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Prediction of the Higher Heating Value of Charcoal

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Abstract

A statistical analysis of the relationship between the indicators of proximate and ultimate analyzes, as well as the HHV of 73 charcoal samples has been carried out. It was found that the indicators of carbon and oxygen content are most closely related in the organic mass of charcoal (R^2=0.987). The dependence of the atomic ratios (C/H and C/O) on the content of carbon and oxygen has a power-law character, as well as the dependence of the HHV on these ratios. Prediction of the HHV with the highest accuracy can be carried out according to the data of determining the volatile matter (R^2=0.8002) or the fixed carbon (R^2=0.8002) in charcoal.

Keywords: *Charcoal; Higher heating value; Correlations; Proximate and ultimate analyzes.*

1. Introduction

According to [1], charcoal, the main product of carbonization (slow pyrolysis) of biomass, has a wide range of applications in various industries. It can be used as a heat source for direct combustion, gasification for synthesis gas, sorbent for cleaning industrial gases, desulfurizer of gases or water, and also as an alternative to blast furnace coke in the metallurgical industry. Based on the foregoing, it seems appropriate to study the effect of various indicators of charcoal quality on the value of its higher heating value (HHV).

In [2–6], mathematical equations are given that make it possible to assess the influence of raw material and technological factors on the value of the heat of combustion of hard coal and coke, which take into account the data of proximate and ultimate analyzes, as well as the conditions for the preparation and coking of coals and quenching of the obtained coke.

It is shown in [7] that the existing equations describing the influence of various factors on the heat of combustion of plant raw materials cannot fully assess the effect of these indicators on the HHV of charcoal.

To predict the HHV of charcoal, the following mathematical relationships were proposed:

$$HHV^d = 0.1846 \cdot V^d + 0.3525 \cdot FC^d, \quad (1)$$

$$HHV^d = 32.7934 + 0.0053 \cdot (C^d)^2 - 0.5321 \cdot C^d - 2.8769 \cdot H^d + 0.0608 \cdot C^d \cdot H^d - 0.2401 \cdot N^d, \quad (2)$$

Mathematical dependences (1) and (2) were tested on a separate sample (26 samples) of charcoal samples and showed high calculation accuracy.

In work [8], when mathematical processing of the results of determining the proximate analysis of charcoal, equations (3) and (4) were obtained:

$$HHV^d = 354.3 \cdot FC^d + 170.8 \cdot V^d, \quad (3)$$

$$HHV^d = 35.430 - 183.5 \cdot V^d - 354.3 \cdot A^d. \quad (4)$$

In work [9], to calculate the HHV of charcoal, equation (5) was used, developed based on the results of work [10]:

$$HHV^d = 0.3491 \cdot C^d + 1.1783 \cdot H^d + 0.1005 \cdot S^d - 0.1034 \cdot O^d - 0.0151 \cdot N^d - 0.0211 \cdot A^d. \quad (5)$$

2. Materials and methods

For the analysis, we used a unique database [11], which contains information on the composition and properties of charcoal samples obtained from raw materials such as coconut shell, beech, pepper, oak, straw, eucalyptus, sequoia, willow, etc. In addition, we used the results of analyzing the quality of charcoal obtained from waste spruce, straw, various types of wood, etc., described in [8, 12]. A total of 73 samples were studied.

Determination of quality indicators of plant raw materials was carried out according to the following regulatory documents: ash content (A) according to CEN/TS 14775:2004 «Solid biofuels. Method for the determination of ash content»; volatile matter (V) according to CEN/TS 15148:2005 «Solid biofuels. Determination of the content of volatile matter»; content of carbon (C), hydrogen (H) and nitrogen (N) according to CEN/TS 15104:2005 «Solid biofuels. Determination of total content of carbon, hydrogen and nitrogen. Instrumental methods»; sulfur content according to CEN 15289:2006 «Solid biofuels. Determination of total content of Sulfur and chlorine»; the higher heating value (HHV) according to CEN/TS 14918:2005 «Solid biofuels. Method for the determination of calorific value».

The oxygen content (O^{daf}) was calculated using the formula (6):

$$O^{daf} = 100 - C^{daf} - H^{daf} - N^{daf} - S^{daf}. \quad (6)$$

Table 1 shows the maximum, minimum, arithmetic mean, as well as the range of values of quality indicators of charcoal samples. Analyzing the data in the table 1, it can be stated that they are characterized by a wide range of values, in particular, the ash content varies from 0.6 to 49.6%; the volatile matter - from 6.7 to 68.5%; fixed carbon content - from 31.5 to 93.3%; carbon - from 58.15 to 97.05%; hydrogen - from 0.75 to 6.06%; nitrogen - from 0.01 to 3.08%; sulfur - from 0.00 to 1.01%; oxygen - 0.85 to 36.72%.

Table 1. Values of charcoal quality indicators

Indicator	Value			
	minimum	maximum	interval	average
A^d, %	0.6	49.6	49.0	9.7
V^{daf}, %	6.7	68.5	61.8	28.1
FC^{daf}, %	31.5	93.3	61.8	71.9
C^{daf}, %	58.15	97.05	38.90	82.05
H^{daf}, %	0.75	6.06	5.31	3.10
N^{daf}, %	0.01	3.08	3.07	0.73
S^{daf}, %	0.00	1.01	1.01	0.02
O^{daf}, %	0.85	36.72	35.87	14.00
C/H	0.95	10.18	9.23	2.87
C/N	33.85	11071.21	11036.36	1550.42
C/O	2.11	152.24	150.13	14.79
HHV^{daf}, MJ/kg	22.98	40.08	17.10	30.62

The atomic ratios also show the following changes: C/H - from 0.95 to 10.18; C/N 33.85 to 11071.21; C/O - from 2.11 to 152.24. The indicated changes in the indicators of proximate and ultimate analyzes were reflected in the higher heating value (HHV) of the studied samples: it varied from 22.98 to 40.08 MJ/kg.

3. Results and discussion

For the studied sample of charcoal samples, the coefficients of pair correlation between different qualities indicators were calculated (Table 2).

Table 2. Coefficients of pair correlation of the investigated relationships

	A^d	V^{daf}	FC^{daf}	C^{daf}	H^{daf}	N^{daf}	S^{daf}	O^{daf}	C/H	C/N	C/O	HHV^{daf}
A^d	1.000											
V^{daf}	0.024	1.000										
FC^{daf}	-0.024	-1.000	1.000									
C^{daf}	0.138	-0.932	0.932	1.000								
H^{daf}	-0.164	0.817	-0.817	-0.877	1.000							
N^{daf}	0.731	0.013	-0.013	0.131	-0.187	1.000						
S^{daf}	0.450	-0.098	0.098	0.056	-0.049	0.239	1.000					
O^{daf}	-0.190	0.923	-0.923	-0.993	0.842	-0.204	-0.095	1.000				
C/H	0.151	-0.696	0.696	0.785	-0.879	0.292	-0.058	-0.760	1.000			
C/N	-0.356	-0.148	0.148	0.062	-0.078	-0.493	-0.157	-0.014	0.048	1.000		
C/O	0.185	-0.503	0.503	0.587	-0.474	0.045	0.091	-0.589	0.478	-0.030	1.000	
HHV^{daf}	0.130	-0.895	0.895	0.832	-0.674	0.046	0.219	-0.842	0.553	0.137	0.514	1.000

The significance of the correlation coefficients was checked by comparing the absolute value of the product $|r| \cdot \sqrt{n-1}$ with its critical value (H) for a given output reliability (P) [13]. The critical value of H at a probability of P=0.999 for 73 samples is 3.198.

Substituting the value 3.198 in the expression $|r| \cdot \sqrt{n-1}$, we find that the relationship between charcoal quality indicators, which is characterized by the value of the correlation coefficient $|r| > 0.377$, is significant. In Fig. 1-17 shows the main graphic, and in Table. 3 mathematical relationships between charcoal quality indicators.

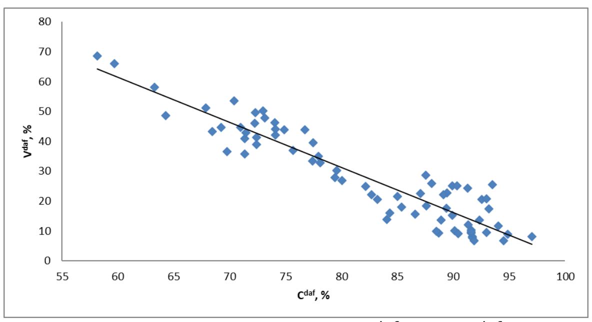

Fig. 1. Dependency between C^{daf} and V^{daf}

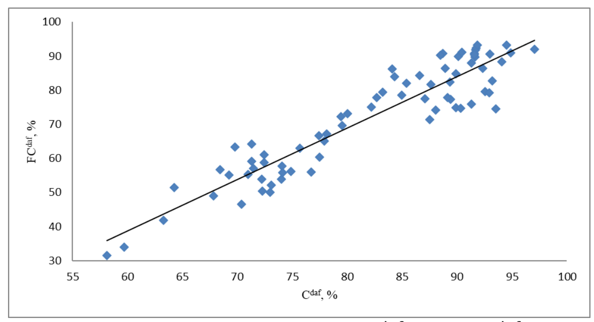

Fig. 2. Dependency between C^{daf} and FC^{daf}

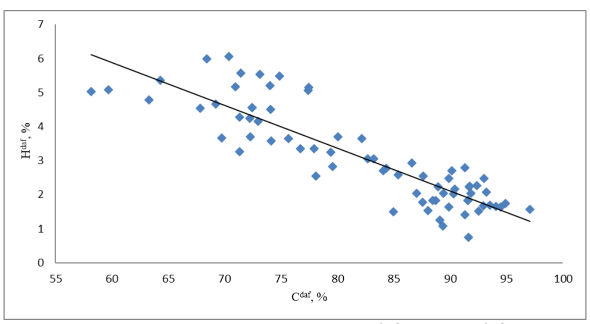

Fig. 3. Dependency between C^{daf} and H^{daf}

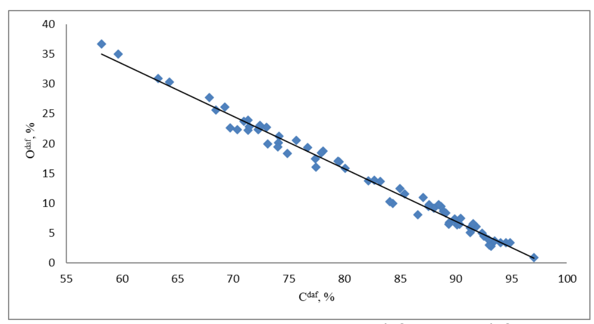

Fig. 4. Dependency between C^{daf} and O^{daf}

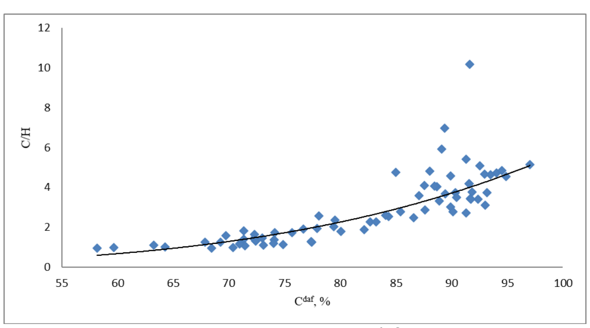

Fig. 5. Dependency between C^{daf} and C/H

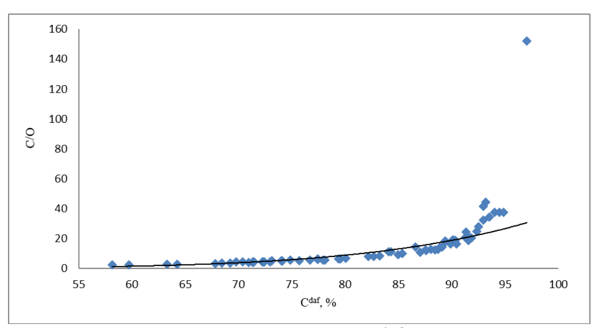

Fig. 6. Dependency between C^{daf} and C/O

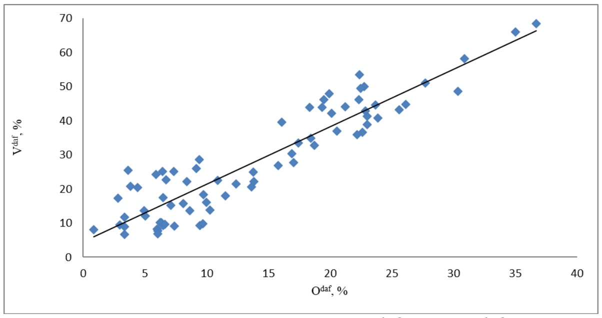

Fig. 7. Dependency between O^{daf} and V^{daf}

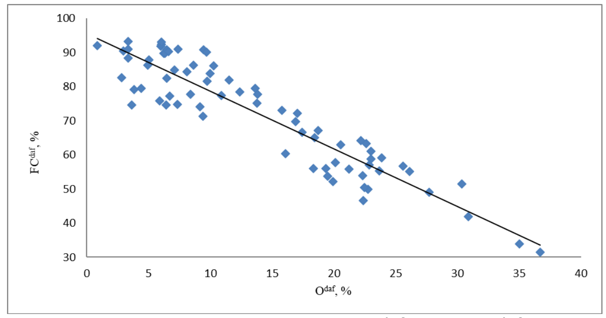

Fig. 8. Dependency between O^{daf} and FC^{daf}

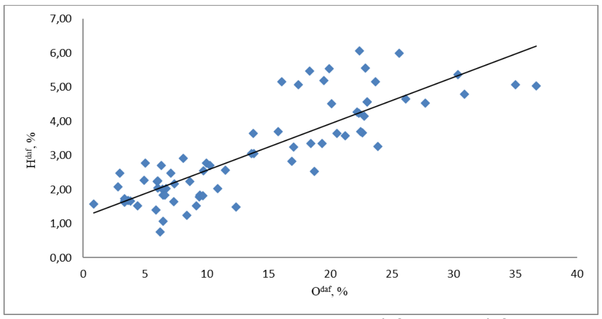

Fig. 9. Dependency between O^{daf} and H^{daf}

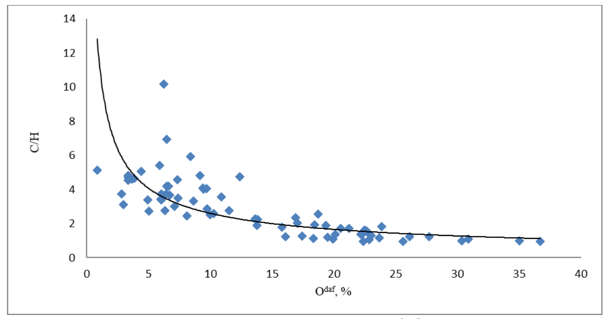

Fig. 10. Dependency between O^{daf} and C/H

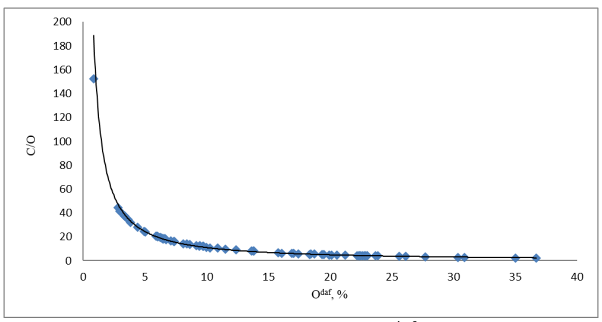

Fig. 11. Dependency between O^{daf} and C/O

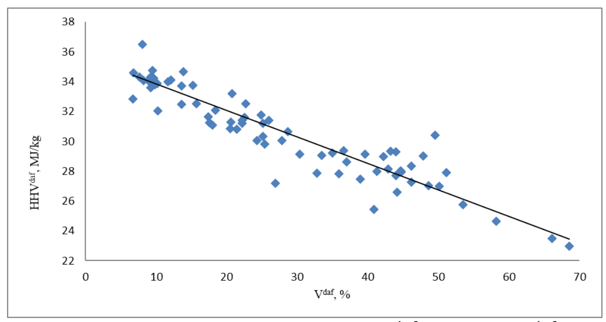

Fig. 12. Dependency between V^{daf} and HHV^{daf}

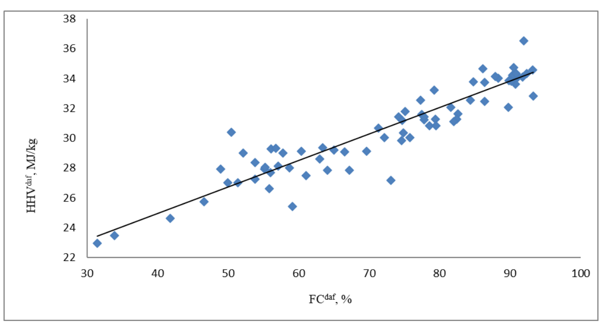

Fig. 13. Dependency between FC^{daf} and HHV^{daf}

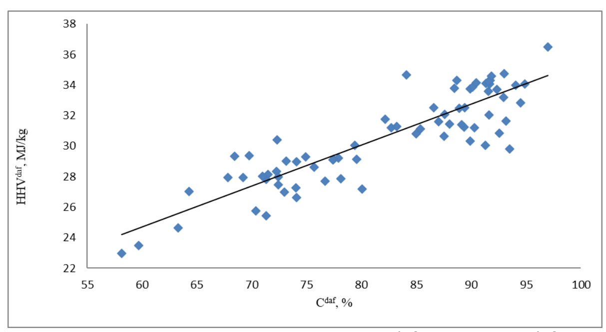

Fig. 14. Dependency between C^{daf} and HHV^{daf}

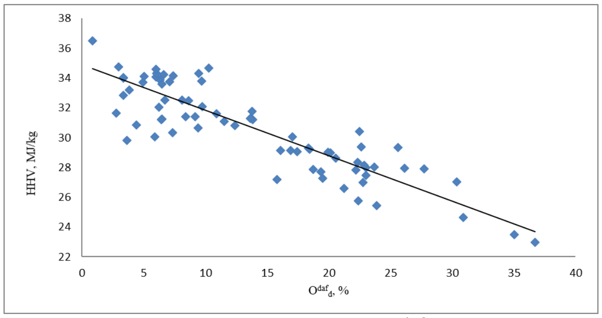

Fig.. 15. Dependency between O^{daf}_{d} and HHV

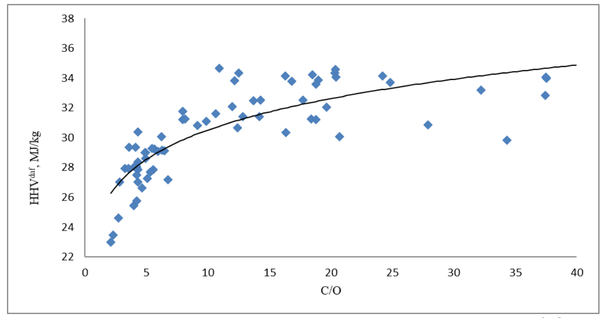

Fig. 16. Dependency between C/O and HHV^{daf}

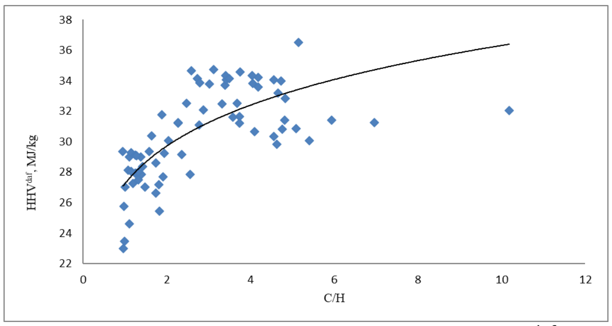

Fig. 17. Dependency between C/H and HHV^{daf}

The analysis of these relationships allows us to state that they are predominantly linear (equations 7-10, 13-15, 18-21). An exception is the relationship between the atomic ratios of elements and the quality indicators of coals (equations 11, 12, 16, 17, 22, 23), for which a power-law dependence is noted.

Statistical analysis of the investigated dependences shows that they are generally characterized by satisfactory accuracy, as evidenced by the high values of the correlation and determination coefficients.

Based on those given in Table 3 data, it can be concluded that the prediction of the HHV with satisfactory accuracy can be carried out according to the data on the volatile matter or the fixed carbon in charcoal. The coefficient of determination in this case is 0.8002.

Table 3. Mathematical equations and their statistical evaluation

№	Equations	Statistical evaluation	
		r	R^2
7	$V^{daf} = -1.5088 \cdot C^{daf} + 151.89$	0.9324	0.8693
8	$FC^{daf} = 1.5089 \cdot C^{daf} - 51.898$	0.9325	0.8695
9	$H^{daf} = -0.1257 \cdot C^{daf} + 13.416$	0.8768	0.7688
10	$O^{daf} = -0.881 \cdot C^{daf} + 86.283$	0.9935	0.987
11	$\frac{C}{H} = 0.0000000208 \cdot (C^{daf})^{4.2216719326}$	0.8945	0.8055
12	$\frac{C}{O} = 0.000000000004 \cdot (C^{daf})^{6.4759451770261}$	0.9335	0.8715
13	$V^{daf} = 1.6844 \cdot O^{daf} + 4.5133$	0.9230	0.8519
14	$FC^{daf} = -1.6845 \cdot O^{daf} + 95.495$	0.9231	0.8521
15	$H^{daf} = 0.1361 \cdot O^{daf} + 1.1983$	0.8422	0.7093
16	$\frac{C}{H} = 11.544 \cdot (O^{daf})^{-0.647}$	0.8272	0.6843
17	$\frac{C}{O} = 156.37 \cdot (O^{daf})^{-1.152}$	0,9981	0.9964
18	$HHV^{daf} = -0.1777 \cdot V^{daf} + 35.609$	0.8945	0.8002
19	$HHV^{daf} = 0.1777 \cdot FC^{daf} + 17.836$	0.8945	0.8002
20	$HHV^{daf} = 0.2676 \cdot C^{daf} + 8.6568$	0.8323	0.6928
21	$HHV^{daf} = -0.3051 \cdot O^{daf} + 34.888$	0.8415	0.7081
22	$HHV^{daf} = 24.451 \cdot (\frac{C}{O})^{0.0963}$	0.7974	0.6358
23	$HHV^{daf} = 27.265 \cdot (\frac{C}{H})^{0.1244}$	0.6990	0.4886

4. Conclusions

A statistical analysis of the relationship between the indicators of proximate and ultimate analyzes, as well as the HHV of 73 charcoal samples has been carried out. It was found that the indicators of carbon and oxygen content are most closely related in the organic mass of charcoal (R^2=0.987). The dependence of the atomic ratios (C/H and C/O) on the content of carbon and oxygen has a power-law character, as well as the dependence of the HHV on these ratios. Prediction of the HHV with the highest accuracy can be carried out according to the data of determining the volatile matter (R^2=0.8002) or the fixed carbon (R^2=0.8002) in charcoal.

Symbols

A – ash, %;
V – volatile matter, %;
FC – fixed carbon, %;
C – content of carbon, %;
H – content of hydrogen, %;
N – content of nitrogen, %;
S – content of sulfur, %;
O – content of oxygen, %;
C/H, C/N, C/O – atomic ratios;
HHV – higher heating value, MJ/kg;
^{d} *– dry basis;*
^{daf} *– dry ash free basis.*

References

[1] Pyshyev S, Miroshnichenko D, Malik I, Contreras AB, Hassan N, ElRasoul AA. Chemistry and Chemical Technology, 2021; 15(1): 61–73.
[2] Miroshnichenko IV, Miroshnichenko DV, Shulga IV, Balaeva YS, Pereima VV. Coke and Chemistry, 2019; 62(4): 143–149.
[3] Balaeva YS, Miroshnichenko DV, Kaftan YS. Solid fuel Chemistry, 2018; 52(5): 279–288.
[4] Balaeva YS, Kaftan YS, Miroshnichenko DV, Kotlyarov EI. Coke and Chemistry, 2018; 61(1): 4–11.
[5] Balaeva YS, Miroshnichenko DV, Kaftan YS. Solid Fuel Chemistry, 2017; 51(3): 141–146.
[6] Balaeva YS, Miroshnichenko DV, Kaftan YS. Pet Coal, 2017; 59(2): 250–256.
[7] Nhuchhen DR, Muhammad TA. Bioengineering,. 2017; 4: 7.
[8] Cordero T, Marquez F, Rodriguez-Mirasol J, Rodriguez JJ. Fuel, 2001; 80: 1567–1571.
[9] Theppitak S, Xin Dai, Hungwe D, Yoshikawa K. IOP Conf. Series: Earth and Environmental Science, 2019; 265: 012005.
[10] Channiwalaa SA, Parikhb PP. Fuel, 2002; 81: 1051–1063.
[11] Database for the physic-chemical composition of (treated) lignocellulosic biomass, micro- and macroalgae, various feedstocks for biogas production and biochar //https://Phyllis.nl/
[12] Crombie K, Masek O. Pyrolysis biochar systems, balance between bioenergy and carbon sequestration. GCB Bioenergy, 2015; 7. 749–361.
[13] Rumshinsky LZ. Mathematical processing of experimental results: a reference manual. Moscow. Nauka. 1971.

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