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Assessment of the Low Heat Values of Plant Biomass, Peat and Fossil Coal Based on Technical Analysis

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Abstract

The paper demonstrates an opportunity to determine the elemental composition of the combustible mass of plant biomass, peat, and fossil coal based on technical analysis findings followed by the assessment of the low heat value of solid fuel. This approach may be useful with the absence of elemental analysis findings and the lower heat of combustion of solid fuel. The content of carbon as the main element that forms the structure of solid fuel may be assessed *via* the yield of volatile matter, as demonstrated in the first case. Empirical dependencies of H_{at}/C_{at} and O_{at}/C_{at} ratios on carbon content in solid fuel, against which the low heat value of solid fuel with a sulphur content of no more than 2 % is calculated, are defined. Herewith, the deviation from the literature data did not exceed 10 %. The second option examines an opportunity to determine H_{at}/C_{at} and O_{at}/C_{at} ratios *via* the yield of volatile matter. The low heat values of solid fuels with sulphur contents of no more than 2 % were calculated on the basis of the resulting empirical dependencies; herewith, the deviation from the known values does not exceed 6 %.

The use of the resulting empirical dependencies to define the low heat values of solid fuels with a sulphur content of 2.1–8.4 % in some cases, gives an increase in deviations from the literature data within 12–14 %.

Key words: technical analysis, solid fuel, biomass, peat, fossil coal, lower heating value

ВВЕДЕНИЕ

Technical analysis of solid fuel allows determining such characteristics as total moisture [1], the contents of ash [2] and volatile matter [3]. In the absence of the data on the heat value of solid fuel, which is defined in the bomb, [4], based on the information on the elemental composition of the combustible mass of solid fuel, the high heat value can be determined by Mendeleev's formula [5]:

$$Q_s^{daf} = 81C^{daf} + 300H^{daf} - 26\ (O^{daf} - S^{daf}) \qquad (1)$$

where Q^{daf} is high heat value of the fuel mass, kcal/kg; C^{daf} is carbon content in the combustible mass of solid fuel, %; H^{daf} is hydrogen content in the combustible mass of solid fuel, %; O^{daf} oxygen content therein, %; S^{daf} is sulfur content therein, %.

When determining the low heat value considering the combustion heat of water formed during hydrogen combustion contained in fuels, the formula is as follows [6]:

$$Q_i^r = 81C^r + 246\ H^r - 26(O^r - S^r) - W_t^r \qquad (2)$$

where Q_i^r is low heat value of fuels, kcal/kg; C^r is carbon content in the operating mass of solid fuel, %; H^r is hydrogen content therein, %; O^r is oxygen content in therein, %; S^r is sulphur content therein, %; W_t^r is total moisture content therein, %.

The heat of combustion may also be defined by other factors obtained when studying deposits of Siberia and the Far East [7] or by other formulas obtained set out in [6, 8].

The knowledge of the elemental composition of solid fuels also allows determining the amount of volatile matter, that may be expressed via structural parameters H_{at}/C_{at} and O_{at}/C_{at}, where

H_{at}/C_{at} is the atomic ratio of hydrogen to carbon in the combustible mass of solid fuel; O_{at}/C_{at} is the atomic ratio of oxygen to carbon in the combustible mass of solid fuel, as noted in [9]. Based on the data of the elemental composition, these values may be determined as follows: $H_{at}/C_{at} = A_C H^{daf}/A_H C^{daf}$; $O_{at}/C_{at} = A_C O^{daf}/A_O C^{daf}$, where A_C, A_H ,A_O are atomic mass of carbon, hydrogen, and oxygen, respectively. The yield of volatile matter in case of deposits of Siberia and the Far East may be determined directly from the data of the elemental composition of the combustible mass in solid fuel, as demonstrated in [7]. Thus, there is a relation between the elemental composition of the combustible mass of solid fuel and the yield of volatile matter . In this regard, solving the reverse task is of interest: determining the elemental composition of the mass of solid fuel based on technical analysis data followed by the assessment of low heat values of solid fuel. This approach may be useful with the absence of the data of the elemental composition and the low heat value of solid fuel.

DETERMINATION OF LOW HEAT VALUES OF SOLID FUELS BASED ON THE DEPENDENCE BETWEEN THE YIELD OF VOLATILE MATTER AND CARBON CONTENT IN THE COMBUSTIBLE MASS

Carbon is the main structure-forming element in solid fuel. The bulk of hydrogen H^{daf}, oxygen, $O^{daf,}$ nitrogen N^{daf} and nonaromatic carbon C^{daf} belonging to the composition of the combustible mass of solid fuel turns into the gas phase [8] with the formation of the coke residue during pyrolysis.

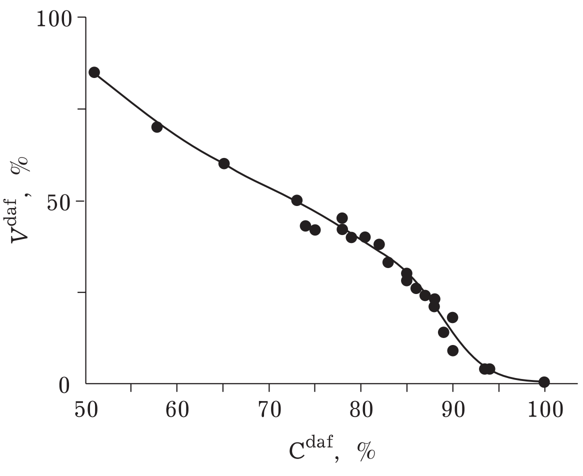

Fig. 1. Change in the yield of volatile matter depending on carbon content in solid fuel. The dots show V^{daf} and C^{daf} values given in [14]. The line corresponds to the trend of changing V^{daf} with a change of C^{daf} in solid fuel.

Therefore, one may assume that the coking level should depend on carbon content in the combustible mass of solid fuel and its aromaticity. Herewith, the yield of volatile matter V_{daf} is defined by the number of the peripheral carbon atoms, the substitution degree of aromatic clusters, the amount of hydrogen in aliphatic groups and oxygen content [10]. Since the amount of formed coke is interrelated with the yield of volatile matter, carbon content in the combustible mass can be defined via the yield of volatile matter. The mass loss of solid fuel when defining the yield of volatile matter is folded from the losses of the organic and mineral mass. Herewith, carbon dioxide of carbonates and hydrate moisture of the mineral mass are removed from the mineral mass; a partial loss of pyrite sulphur also happens [11]. Additionally, the constituent mineral components may exert catalytic effect for the pyrolysis process of organic part of solid fuel [12, 13]. Apparently, all this defines the deviations in the yield of volatile matter for coal from different deposits with the identical content of carbon in the combustible mass. To verify an opportunity to define the elemental composition of fossil coal, including biomass and peat, the data of the All-Russian Thermal Engineering Institute (VTI) on the composition, technical analysis and the heat value were used [14]. The data, where sulphur contents do not exceed 2 %, were used to reduce the error due to high sulphur contents in coal from some deposits.

Figure 1 demonstrates a change in the yield of volatile matter (V^{daf}) depending on carbon content in solid fuel C^{daf}. It can be seen that the yield of volatile matter decreases with an increasing carbon content in solid fuel. Paper [12] describes a similar dependence.

Carbon content in solid fuel may be defined via the function $f_V = V/(1 - V)$, where $V = V^{daf}/100$, as proposed in this work. Figure 2 demonstrates carbon content in the combustible mass of solid fuel C^{daf} versus f_V. To define carbon content in the combustible mass of solid fuel (C^{daf}) an empirical formula has been proposed:

$$C^{daf} = 100 - 27 f_V^n \quad (3)$$

where $n = 0.6-0.0454 f_V^n$.

The formula (3) is applicable up to $V^{daf} = 85$ %, which corresponds to the amount of volatile matter in case of biomass (wood). The coefficient in the formula (3) has been obtained with $V^{daf} = 50$ %, when $f_V = 1$. A change of the degree n depending on f_V was determined using the value of the obtained coefficient.

Figure 3 shows the data on carbon content in solid fuels C^{daf} (%) and those calculated by the

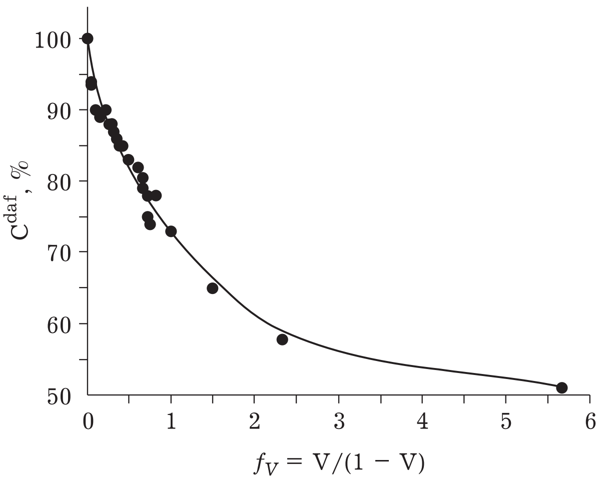

Fig. 2. Carbon content (C^{daf}) in solid fuel versus $f_V = (V/(1 - V)$, where $V = V^{daf}/100$. The line indicates calculations by formula (3), points – literature data [14].

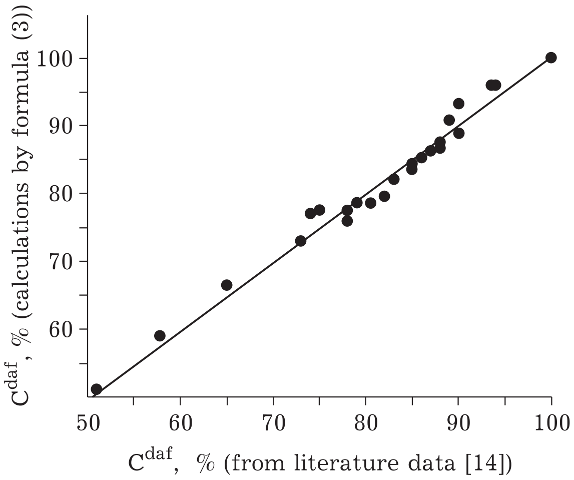

Fig. 3. The ratio of the literature data on the carbon content of solid fuels C^{daf} (%) and calculated by the formula (3). The straight line corresponds to the coincidence of Cdaf values calculated by the formula (3) and the literature data [14]. The dots show the deviation of the calculated C^{daf} values from the literature data.

formula (3). There is a clear correlation between calculated and literature data on carbon content in the combustible mass of solid fuels.

To establish H_{at}/C_{at} and O_{at}/C_{at} relations with a carbon content in the combustible mass of solid fuels (coal, peat, plant biomass) the following empirical formulas were suggested:

$$H_{ат}/C_{ат} = 1.48\, f_C^{0.45} \quad (4)$$

$$O_{ат}/C_{ат} = 0.655\, f_C^{1.3} \quad (5)$$

where fc = (100 − Cdaf)/Cdaf, Cdaf ≥ 51 %.

To define coefficients curves were extrapolated up to the value of $f_C = 1$. Afterwards, the function degree was defined for solid fuels and the values of coefficients and degrees for reaching the maximum deviations were specified based on the literature data [14] for H_{at}/C_{at} and O_{at}/C_{at} values.

The obtained dependencies are presented in Fig. 4 and 5; points show the atomic ratios H_{at}/C_{at} and O_{at}/C_{at} obtained by the data of [14].

The mass ratio of the elements in solid fuel may be defined by the atomic ratios H_{at}/C_{at} and O_{at}/C_{at}. In other words, the mass of hydrogen $A_H(H_{at}/C_{at})$ with the relative atomic mass A_H and the mass of oxygen $A_O(O_{at}/C_{at})$ with the relative atomic mass of A_O will correspond to one carbon atom with the relative atomic mass A_C.

The formulas are applicable for solid fuels (biomass, peat, coal of different metamorphic stages with contents $C^{daf} \geq 51$ %, $V^{daf} \leq 85$ %).

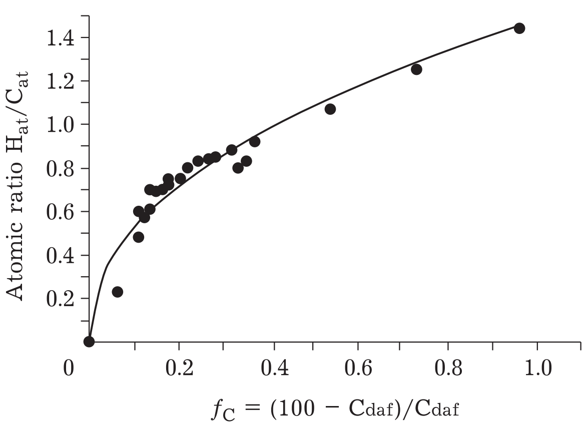

Fig. 4. Atomic ratio H_{at}/C_{at} in solid fuels versus $f_C = (100 - C^{daf})/C^{daf}$. The line indicates calculations by formula (5), the points – the literature data [14].

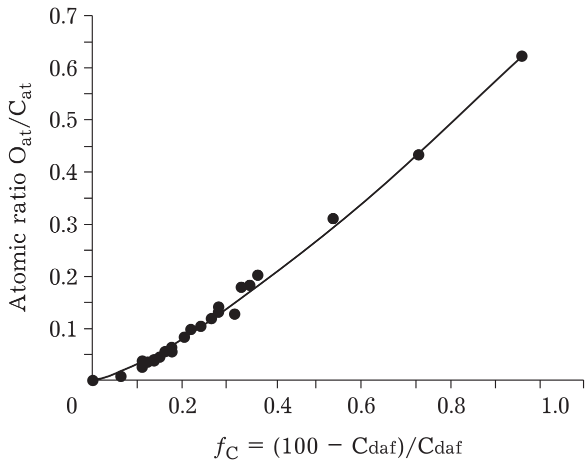

Fig. 5. O_{at}/C_{at} versus $f_C = (100 - C^{daf})/C^{daf}$. The line indicates calculations by formula (5), the points – the literature data [14].

The values of the lower heat value (Q_i^r) for solid fuels considering ash and total moisture contents were calculated by the formula (2) in accordance with the obtained values of carbon, hydrogen, and oxygen contents. Figure 6, *a* demonstrates the ratio of the calculated values and Q_i^r amounts for solid fuels with a sulphur content of no more than 2 % given in [14]. The standard deviation was 3.9 %; the maximum deviation of the calculated values from the literature data did not exceed 10 %.

Thus, the percentages of carbon, hydrogen and oxygen in the combustible mass based on the resulting atomic ratios H_{at}/C_{at} and O_{at}/C_{at} and formulas (4) and (5) and considering the relative atomic masses of the elements are determined by formulas:

$$C^{daf} = KA_C/(A_H(H_{ат}/C_{ат}) + A_O(O_{ат}/C_{ат}) + A_C) \quad (6)$$

$$H^{daf} = KA_H(H_{ат}/C_{ат})/(A_H(H_{ат}/C_{ат}) + A_O(O_{ат}/C_{ат}) + A_C) \quad (7)$$

$$O^{daf} = KA_O(O_{ат}/C_{ат})/(A_H(H_{ат}/C_{ат}) + A_O(O_{ат}/C_{ат}) + A_C) \quad (8)$$

where $K = 100 - N^{daf} - S^{daf} = 97.4$ % is normalization coefficient taking into account the contents of sulphur and nitrogen in coal and peat (average sulphur content $S^{daf} = 0.8$ %, nitrogen $N^{daf} = 1.8$ %); normalization coefficient of 99.4 taking into account the content of nitrogen $N^{daf} = 0.6$ % and sulphur $S^{daf} = 0$ % was used for biomass (wood).

The resulting formulas to determine carbon, hydrogen, and oxygen contents can also be used to assess the low heat value of solid fuels with a sulphur content of over 2 %. However, a stronger deviation from the literature data is likely due to the redistribution of the content of unaccounted sulphur by other elements with greater coefficients in the Mendeleev formula (carbon and hydrogen). Figure 6*b* demonstrates the ratio of the Q_i^r values calculated and given in [14] for coal with a sulphur content of 2.1–8.4 %. Standard and maximum deviations were 5.9 % and 13.4 %, respectively.

Thus, the low heat value for solid fossil fuels with a sulphur content of no more than 2 % and biomass with the accuracy up to 10 % can be assessed based on technical analysis of solid fuels on the assumption of the dependence of carbon content on the yield of volatile matter. The use of the resulting formulas to determine the main components of the combustible mass of solid fuels in case of a sulphur content of 2.1–8.4 % at subsequent calculations of the low heat value in some cases leads to a more significant deviation from the literature data (the maximum deviation is 13.4 %).

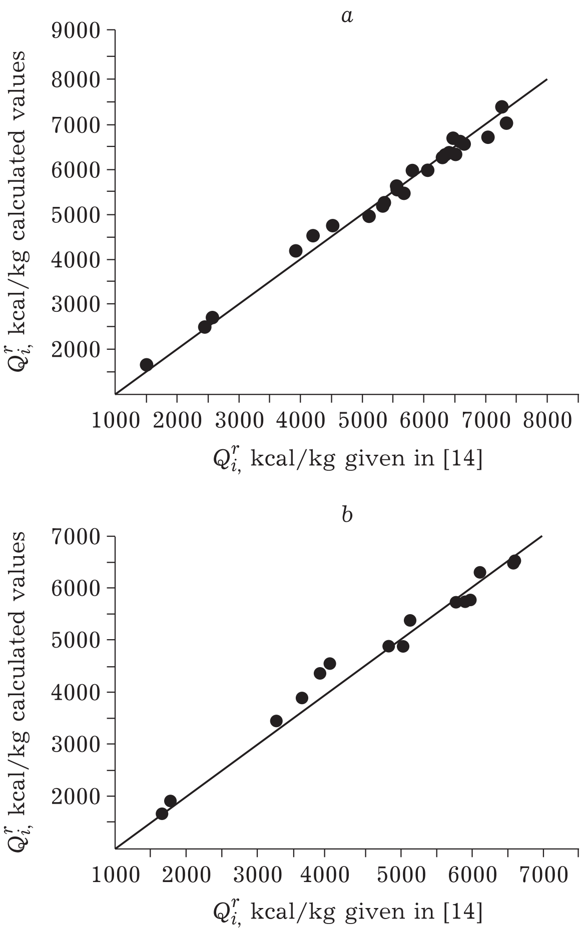

Fig. 6. The ratio of Q_i^r values for solid fuels with a sulphur content up to 2 % (*a*) and 2.1–8.4 % (*b*) calculated and given in [14].

DETERMINATION OF LOW HEAT VALUES OF SOLID FUELS BASED ON THE DEPENDENCE BETWEEN THE YIELD OF VOLATILE MATTER AND STRUCTURAL PARAMETERS, SUCH AS H_{AT}/C_{AT} AND O_{AT}/C_{AT}

Another option of assessment of the elemental composition of solid fuels and biomass assumes that the atomic ratios H_{at}/C_{at} and O_{at}/C_{at} can be determined directly via the yield of volatile matter. Coke is either not formed or generated insignificantly during pyrolysis of aliphatic compounds and substances containing isolated aromatic rings, while volumes of the coke residue during pyrolysis of aromatic compounds with large contents of condensed rings are insignificant, as demonstrated by the results of studying pyrolysis of various compounds [8]. The cleavage of side chains containing the bulk of hydrogen and oxygen occurs during pyrolysis in the last case. Thus, one should expect nonlinear dependencies of the atomic ratios H_{at}/C_{at} and O_{at}/C_{at} on the yield of volatile matter V^{daf} during pyrolysis of hydrocarbon raw materials heterogeneous by aromaticity. The de-

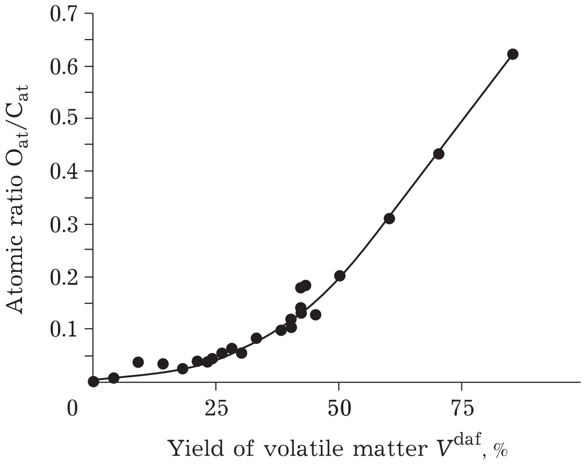

Fig. 7. Atomic ratio O_{at}/C_{at} in solid fuels versus the yield of volatile matter V^{daf}. The points indicate H_{at}/C_{at} values obtained on the basis of the data from [14]. The solid line reflects the trend of changing H_{at}/C_{at} with increasing the amount of volatile matter in solid fuels.

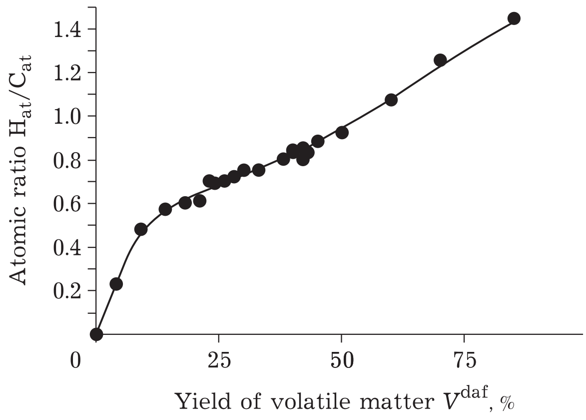

Fig. 8. Atomic ratio O_{at}/C_{at} in solid fuels versus the yield of volatile matter V^{daf}. The points indicate O_{at}/C_{at} values on the basis of the data from [14]. The solid line reflects the trend of changing O_{at}/C_{at} with increasing the amount of volatile matter in solid fuels.

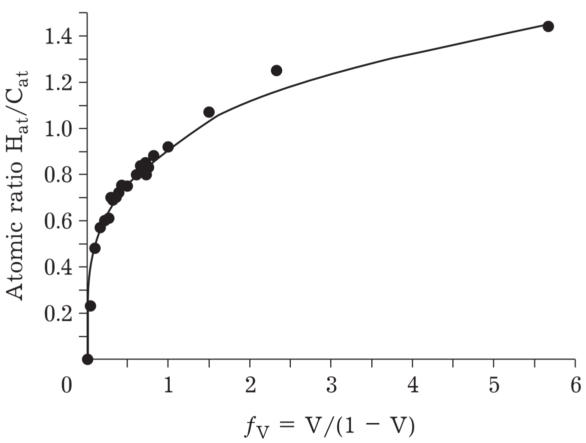

Fig. 9. Atomic ratio H_{at}/C_{at} in solid fuels versus f_v function. The line indicates calculations by formula (9), the points – the literature data [14].

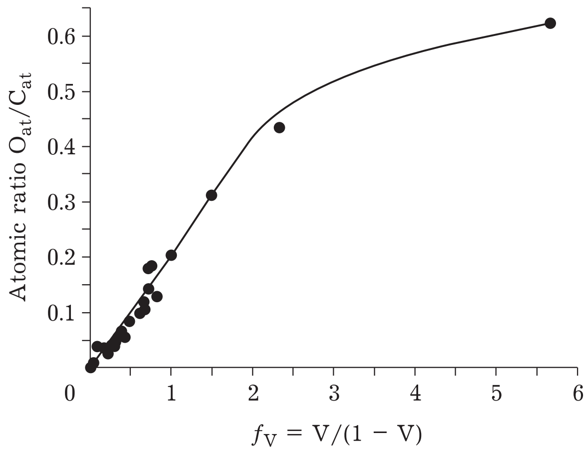

Fig. 10. The line indicates calculations by formula (10), the points – the literature data [14].

pendencies H_{at}/C_{at} and O_{at}/C_{at} on V^{daf} are demonstrated in Fig. 7 and 8 by the data of elemental analysis of solid fuels [14].

The atomic ratios H_{at}/C_{at} и O_{at}/C_{at} for various solid fuels are determined in this work based on the dependencies H_{at}/C_{at} and O_{at}/C_{at} on f_V function. The resulting dependencies are given in Fig. 9 and 10. The dots show the values of atomic ratios obtained on the basis of literature data of the elemental analysis of the combustible mass of solid fuels and biomass [14]; the lines show the values obtained by empirical formulas:

$$H_{ат}/C_{ат} = 0.92\, f_V^n \quad (9)$$

where $n = (0.28 - 0.0036 f_V)(f_V^2 + 0.0009)/f_V^2$

$$O_{ат}/C_{ат} = 0.202\, f_V^n \quad (10)$$

where $n = 1.2 - 0.0971 f_V$

$f_V = V/(1 - V)$, $V = V^{daf}/100$, $V^{daf} = 85$ %.

The values of coefficients correspond to the magnitudes at $f_V = 1$. Afterwards, degree n depending on f_V was determined and functions that reflect most precisely a change of the degree in each case were selected.

The resulting atomic ratios H_{at}/C_{at} and O_{at}/C_{at} were used to assess the elemental composition of solid fuels and biomass by formulas (6)–(8) using formulas (9) and (10). The heat value of solid fuels and biomass was determined by formula (2) on the basis of the calculated elemental composition of the combustible mass considering ash and total moisture contents. The ratio of the calculated values of the low heat value Q_i^r for solid fuels, biomass, and literature data of [14] is demonstrated in Fig. 11, *a*.

The standard and maximum deviations are 2.9 % and do not exceed 6 %, respectively. The standard deviation in the case of using this method to

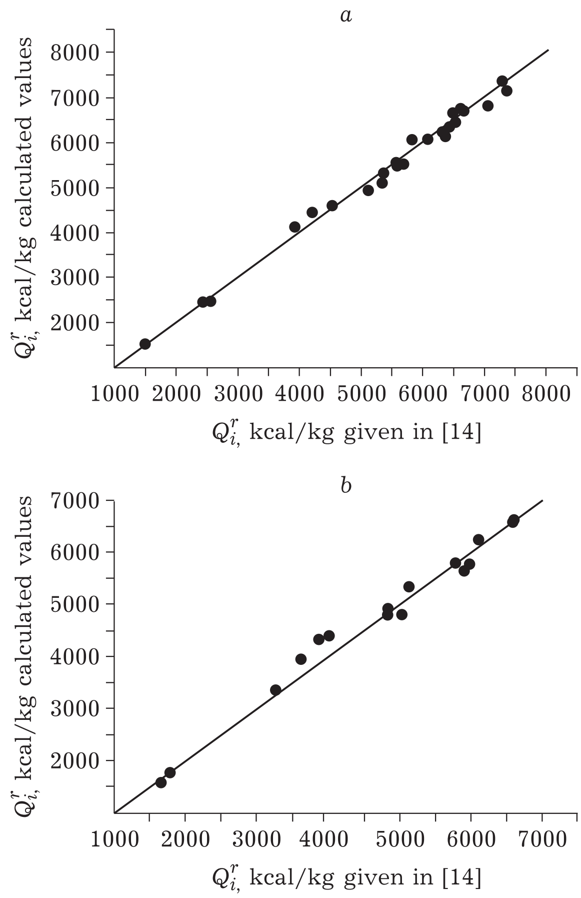

Fig. 11. The ratio of Q_i^r values for solid fuels with sulfur content up to 2 % (*a*) and 2.1–8.4 % (*b*) calculated and given in [14].

assess the heating value of solid fuels with a sulphur content of 2.1–8.4 % was 5.2 %, the maximum deviation – 12.3 %. Figure 11, *b* demonstrates the ratio of the calculated values of the low heat value for solid fuels with a sulphur content of 2.1–8.4 % and Q_i^r values given in [14].

Thus, one can assess the low heat value of solid fuels and biomass with the accuracy to 6 % based on the atomic ratios H_{at}/C_{at} and O_{at}/C_{at} obtained using the data on the yield of volatile matter. The maximum deviation was 12.3 % in the case of solid fuels with sulphur contents of 2.1–8.4 %.

CONCLUSION

An opportunity to determine the elemental composition of the combustible mass of fossil coal, biomass and peat based on technical analysis data followed by determination of the low heat value of solid fuel was demonstrated. This approach might be useful with the absence of data on the elemental composition and low heat value of solid fuel. Two options to solve the stated objective were considered.

The content of carbon as the main element that forms the structure of solid fuels could be determined via the yield of volatile matter, as demonstrated in the first option. The empirical dependencies H_{at}/C_{at} and O_{at}/C_{at} on carbon content in solid fuel were defined, against which the low heat value of solid fuels with a sulfur content of not more than 2 % was calculated. Herewith, the deviation from the values given in literature did not exceed 10 %.

The second option examined an opportunity to determine the ratios H_{at}/C_{at} and O_{at}/C_{at} via the yield of volatile matter. The low heat values of solid fuels with a sulphur content of no more than 2 % was calculated on the basis of the resulting empirical dependencies. Herewith, the deviation from the values given in the literature did not exceed 6 %.

The use of the resulting empirical dependencies to determine the low heat value of solid fuels with a sulphur content of 2.1–8.4 % in some cases, leads to increasing the deviation from the literature values within 12–14 %.

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