



# Rank-dependent formation enthalpy of coal



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## ABSTRACT

In the study, the enthalpy of formation of a complex chemical compound, such as coal, was defined as the difference between the experimentally determined heat of combustion and the thermodynamically calculated heat of combustion of the elementary reactants. The boundary conditions for the approach were defined by the enthalpy of formation of graphite; thus, the aforementioned method should produce a value of zero for graphite. Using the developed correlation for the enthalpy of formation, a model of coal classification was developed based on this thermodynamic quantity, which reflects the structure and technological suitability of coal. According to the analysis of the enthalpy of formation with respect to the composition of coal, the enthalpy of formation may have negative or positive values, depending on the type of fuel. Furthermore, changes in the formation enthalpy are continuous but correspond to different chemical structures. The following values for the enthalpy of formation were obtained: anthracite = +250 kJ/kg, peat < −3200 kJ/kg and medium volatile bituminous coal ~zero.

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## 1. Introduction

The final state of the geochemical transformation of plant debris is coal, a complex form of organic matter contaminated with dispersed mineral substances. Geochemical changes lead to the formation of specific coal structures that are dependent on the composition and temperature–pressure history of the original substance and its transformation. In general, coal organic matter is not defined as a chemical compound; rather, a model form is used to describe coal, depending on its rank. Thus, coal cannot be characterized by a defined thermodynamic state at a standard pressure and temperature, which is referred to as the enthalpy of formation and is easily determined for pure species using proper thermodynamic tables or by measuring the heat of individual reactions. However, this strategy is not relevant for coal due to the complexity of its composition. According to the particular chemical structure of coal, one can construct an indirect method for determining the enthalpy of formation and classify coal with respect to that quantity.

Established classification systems guide the interpretation of the results of scientific research and allow for the comparison of operating conditions and coal selection for chemical processing. However, the analysis of such classification systems and the resulting parameters show that these systems are inconsistent. In addition, when classifying coal for processing in the chemical and power industry, technological needs are not directly reflected,

and operational parameters such as the caking ability, ash content or calorific value are the primary focus [1,2].

Previous studies suggest that existing classification systems are not related to the thermodynamics that characterize the work potential of coal. In the present study, a key thermodynamic parameter – the enthalpy of formation – was used to characterize coal.

The enthalpy of formation represents the energy obtained from reactions that produce coal. For pure substances, the enthalpy of formation is a single, defined value. However, due to the various chemical structures of coal, the enthalpy of formation depends on the rank of coal and the specific structure of a given type of coal. Thus, the enthalpy of formation can be used in classification systems to characterize coal.

To maintain consistency with chemical thermodynamics, a nascent model should take into account the fact that increasingly metamorphous coal approaches the structure of graphite, for which the heat of calorimetric combustion and the thermodynamic enthalpy of combustion are equal and the enthalpy of formation is zero.

To develop a new coal classification approach, knowledge of the formation enthalpy is needed to model various processes. In current computer models, the formation enthalpy is taken as zero because coal is split into basic elements in the absence of heat effects. That approach can result in substantial errors, particularly in the modeling of pyrolysis and gasification.

## 2. Experimental

The objective of the present study was to determine the influence of coal (described by the elemental composition) on the

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**Table 1**  
Range of elemental compositions and heats of combustion.

Parameter	Min. value	Max. value
Content (%) (daf)		
C	69.87	91.26
H	2.61	6.66
O	2.08	23.08
N	0.07	2.53
S	0.39	9.37
$Q_{\text{daf}}^s$ , MJ/kg	27.27	36.98

change in the enthalpy of formation. It was assumed that the enthalpy of formation for coal, which is a complex fuel, is equal to the difference between the measured heat of combustion and the thermodynamically calculated heat of combustion of the elements of coal (C, H and S). The difference between the measured heat of combustion and the calculated thermal effect of combustion was based on 224 sets of data describing the properties of Russian [3], American [4] and Polish [5] coal and char/coke. For computational and comparative purposes, the elemental composition data were converted into a dry and ash-free basis, and the heat of combustion was treated similarly. The oxygen content was obtained by subtracting the determined contents of other elements (C, H, N, and S), and the combustible fraction of sulfur was taken into account. The database comprised a wide spectrum of fuel properties, and the ranges are presented in Table 1.

The data were used to verify the available correlations for the calculation of the heat of combustion for coal or char. As a result, a new correlation that takes into account the expected consistency between the enthalpy of the combustion of coal elements and the calorimetrically determined value of the heat of coal combustion was developed. Thus far, according to the state of knowledge published in the literature, such a relationship has not yet been developed. Therefore, in the present study, the enthalpy of formation was calculated and described by a correlation equation for the entire coalification range.

### 2.1. The dependence of the heat of combustion on the composition of coal

In Figs. 1–3, the basic relationships between the measured heat of combustion and the content of individual elements are presented. The heat of combustion of solid fuels for a wide range of coalification stages showed that the maximum heating value is achieved at a carbon content of 85–90% (Fig. 1), which corresponds to an oxygen content of 3–4% (Fig. 2) and a hydrogen content of

5–6% (Fig. 3). The observed maxima correspond to the following atomic ratios – C:H:O = 28:20:1 – and are observed for the range of coking coal. The value of the heat of combustion  $Q_s$  approaches the heat of graphite combustion (32.84 MJ/kg) as the oxygen and hydrogen content decrease to zero (Figs. 2 and 3). Basically, hydrogen strengthens  $Q_s$  by binding with carbon and weakens  $Q_s$  by binding with oxygen. As a result, the correlation between  $Q_s$  and the H content is poor.

## 3. Results and discussion

### 3.1. Heat of combustion – literature correlation analysis

The heat of combustion is a basic quantity that characterizes the energy potential of fuels. The heat of combustion can be experimentally determined using standard calorimetric procedures, and its actual value can be obtained [6].

However, in most cases, computational methods based on the elemental composition of fuel are employed to obtain the heat of combustion. A significant number of correlations have been developed and have been comprehensively reviewed by Channiwala and Parikh [7]. These correlations have been applied to both coal and biomass. The existing correlations can be used for calculating the high heating values (HHVs) of coal but not those of the char that is a product of coal pyrolysis and is enriched in carbon. For fuels that contain less than 5% oxygen, as the carbon content approaches 100%, the calculated HHV deviates significantly from the expected values. This result indicates that all of the correlation values do not produce the proper value of HHV for graphite, and they do not cover the entire range of carbon content, which is critically important for process modeling.

To identify a relationship between the enthalpy of coal combustion, which is taken as a physical mixture of elements, and the calorimetric heat of combustion, the existing correlations must be considered. Thus, the relationships for coal under dry and ash-free conditions (dafs) were verified. Dulong [8] Eq. (1), which considers the amount of hydrogen available for combustion by deducting the equivalent oxygen content, is the most well-known relationship. In addition, the Strache and Lant (2) [9] and Steuer (3) [10] correlations were also considered. The other correlations evaluated in the present study take into account the effects of oxygen on the binding of carbon and hydrogen. These relationships include D'Huart (4) [11], Seylor (5) [12] and Gumz (6) relationships [13]. The Boie (7) [14], Dulong-Berthelot (8) [15] and IGT relationships (9) [16], which average the results of more than 700 samples of coal and char, are the most frequently used equations. Taking into account all of the

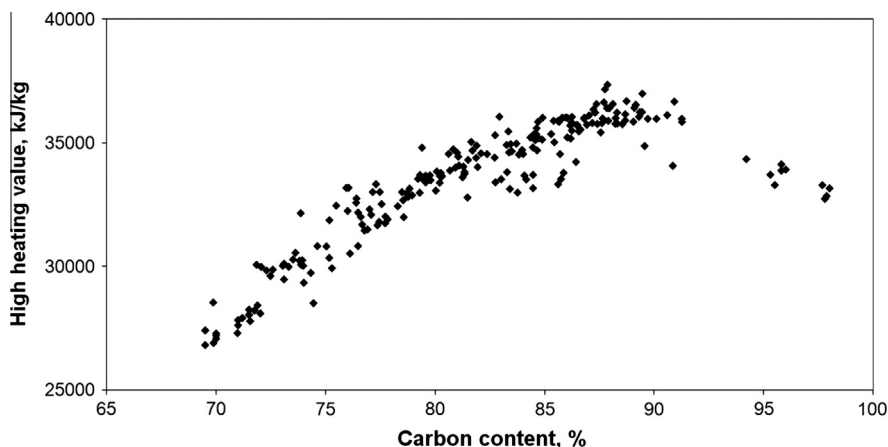


Fig. 1. The dependence of the heat of combustion on the carbon content (daf).

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