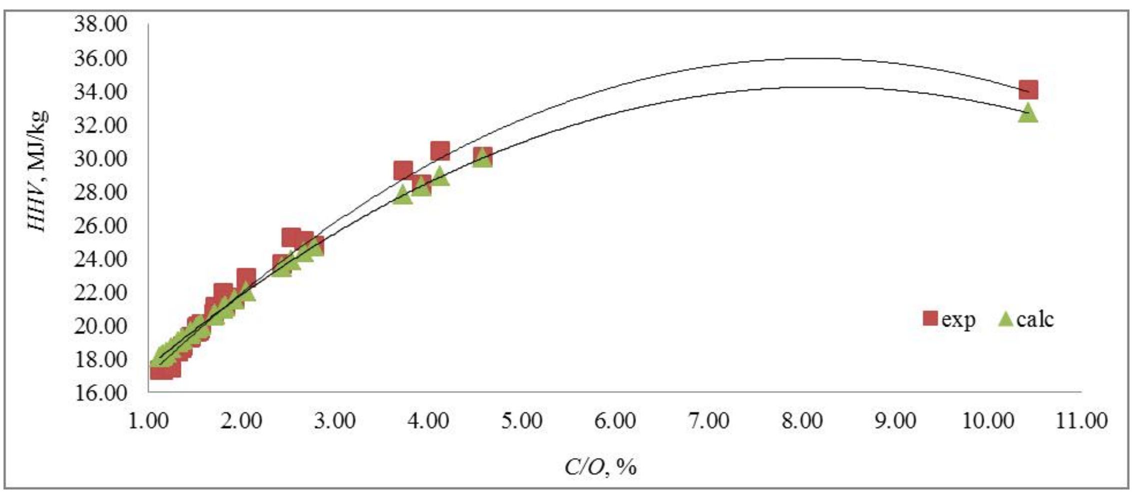

Fig. 4. Dependence between *HHV* and *C/O*

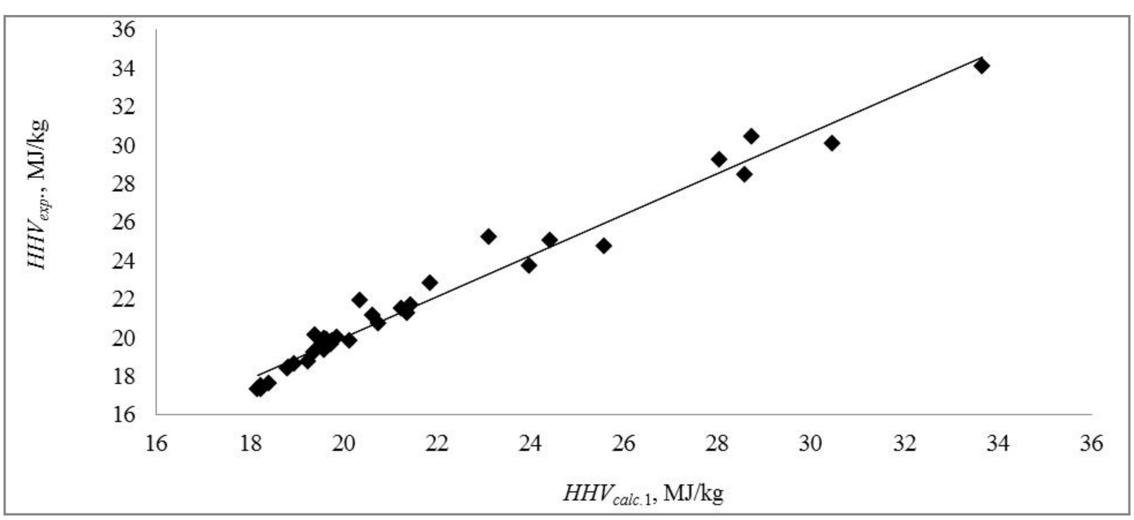

Fig. 5. Dependence between $HHV_{exp.}$ and $HHV_{calc.1}$

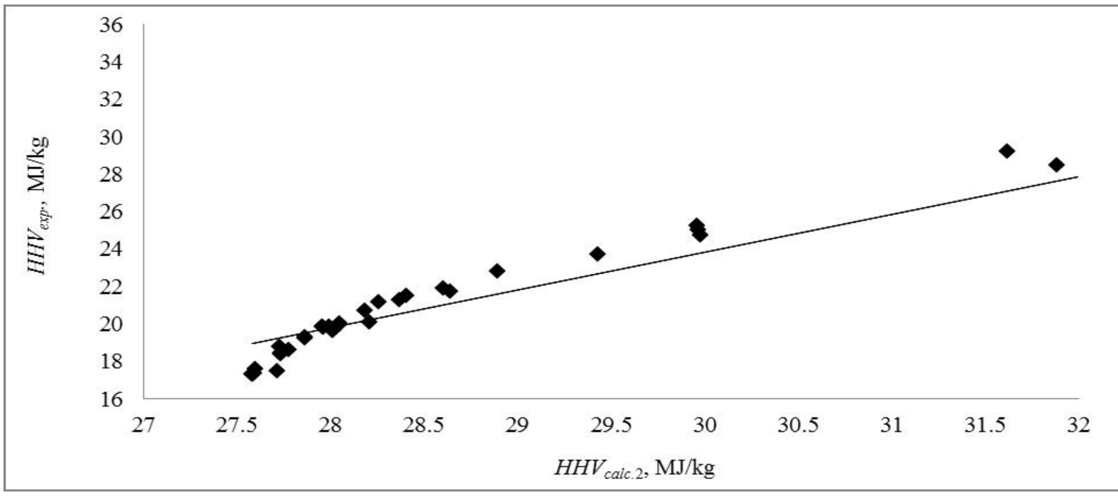

Fig. 6. Dependence between $HHV_{exp.}$ and $HHV_{calc.2}$

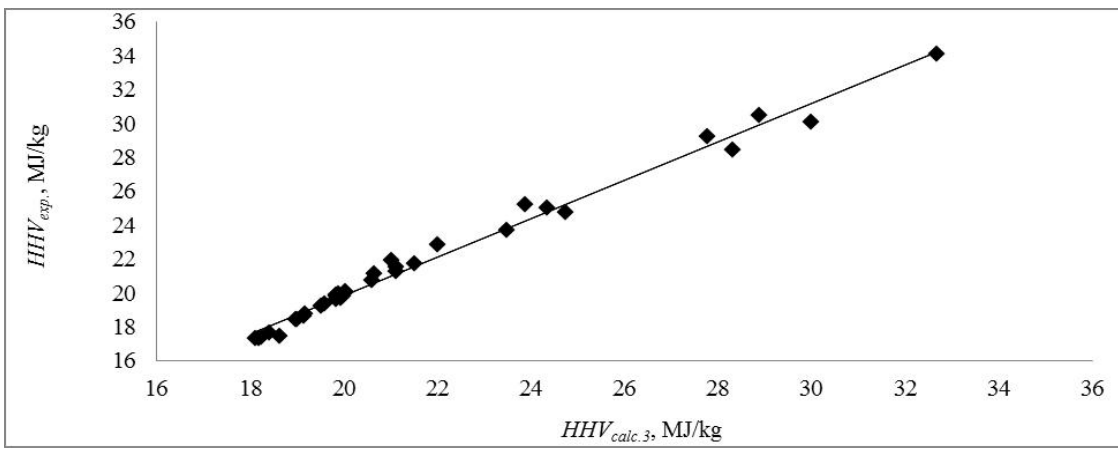

Fig. 7. Dependence between $HHV_{exp.}$ and $HHV_{calc.3}$

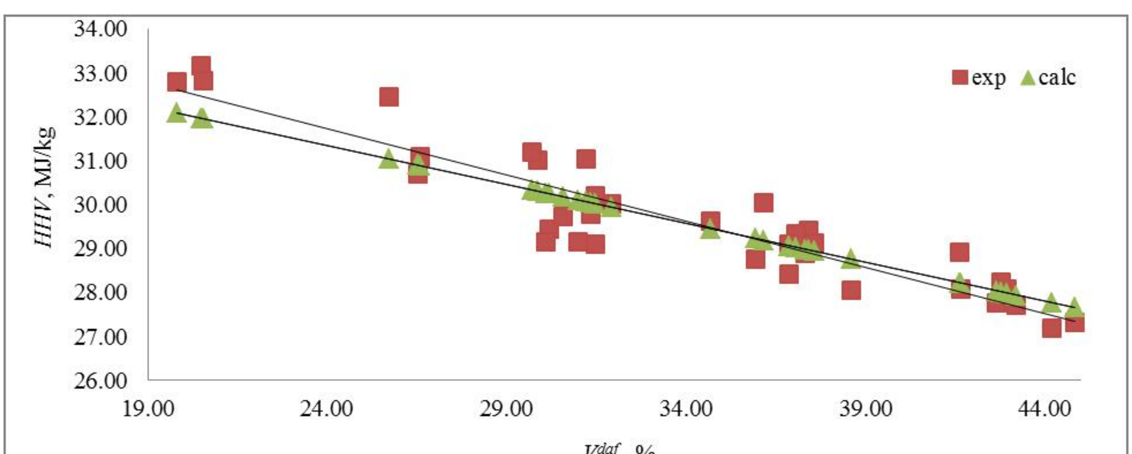

Fig. 8. Dependence of HHV on V^{daf}

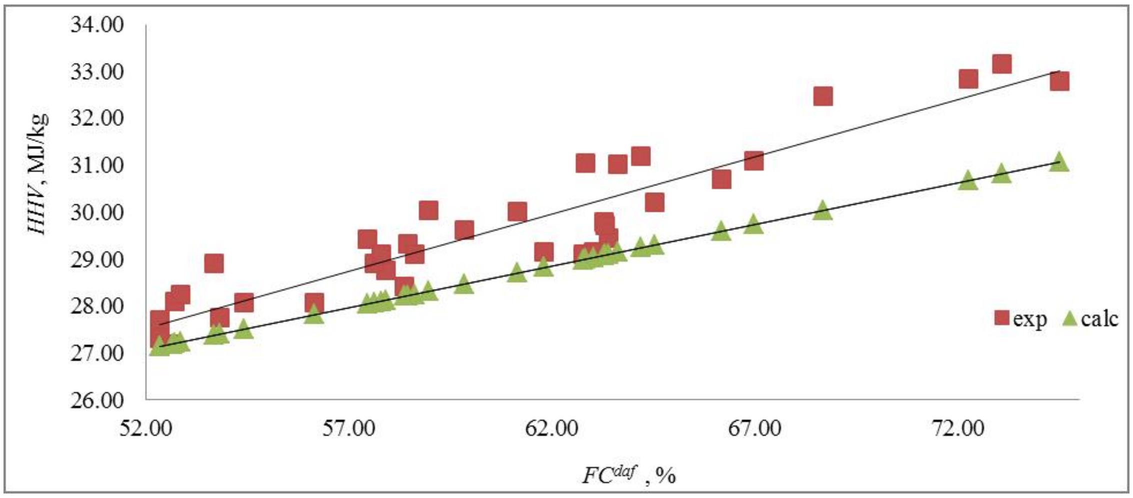

Fig. 9. Dependence of *HHV* on FC^{da}

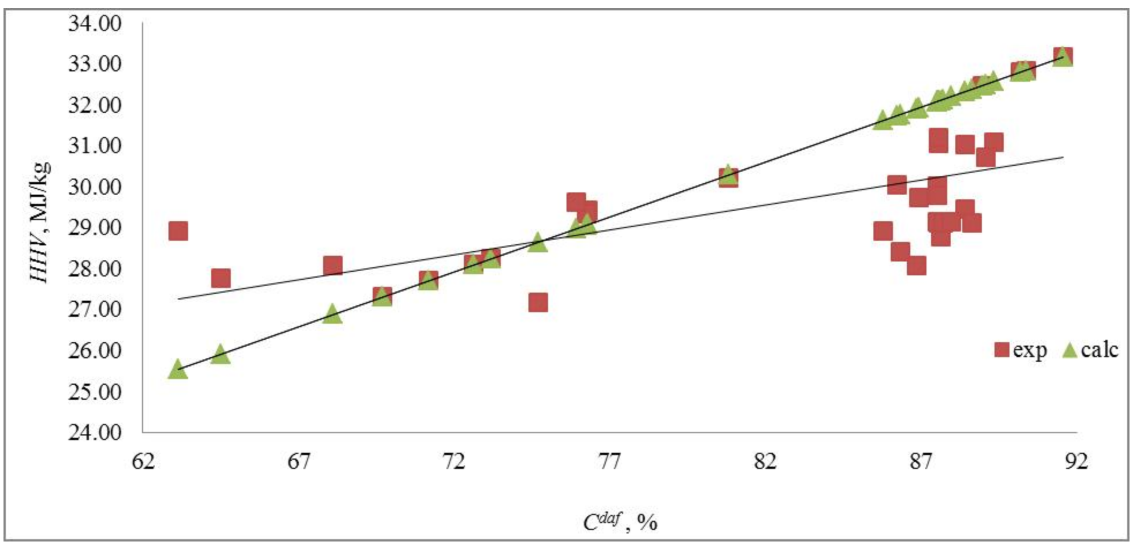

Fig. 10. Dependence of *HHV* on C^{daf}

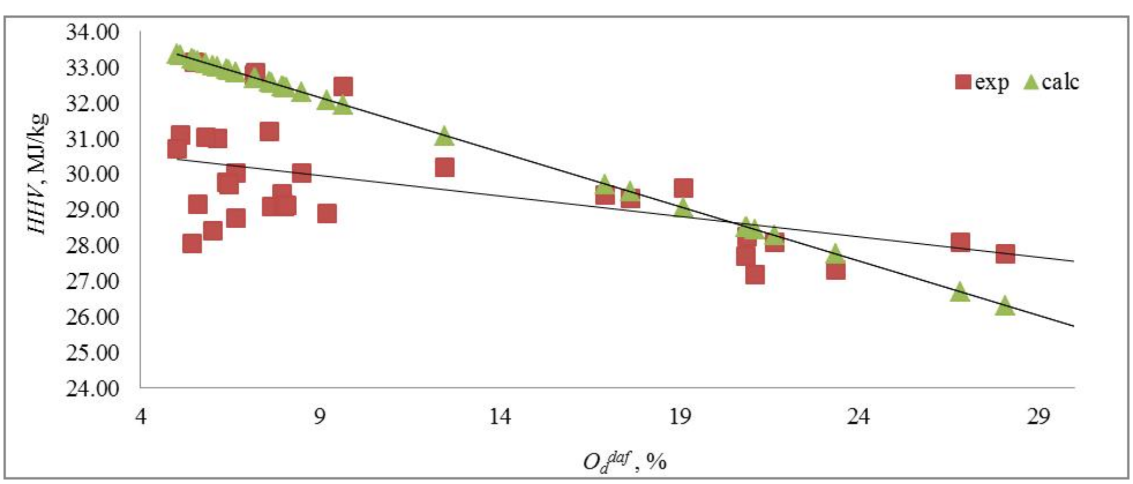

Fig. 11. Dependence of *HHV* on O_d^{daf}

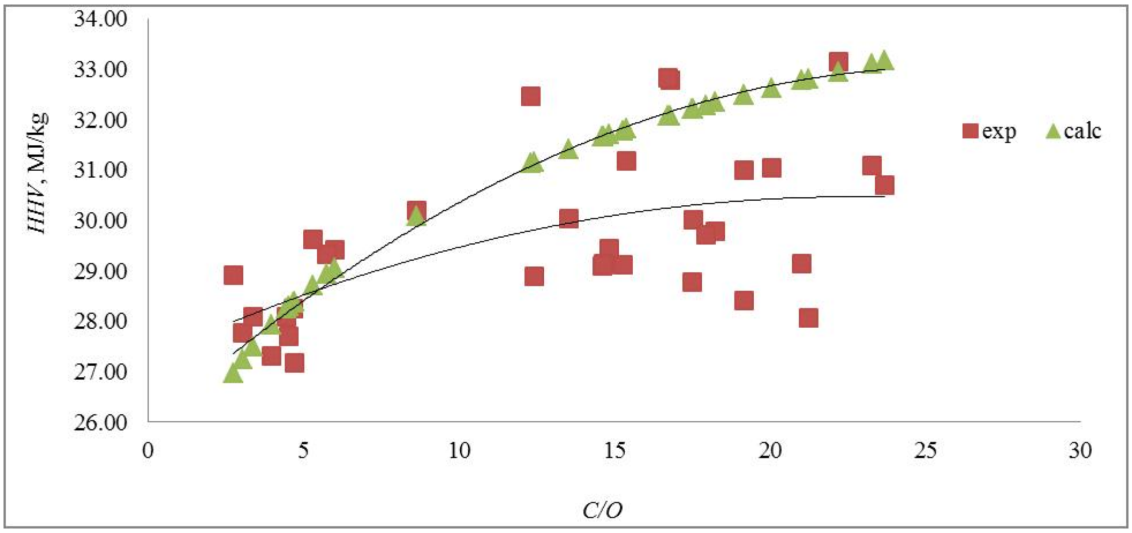

Fig. 12. Dependence of *HHV* on *C/O*

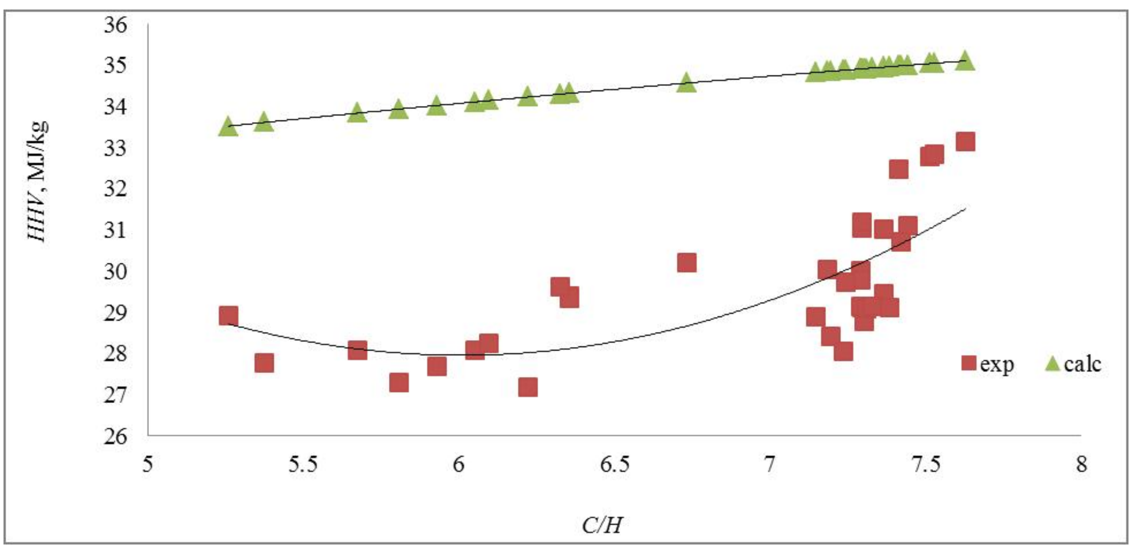

Fig. 13. Dependence of *HHV* on *C/H*

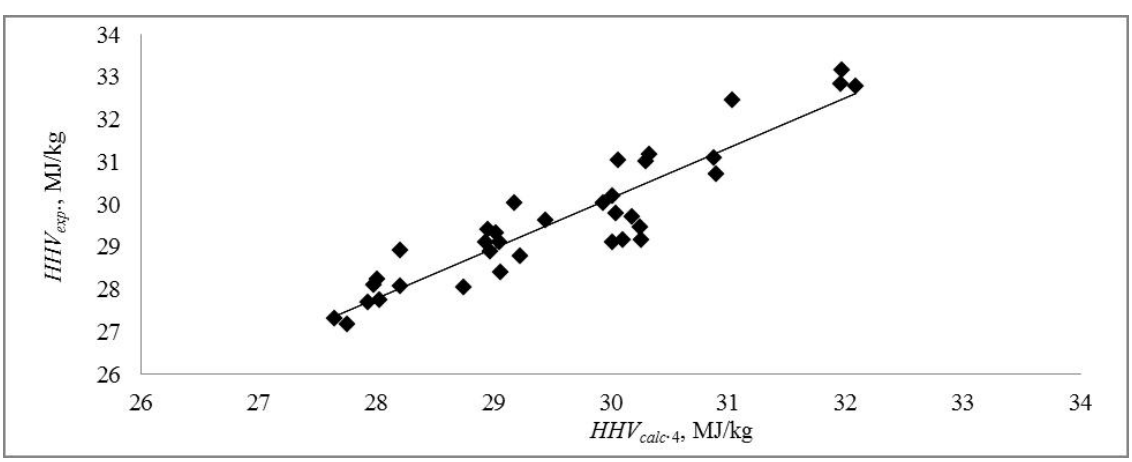

Fig. 14. Dependence between $HHV_{exp.}$ and $HHV_{calc.4}$

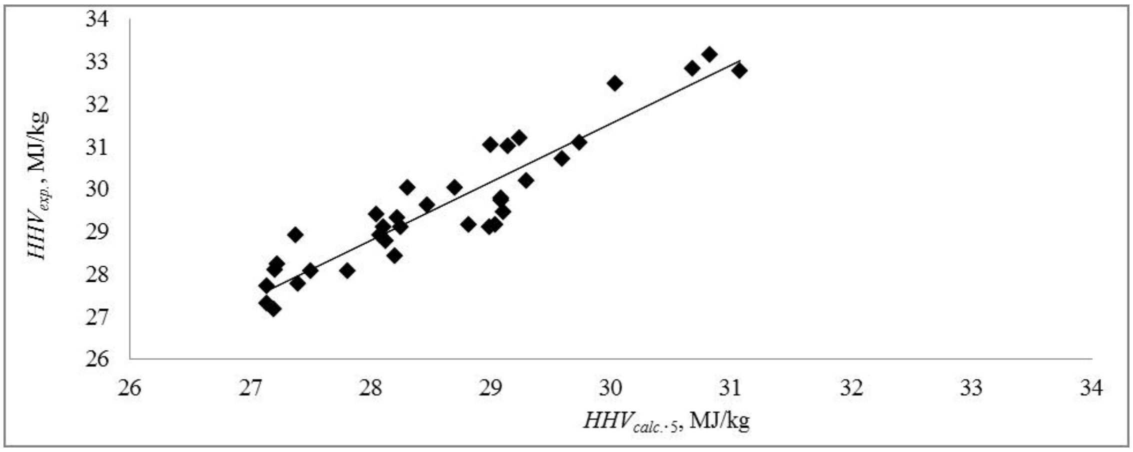

Fig. 15. Dependence between $HHV_{exp.}$ and $HHV_{calc.5}$

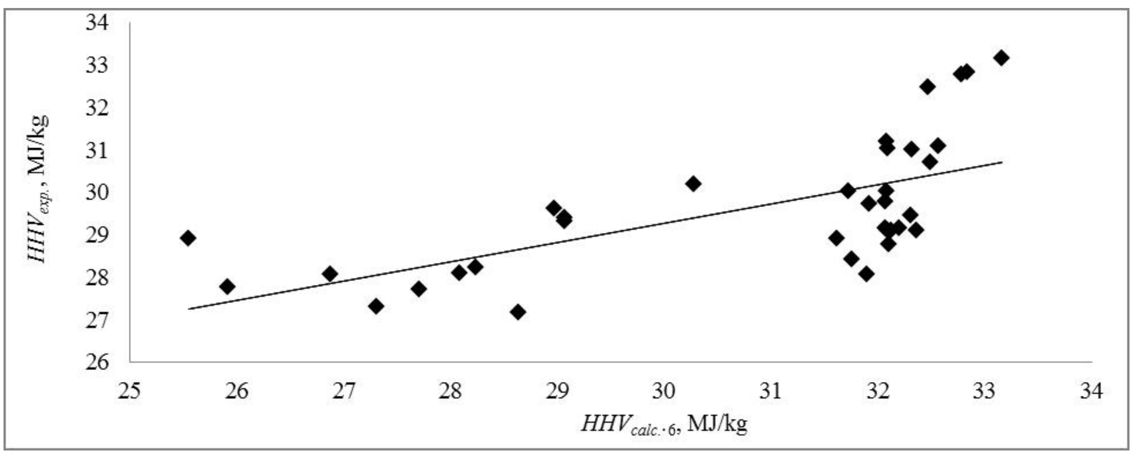

Fig. 16. Dependence between $HHV_{exp.}$ and $HHV_{calc.6}$

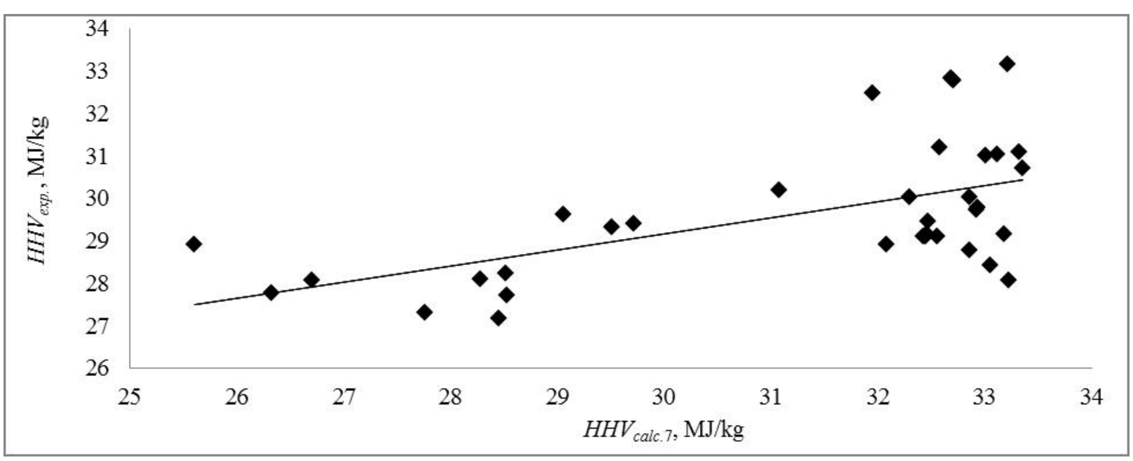

Fig. 17. Dependence between $HHV_{exp.}$ and $HHV_{calc.7}$

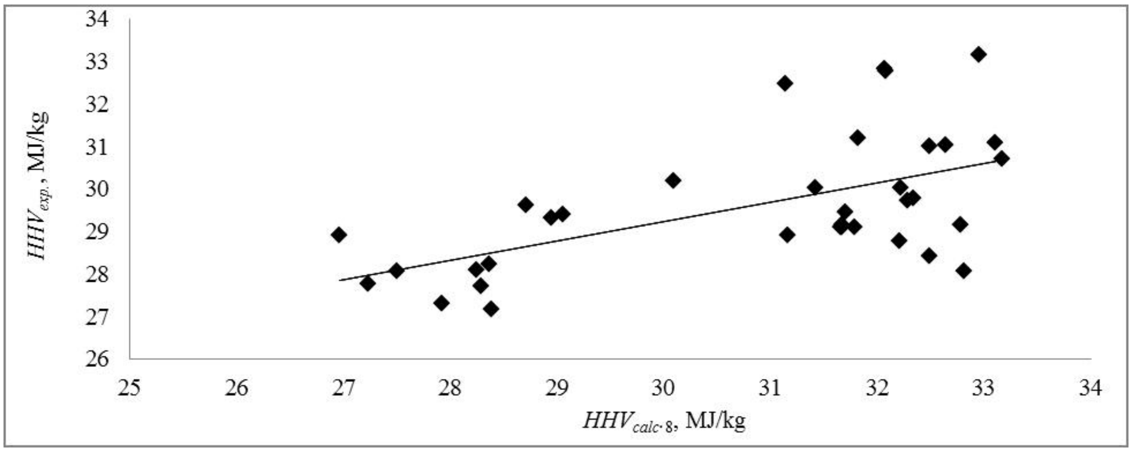

Fig. 18. Dependence between $HHV_{exp.}$ and $HHV_{calc.8}$

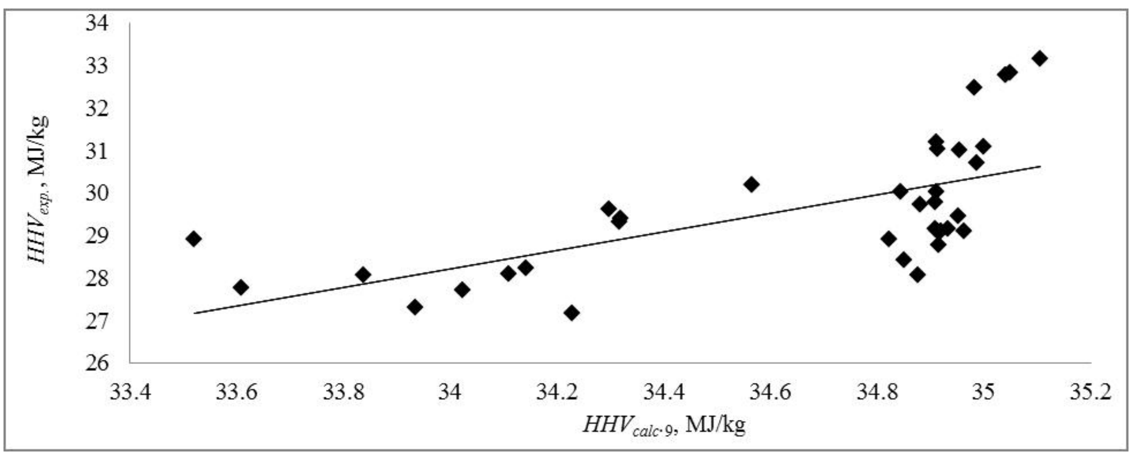

Fig. 19. Dependence between $HHV_{exp.}$ and $HHV_{calc.9}$

Table 3. Mathematical dependencies and their statistical evaluation

No.	Dependency	Statistical evaluation [1]		
		r	R^2	σ, MJ/kg
Vegetable raw material				
(11)	$HHVexp. = 1.2962 \cdot HHVcalc.1 - 6.0416$	0.959	0.92	4.632
(12)	$HHVexp. = 12.6165 \cdot HHVcalc.2 - 53.723$	0.991	0.98	5.290
(13)	$HHVexp. = 12.6165\ HHVcalc.3 - 53.723$	0.959	0.92	4.547
Charcoal				
(14)	$HHVexp. = 1.1838 \cdot HHVcalc.4 - 5.3728$	0.923	0.85	1.395
(15)	$HHVexp. = 1.3713 \cdot HHVcalc.5 - 9.6073$	0.933	0.87	1.425
(16)	$HHVexp. = 0.4551 \cdot HHVcalc.6 + 15.624$	0.642	0.41	1.987
(17)	$HHVexp. = 0.3776 \cdot HHVcalc.7 + 17.83$	0.566	0.32	2.140
(18)	$HHVexp. = 0.4557 \cdot HHVcalc.8 + 15.57$	0.574	0.33	1.873
(19)	$HHVexp. = 2.1802 \cdot HHVcalc.9 - 45.898$	0.631	0.39	2.774

[1] r is a multiple correlation coefficient; R^2 is a coefficient of determination; σ is a standard deviation, MJ/kg

As can be seen, the obtained dependencies of the experimental higher heating values of vegetable raw materials are characterized by high values of the coefficient of determination (0.92–0.98) and multiple correlation coefficients (0.959–0.991).

For biochar, satisfactory values of the coefficients of determination and multiple correlation coefficients characterize the obtained dependencies of the experimental higher heating values on a dry ashless state on its values calculated according to equation (4) from V^{daf} – (R^2 = 0.85; r = 0.923) and according to the equation (5) from FC^{daf} – (R^2 = 0.87; r = 0.933).

Thus, the proposed regression Eqs. (1)–(6), which define the dependence of the higher heating values of vegetable raw materials on the content of carbon, oxygen, or their atomic ratio ($\frac{C}{O}$), as well as Eqs. (4) and (5), defining the dependencies of the higher heating values of charcoal on the volatile matter V^{daf} and non-volatile carbon FC^{daf}, respectively, adequately describe the corresponding dependencies and allow to predict the higher heating values with high accuracy.

Ahmaruzzaman[26] used 4 equations to predict the higher heating value using indicators of proximate analysis of hydrocarbons. These equations were proposed in such works as Parikh *et al.*[27], Cordero *et al.*[28], Jimenez and Gonzalez[29], Han *et al.*[30], and tested on oil residue mixtures, coal, polymers, and plant waste. The average value of the coefficient of determination (R^2) was 0.965. Based on this, it can be concluded that the equations we proposed for predicting the higher heating value of vegetable raw materials are on the same level as other analogs.

In addition, the equations we proposed prove that the carbon content most describes the higher heating value of vegetable raw materials. This coincides with the opinion of Noushabadi *et al.*[31], who analyzed 69 different mathematical equations for predicting the higher heating value of vegetable raw materials, as well as Telmo and Lousada[32] who proved that The Higher Heating Value (HHV) of 17 wood fuels was correlated with their lignin (L) and extractive contents (Ext).

4. Conclusions

The higher heating values on a dry ashless state of 35 samples of vegetable raw materials and the same number of biochar samples were determined. Biochar was obtained using a patented modern industrial installation.

The parameters of their proximate, ultimate, and calorimetric analyses necessary for calculation were established. Graphical dependencies of the experimental and calculated higher heating values of vegetable raw materials and charcoal on the content of indicators of proximate and ultimate analyses are established.

Mathematical and graphical dependencies between the experimental and calculated higher heating values of vegetable raw materials and biochar were developed, and a statistical analysis of the obtained dependencies was performed.

The obtained dependencies of the experimental higher heating values of vegetable raw materials are distinguished by high values of coefficients of determination and multiple correlation coefficients. For vegetable raw materials, the coefficient of determination for the equation of HHV on C^{daf} dependence is 0.92, and the multiple correlation coefficient is 0.960; for the equation of HHV on O_d^{daf} dependence, the coefficients of determination and multiple correlation are 0.98 and 0.991, respectively; and for equation (3) of HHV on $\frac{C}{O}$ atomic ratio dependence, the coefficients of determination and multiple correlation are 0.92 and 0.959, respectively.

Also, the satisfactory values of the coefficients of determination and multiple correlation coefficients characterize the obtained dependencies of the experimental higher heating values on a dry ashless state of biochar on the values calculated according to the equation with V^{daf} – (R^2 = 85.14 %; r = 0.923) and according to the equation with FC^{daf} – (R^2 = 87.02 %; r = 0.933).

The obtained results confirm the adequacy of the developed dependencies and show the possibility of using them for predicting with high accuracy the higher heating value of:

– vegetable raw materials (based on the content of carbon, oxygen, or their atomic ratio);

– charcoal (based on the volatile matter or non-volatile carbon).

Accurate forecasting (on an industrial scale) of the higher heating values of the raw materials and biochar will enable effective improvement of the circular economy and increase the importance of using biomass. The obtained data have considerable practical significance, because the use of the results proposed by the authors in industry will significantly improve the efficiency of the biowaste processing process.

List of abbreviations and symbols

NCRES – non-conventional and renewable energy sources;

NES – New Energy Strategy;

TPES – total primary energy supply.

FC^{daf} – content of fixed carbon in the dry ashless condition;

R^2 – coefficient of determination;

V^{daf} – volatile matter in the dry ashless condition;

r – coefficient of correlation;

HHV – the higher heating value;
$\frac{C}{O}$ – atomic ratio;
O_d^{daf} – content of oxygen in the dry ashless condition;
C^{daf} – content of carbon in the dry ashless condition;
σ – standard deviation;
S^{daf} – content of Sulphur in the dry ashless condition;
N^{daf} – content of nitrogen in the dry ashless condition;
H^{daf} – content of hydrogen in the dry ashless condition;
A^d – ash in dry condition;
W^a – water in analytical condition;
CO_2 – carbon dioxide.

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ПРОГНОЗУВАННЯ ВИЩОЇ ТЕПЛОТВОРНОЇ ЗДАТНОСТІ СИРОВИНИ ТА БІОВУГІЛЛЯ

Анотація. *Однією із найважливіших характеристик біовугілля (деревного вугілля) є його висока теплотворна здатність. Визначено вищу теплотворну здатність на сухий беззольний стан 35 зразків рослинної сировини та деревного вугілля для встановлення залежності між якістю сировини та виготовленими зразками біовугілля. Виробництво біовугілля здійснено на модернізованому обладнанні за запатентованою технологією. Встановлено математичні та графічні залежності експериментальних і розрахункових вищих теплотворних здатностей рослинної сировини для отримання піролізного газу та деревного вугілля. Результати аналізу свідчать про прийнятність встановлених залежностей і дають підстави для висновку про можливість прогнозування вищих теплотворних властивостей рослинної сировини та деревного вугілля. Отримані дані мають важливе практичне значення. Використання запропонованих авторами результатів у промисловості істотно покращить перероблення біовідходів і збільшить частку рециркулярної економіки.*

Ключові слова: *біомаса, деревне вугілля, висока теплотворна здатність, математичні залежності, технічний і елементний аналіз.*