Influence of ash content on combustion heat, volatile yield and sulfur content in the energy coals of Ukraine

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Abstract

The paper deals with the problem of reliable definition of heating value, volatile yield and sulfur content in coal organic matter and develops the methods of calculation evaluation of these parameters for coals with real ash content. The amendments due to mineral matter thermal decomposition are accounted. 8 power coals of Donetsk and Lvov-Volyn basins are studied having volatile yield from1 to 40% in frameworks of ash content from 10 to 40%. Calculations based on parameters defined more precisely differ from laboratory results not more than allowed laboratory test error value.

Keywords: ash content; coal; heating value; mineral impurities; sulfur; volatile yield

1. Introduction

To determine the quality of power-generating coals, the simplest and most common is technical analysis with determination of total moisture W_t^r, ash content on dry weight A_d and volatiles yield on dry weight V_d. Determination of the lowest calorific value Q_i^r is much more time consuming and laborious, and, in contrast to thermal power plants, coal enterprises are not sufficiently provided with calorimeters. The analysis of the content of total sulfur S_t^d is even more laborious, in connection with which it is most often performed only in collective samples of coal products per month. Meanwhile, the heat of combustion of coal and the sulfur content in batches supplied to TPPs are the main parameters by which the fuel supply of power units is planned, and for coal going to production, the efficiency and environmental indicators of combustion depend on them.

For coals of one grade, there are formulas for recalculating Q_i^r from one ash content to another [1]. There are also methods for calculating the net calorific value for ash content and moisture content, which are based on the averaged values of the net calorific value per dry ash free mass of fuel Q_s^{daf} [2]. However, these methods give an error of 50 to 300 kcal/kg compared to laboratory determination. Methods for calculating the yield of volatiles also give a significant error [1]. There are no calculated methods of conversion to actual ash content for sulfur content.

The physical meaning of the influence of ash content on the results of determining the heat of combustion of coal and the yield of volatiles is known in principle. In [3] it is noted that the determination of ash content by calcining in an atmosphere of air or oxygen (according to GOST 11022-95) gives results that do not correspond exactly to the amount of mineral impurities, in particular, due to the following transformations of the components of the mineral mass:

- decomposition of carbonates with the release of carbon dioxide (1)
- losses of crystallization water by sulfates (2)
- oxidation of iron sulfides (3)

$$CaCO_3 \rightarrow CaO+CO_2 \quad (1)$$

$$CaSO_4 \cdot 2H_2O \rightarrow CaSO_4+2H_2O \quad (2)$$

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$$4FeS_2+11O_2 \rightarrow 2Fe_2O_3+8SO_2 \quad (3)$$

Even if we neglect the thermal effects of these reactions, one cannot fail to take into account that they change both the content of mineral ballast, on the basis of which $Q_i{}^r$ is calculated, and the observed release of volatiles. In [4] it is indicated that the discrepancy between the ash content and the proportion of mineral mass in coal can exceed 5%. Of course, the most reliable would be the determination of the mineral substance in coal by chemical means (according to GOST 29086-91). However, these methods are complex; as a rule, they are not used in chemical laboratories of thermal power plants and coal enterprises. For the same reason, an analysis is not carried out separately for organic and mineral sulfur, according to which it would be possible to estimate the change in its total content with a change in ash content.

2. Results and discussion

The complexity of calculating the yield of volatiles and the heat of combustion for the actual ash content of coal supplied to TPPs A^d = 20 – 30% is aggravated by the fact that the V^{daf} and $Q_s{}^{daf}$ values, on the basis of which such estimates are made, for coals of specific suppliers are usually determined by ash-free samples ($A^d \leq 10\%$) [5], i.e. far from the actual range of ash content. To increase the reliability of the calculation of the net calorific value, the influence of the difference between the ash content and the mineral part in [6] was taken into account by the correction factor K_{mm}, by which the ash content is multiplied in the calculation formula for $Q_i{}^r$, kcal/kg:

$$Q_i{}^r = Q_s^{daf} \times (1 - K_{mm} \times A^d / 100) \times (1 - W_t{}^r / 100) -$$
$$- 583 \times [W_t{}^r / 100 + k \times (1 - K_{mm} \times A^d / 100) \times (1 - W_t{}^r / 100)] \quad (4)$$

where k is a coefficient that takes into account the hydrogen content in coal with conversion to water (averaged values of 0.46 for brown and bituminous coal, 0.21 for anthracite). On the basis of taking into account only the average content of carbonates, the value of K_{mm} in [6] is recommended to take 1.083 for Lvov-Volyn coals, 1.044 for Donetsk lean coals, 1.025 for Donetsk coals of other grades.

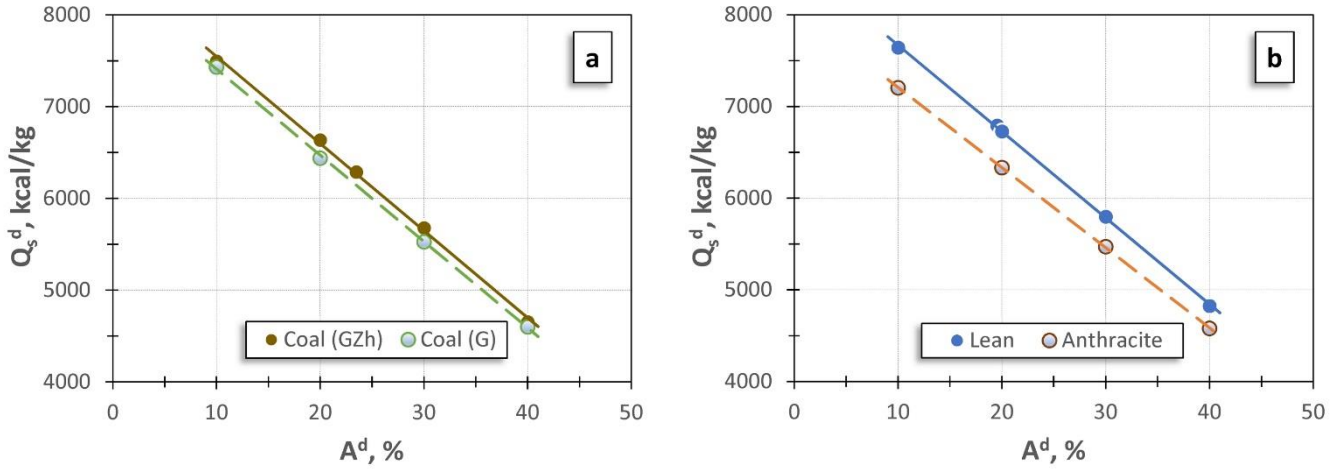

Fig. 1. Dependences $Q_s{}^d = f(A^d)$ for coals from Lvovsko-Volynskiy (a; solid points – GZH, transparent – G) and Donetsk basins (b; solid points – L, transparent – A).

In [7], it was proposed for the first time to determine the refined values of $Q_s{}^{daf}$ and K_{mm} by stratifying a coal sample in a heavy liquid, analyzing fractions of different ash content, and plotting dependencies $Q_s{}^d = f(A^d)$. This procedure was carried out with the bulk samples of the largest suppliers of coal from the gas group – SE Dobropolyeugol, SE DUEK and the

Yuzhnodonbasskoe #1. She showed that these dependences are approximated by linear ones ($A - B \times A^d$) with a correlation coefficient $R^2 > 0.9995$.

Intersections of linear approximations with the ordinate axis (at "zero" ash content) give the refined values of Q_s^{daf}, which for coal grades DG and G turned out to be 100-300 kcal/kg higher than the values averaged in [2] based on the results of the analysis of ash-free samples. The tangents of the angles of inclination of the straight lines to the abscissa axis gave the value $K_{mm} = 1.08 – 1.13$, which is much higher than the recommended ones in [6]. The results suggest that such high K_{mm} values are associated more with the loss of crystallization water and with the decomposition of mineral sulfur compounds than with the decomposition of carbonates.

In this paper, the approach proposed in [7] is used to refine the values of Q^{daf} and K_{mm} Donetsk lean coal (sample of the Zhdanovskaya mine) and anthracite (Krasnopartizanskaya mine), as well as Lvov-Volyn coal of grades G (mine "Chervonogradskaya") and GZh (mine "Stepnaya").

Figure 1 shows the dependences $Q_s^d = f(A^d)$ and their linear approximations with the correlation $R^2 = 0.9995$-0.9998. Table 1 summarizes the refined values of Q_s^{daf} and K_{mm} for all analyzed thermal coals. It can be seen that for all brands and both pools $K_{mm} = 1.08 – 1.13$.

Table 1. Adjusted values of Q_s^{daf} and K_{mm} for different grades of coal

Coal grade	Mine	K_{mm}	Q_s^{daf}
DG	Yuzhnodonbasskoe #1	1.10	8212
G	Yuzhnodonbasskoe #3	1.08	8232
G	Dobropolskaya	1.13	8287
G	Belozerskaya	1.10	8114
G	Chervonogradskaya	1.12	8346
GZH	Stepnaya	1.12	8468
L	Zhdanovskaya	1.10	8604

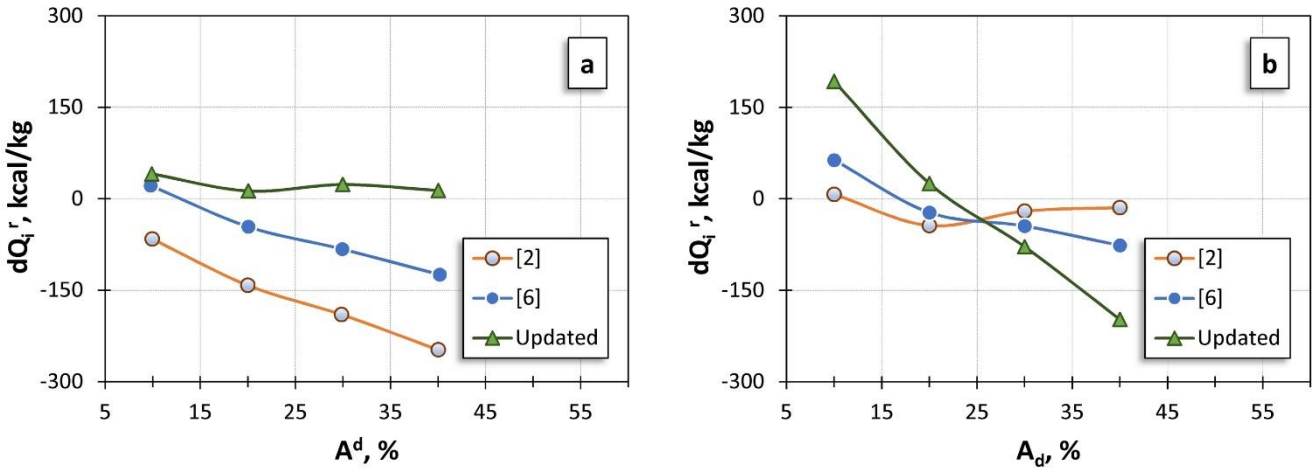

Fig. 2. The difference between the laboratory and calculated calorific value for Donetsk anthracite (a) and Lvov-Volynsk gas coal (b) according to the calculation method: transparent points – [2], solid ones – [6], triangles – using updated values Q_s^{daf} and K_{mm}

The use of refined data can significantly reduce the discrepancy between the calculation and the laboratory determination of Q_i^r. Figure 2 shows this discrepancy ("laboratory value minus calculated") for Donetsk anthracite and Lvov-Volyn gas coal, depending on the ash content. It is seen that the calculation accuracy according to [2] is ±200 kcal/kg, according to [6] ±100 kcal/kg. Calculation according to the formula [6] using the refined values of Q_s^{daf} and K_{mm} increases the accuracy up to ±40 kcal/kg, which

corresponds to the permissible error in determining the calorie content in a laboratory sample.

In our opinion, it is advisable to apply a similar approach to the yield of volatile substances and to the total sulfur content. Considering that both organic and mineral parts are the source of volatile substances and sulfur in a non-ash-free sample, their dependence on ash content can be represented as:

$$V^d = V^{daf} \times (100 - A^d) / 100 + V^{mm} \times A^d / 100 \quad (5)$$

$$S_t{}^d = S^{daf} \times (100 - A^d) / 100 + S^{mm} \times A^d / 100 \quad (6)$$

where V^{mm}, S^{mm} – the yield of volatile substances and the sulfur content in the mineral part of the coal. This is the form of the dependences $V^d = f(A^d)$ and $S_t{}^d = f(A^d)$ for the studied coals (Fig. 3).

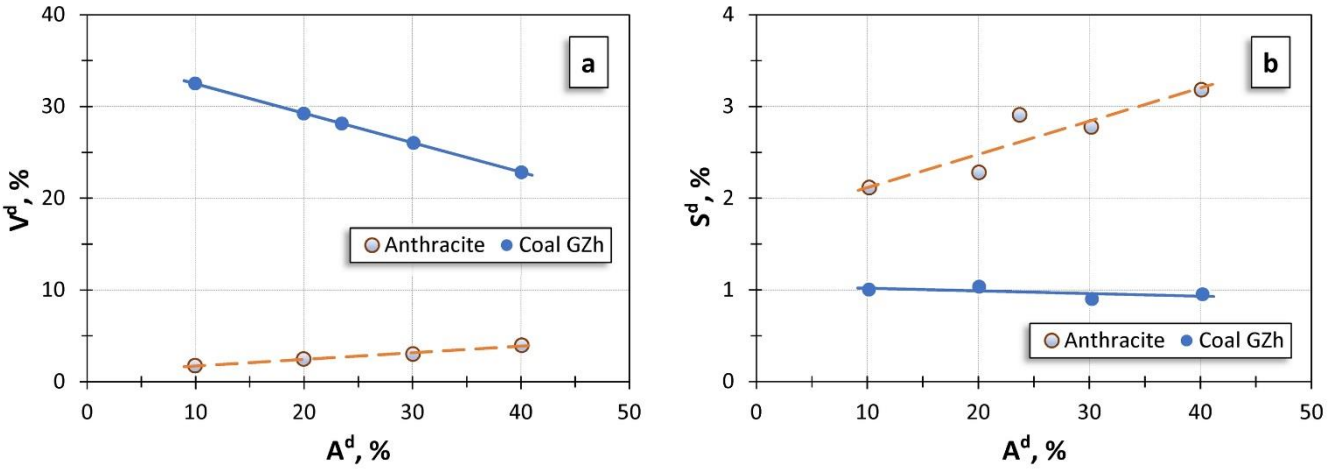

Fig. 3. Dependences $V^d = f(A^d)$ (a) and $S^d = f(A^d)$ (b) for Donetsk anthracite (transparent points) and Lvov-Volynsk coal GZh (solid points)

Experimental points are easily linearized. Slightly larger than in the dependences $Q_s{}^d = f(A^d)$, the scatter of the data is associated only with the lower accuracy of the laboratory determination of sulfur. The intersections of linear approximations with the ordinate axis (at "zero" ash content) give the refined values of V^{daf} and S^{daf}, the slope angles give the values ($V^{daf} - V^{mm}$) and ($S^{daf} - S^{mm}$), from which it is easy to determine V^{mm} and S^{mm} (Table 2).

Table 2 The release of volatiles and the sulfur content in the organic and mineral parts of coals of various grades

Coal grade	Mine	V^{daf}, %	V^{mm}, %	S^{daf}, %	S^{mm}, %
DG	Yuzhnodonbasskoe #1	40.1	3.4	1.15	2.25
G	Yuzhnodonbasskoe #3	38.1	5.1	0.94	1.28
G	Dobropolskaya	35.2	7.4	1.47	2.28
G	Belozerskaya	33.8	8.5	1.68	1.79
G	Chervonogradskaya	32.8	6.8	0.50	0.16
GZH	Stepnaya	35.5	4.0	1.74	5.46
L	Zhdanovskaya	6.40	9.8	1.76	3.04
A	Krasnopartizanskaya	1.10	7.8	1.05	0.77

Reverse substitution of these values into the above calculation formulas gives values that in 95% of cases deviate from laboratory values by no more than the permissible error in determining the volatiles yield and total sulfur content according to the corresponding determination standards. The V^{mm} values (in fractions) turned out to be close to (1 – K_{mm}) = 0.08-0.13. This indicates that the main part

of the mineral substance decomposes even during the determination of volatiles.

3. Conclusions

The results obtained allow us to consider in a new way the usual classification and technical characteristics of power-generating coals. The contribution of the decomposition of the mineral part to the measured yield of volatiles and its effect on the value of Q_i^r turned out to be much larger than previously thought. Taking it into account, the question may arise about refining the classification of some lean coals with V^{daf} less than 8% and dividing grade A into two groups, with V^{daf} more and less than 4%. This is due to the fact that during pulverized combustion, volatiles determine the conditions for the ignition of coal, but it is the volatiles of the organic, and not the mineral, that are capable of burning. At a number of power plants, burning anthracite with V^d = 4-5% at an ash content of 22-25% with forced gas-oil illumination, they do not suspect that the "useful" yield of volatiles in such anthracite does not exceed 2-3%, the rest is not conducive to ignition additive from the decomposition of the mineral part.

As for the sulfur content, which is important for planning the environmental performance of TPP power units, clarification of its distribution in the organic and mineral parts of coal determines the required degree of enrichment. Generally speaking, beneficiation reduces specific sulfur emissions by burning less low ash coal than high ash coal to generate the same amount of electricity. However, for the coals of such mines as Yuzhnodonbasskoe #1, Stepnaya, Zhdanovskaya, which are distinguished by an increased sulfur content in the mineral part, improving the ecological indicators of combustion may require additional enrichment.

In general, the results of this study solve the problem of reliably determining the heat of combustion, the yield of volatile substances and the sulfur content for the organic part of coal and the development of methods for calculating these indicators for coals with real ash content. It is extremely important that this does not require the involvement of complex and expensive methods of analysis. For coals of one manufacturer, as a rule, it is sufficient to separate a sample in a heavy liquid, for example, in carbon tetrachloride, and to determine the desired indicators at 3-4 different ash content levels, which is quite within the power of an ordinary TPP laboratory or coal enterprise.

In further studies using this approach, it is advisable to trace the change in the content of carbon, hydrogen and oxygen in coals, and, based on the results, specify which of the decomposition reactions of the mineral substance prevails in each specific case.

The generalization of the results for the main coal enterprises in Ukraine will provide a basis for clarifying the provisions of regulatory documents concerning the classification, quality and testing of coals for thermal power plants and other consumers.

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