Dependence of the heat of combustion of coals on their degree of metamorphism

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Abstract. The purpose of burning any fuel is to obtain thermal energy, the amount of which is judged by the heat of combustion, their most important thermophysical characteristic. In the modern world, the use of coal as a fuel for the production of heat and electricity leads in terms of consumption. This paper presents the results of measuring the highest heat of combustion of coal in a calorimeter unit. The analysis of the data obtained showed that the value of the highest calorific value depends on the metamorphism stage of coals and their elemental composition.

1. Introduction
In the modern world fuel and energy complex, coal is used mainly as a universal energy carrier and raw material for the production of metallurgical coke. The use of coal as a fuel for the production of heat and electricity takes the leading place in terms of consumption. Differences in the material composition and degree of metamorphism led to the differentiation of the technological properties of coals. To establish the direction of industrial use, coals are subdivided into grades and technological groups [1, 2]. Since there is a significant difference in the technological properties of coals, in order to establish a rational direction for the industrial use of coals in a particular industry, it is necessary to assess their energy potential by determining their heat of combustion [3-5]. It should be noted that the enthalpy of formation of the organic mass of coals is also calculated from the heat of reaction of complete combustion [6, 7].

The purpose of this study is to establish the dependence of the higher heat of combustion of coals on their stages of metamorphism and the elemental composition of organic matter.

2. Results and discussion
As objects of research, we used 10 samples of coal of various technological grades, selected at coal mining enterprises of Kuzbass. Analytical samples of coals (air-dry state, particle size 0.2 mm) were analyzed.

The technical analysis of coals was carried out using standard methods. The composition of the organic matter of the coals was determined by elemental analysis.

Deep changes in the molecular composition and properties of fossil coals in the bowels of the earth's crust are commonly called metamorphism. Transformations of the molecular structure of fossil coals during metamorphism affect not only their chemical and technological properties, but also a number of physical parameters, in particular, the change in their optical properties [2, 8].
Consequently, fairly objective data on the degree of coal metamorphism can be obtained by determining the vitrinite reflectance index, determined in the immersion oil (Ro,r) according to GOST 12113-83.

Petrographic analysis was carried out on an automated complex for assessing the grade composition of coals of the SIAMS-620 system (Russia) in an oil immersion environment. The microcomponents were counted automatically at a magnification of 300 times in reflected light.

The determination of the heat of combustion of analytical coal samples (with a particle size of less than 0.2 mm) was carried out in accordance with GOST 147-95 (ISO 1928-76) on a S2000 IKA Calorimeter. The calculation of the highest heat of combustion of coals for a dry ashless state (Q\text{daf}) was carried out according to the formula: \( Q_{\text{daf}} = Q^a/(1 - W^a)(1 - A^d) \), where \( Q^a \) is the highest calorific value of the analytical sample, \( W^a \) is the analytical moisture, \( A^d \) is the ash content for the dry state of the fuel [9].

The characteristics of the coal samples are given in Tables 1 and 2. It can be seen that the coals differ in ash content and the yield of volatile substances, the sulfur content in the coals is minimal.

**Table 1. Characteristics of the studied coal samples**

| No. sample | Coal grade* | Technical analysis, % |
|------------|-------------|-----------------------|
|            |             | \( W^a \) | \( A^d \) | \( V_{daf} \) | \( S^d \) |
| 1          | LF          | 4.5     | 3.8     | 42.2     | 0.3 |
| 2          | LFG         | 3.9     | 6.2     | 41.2     | 0.4 |
| 3          | G           | 3.0     | 10.1    | 38.7     | 0.6 |
| 4          | GF          | 1.6     | 8.3     | 32.1     | 0.4 |
| 5          | F           | 0.9     | 7.4     | 32.4     | 0.4 |
| 6          | CF          | 1.1     | 7.8     | 28.2     | 0.5 |
| 7          | C           | 1.2     | 8.7     | 25.6     | 0.3 |
| 8          | CWC         | 1.2     | 9.7     | 22.1     | 0.5 |
| 9          | HC          | 0.9     | 6.8     | 19.4     | 0.3 |
| 10         | A           | 0.8     | 10.5    | 5.9      | 0.2 |

*LF-long-flame, LFG-long-flame gas, G- gas, GF-gas fat, F-fat, CF- coking fat, C-coking, CWC-coking weakly caking, HC – hard caking, A- anthracite

**Table 2. Elemental composition and indicators of calorific value of the studied coals**

| Coal grade | Metamorphism stage | Elemental composition, % per daf | Atomic ratio | \( Q^{daf} \), MJ/kg |
|------------|--------------------|-----------------------------------|--------------|----------------------|
| Code       | \( R_{o,r} \), %  | C       | H       | (O + N + S) | H/C     | O/C     |               |
| LF         | I                  | 0.59    | 77.6    | 5.6      | 16.8    | 0.86    | 0.16    | 31.516       |
| LFG        | I                  | 0.63    | 79.2    | 5.7      | 15.1    | 0.86    | 0.14    | 32.370       |
| G          | I-II               | 0.70    | 81.4    | 5.6      | 13.1    | 0.83    | 0.12    | 33.208       |
| GF         | II                 | 0.82    | 84.3    | 5.6      | 10.1    | 0.80    | 0.10    | 34.518       |
| F          | II-III             | 0.96    | 86.1    | 5.5      | 8.4     | 0.75    | 0.07    | 35.205       |
| CF         | III                | 1.10    | 87.5    | 5.4      | 7.1     | 0.74    | 0.07    | 35.677       |
| C          | III-IV             | 1.20    | 89.8    | 5.0      | 5.2     | 0.64    | 0.04    | 36.071       |
| CWC        | IV                 | 1.39    | 89.7    | 4.7      | 5.6     | 0.63    | 0.05    | 35.707       |
| HC         | IV                 | 1.42    | 89.9    | 4.6      | 5.5     | 0.61    | 0.05    | 35.661       |
| A          | VII-VIII           | 2.72    | 95.3    | 2.0      | 2.7     | 0.25    | 0.02    | 34.530       |

The data presented show that coals of various stages of metamorphism were studied, the vitrinite reflectance (\( R_{o,r} \)) of which varies from 0.59% to \( R_{o,r} = 2.72\% \). The elemental composition of the organic matter of coals changes according to their brand identity and genetic maturity. With an increase in the maturity stage, the carbon content increases against the background of a decrease in the content of hydrogen and various heteroatoms (oxygen, nitrogen, and sulfur) (Table 2). Analysis of the
obtained data on the calorific value of coals shows that their calorific value in the series of metamorphism changes extremely (Figure 1).

![Graph showing the relationship between highest calorific value and reflection index of vitrinite](image1)

**Figure 1.** The nature of the relationship of the highest calorific value with the reflection index of vitrinite of coal ($R_o,r$)

It was found that at the initial stages of metamorphism with a change in the vitrinite reflectance $R_o,r$ from 0.52 to 1.10%, an increase in the heat of combustion of coals from 31.516 to 36.071 MJ/kg is observed. In the range of variation of the vitrinite reflectance at $R_o,r = 1.10 - 1.42\%$, the heat of combustion of coal remains approximately at the level of 35-36 MJ/kg. With a further increase in the vitrinite reflectance index ($R_o,r = 2.72\%$), there is a slight decrease in this indicator to 34.530 MJ/kg (Table 2). The decrease in the heat of combustion can probably be explained by a certain ratio of hydrogen and carbon in the organic mass of the coal sample. It is known that of the elements that make up the organic mass of coal, combustible are carbon, hydrogen and part of sulfur [10-14]. In sample No. 10 (coal grade A), the maximum value of the carbon content with the minimum content of hydrogen was determined, and the sample is characterized by the minimum value of the H/C atomic ratio (Table 2).

Figure 2 shows a graphical dependence of the highest heat of combustion of coals on the carbon content in their organic mass.

![Graph showing the dependence of highest calorific value on Cdaf and atomic ratio H/C](image2)

**Figure 2.** Graphical dependence of the highest calorific value of coal on $C_{daf}$ (a) and atomic ratio H/C (b) of their organic mass

It can be seen that for coals of low and medium stages of metamorphism in the range $R_o,r = 0.52 - 1.10\%$, the value of their calorific value is directly proportional to the carbon content. With an increase in the maturity stage of coals, the content of hydrogen in the organic mass decreases and, as a
consequence, the atomic ratio H/C, which leads to a decrease in the calorific value of coals with the $R_{o,r} > 2.5\%$ index.

3. Conclusion
A study of the calorific value of fossil coal, selected at various coal mining enterprises of the Kuznetsk coal basin, has been carried out. It is shown that the value of the highest calorific value depends on the stage of coal metamorphism and their elemental composition. It was found that for coals with a vitrinite reflection index from 0.52 to 1.10\%, a very intensive increase in the heat of combustion from 31 to 36 MJ/kg is observed, with $R_{o,r} > 2.5\%$, this indicator slightly decreases to 34- 35 MJ/kg due to the reduced hydrogen content in their organic mass.

4. References
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