

APPLYING THE CORRECTION FOR UNDECOMPOSED CARBONATES TO GROSS CALORIFIC VALUES OF OIL SHALES FROM DIFFERENT DEPOSITS

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Abstract. *The relationship between the carbon dioxide content of carbonates in the bomb calorimeter combustion residues and that in the corresponding oil shale samples originated from different deposits was investigated. As a result, a criterion for applying a correction for undecomposed carbonates to gross calorific value was established. A suitable standard method for determination of gross calorific value of oil shale samples was also suggested.*

Keywords: *gross calorific value, carbonates in oil shale, carbon dioxide, calorimetric bomb.*

1. Introduction

Calorific value is the most important quality characteristic of fuel. The influence of the composition of mineral matter on the calorific value of low-calorific fuels, e.g. oil shales and lignites, has been widely investigated [1–9]. For instance, Jaber et al. [7] reported that in case of Jordan oil shale, the calcium carbonate content has some influence on its gross calorific value. Such influence was quantitatively evaluated for Israel lignite in which the relatively high CaCO₃ content decreases the calorific value of the fuel due to endothermic decarbonisation. When the sum of ash and carbon dioxide contents was plotted against the sum of high calorific value

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and decarbonisation heat consumption, a good linear relationship was observed [8].

Warne and Dubrawski [9] addressed the possibilities of calculating corrections to the gross calorific values using the differential thermal analysis (DTA) method.

There are some national and international standards covering the determination of calorific value of coals and cokes [10–13]. Oil shale has not been included in the scope of these standards.

GOST 147-95 covers the analysis of coals, peat and oil shale and takes the specificities of oil shale analysis into account [14]. The presence of undecomposed carbonates in the bomb combustion residue requires applying the corresponding correction to the gross calorific value. According to the standard, such correction is required for calorific values below 5.440 MJ/kg. However, the standard only concerns oil shales from the Baltic deposit and the Volga deposit.

The aim of this work was to determine a criterion for applying the correction to gross calorific value for undecomposed carbonates that would be applicable to oil shales from different deposits.

2. Experimental

2.1. Selection of samples

More than 1000 oil shale samples from different deposits were analysed by our research group in the course of previous investigations. About 50 samples were chosen for the present research based on their carbon dioxide content of carbonates, $(\text{CO}_2)_M$, and calorific values by bomb, Q_b^\dagger . The data on oil shale samples from the Baltic deposit obtained in our previous studies along with the data from literature [15] were plotted in Figure 1 to estimate the value of carbon dioxide content which corresponded to the calorific value of 5.440 MJ/kg.

As seen from Figure 1, there is a clear linear dependence between the carbon dioxide content of carbonates and the calorific value in case of oil shale samples from the Baltic deposit (the squared value of the correlation coefficient is 0.9256). It can be explained by the fact that the mineral matter composition of Baltic oil shale samples is rather constant. The plot indicates that for the Baltic oil shale with a calorific value of 5.440 MJ/kg the carbon dioxide content of carbonates is about 25% by mass.

Based on these values, the samples were selected so that each of the following groups would be represented: $Q_b \geq 5.4$ MJ/kg and $(\text{CO}_2)_M \geq 25\%$; $Q_b \geq 5.4$ MJ/kg and $(\text{CO}_2)_M \leq 25\%$; $Q_b \leq 5.4$ MJ/kg and $(\text{CO}_2)_M \geq 25\%$; $Q_b \leq 5.4$ MJ/kg and $(\text{CO}_2)_M \leq 25\%$. Figure 2 illustrates this selection further.

[†] Calorific value by bomb, Q_b , is the heat of combustion in the calorimetric bomb not corrected to acid formation and carbonates decomposition.

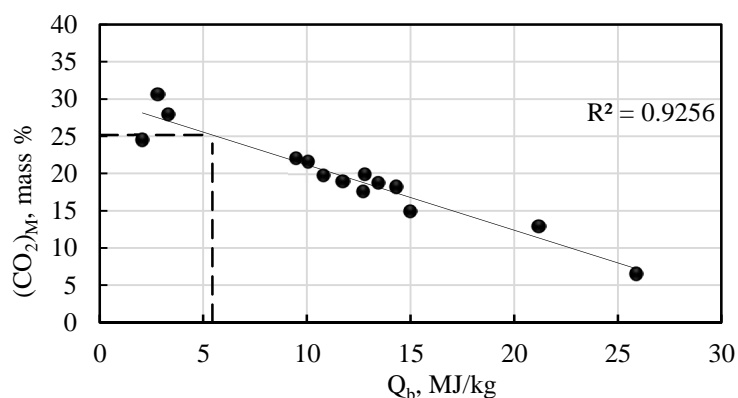


Fig. 1. Data on oil shale samples from the Baltic deposit.

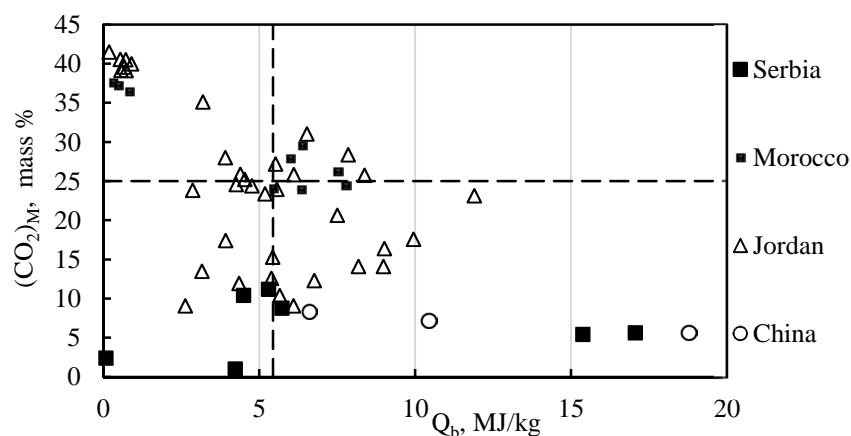


Fig. 2. Characteristics of oil shale samples from different deposits taken for the study.

Thus, the samples from Jordan, Moroccan, Serbian and Chinese oil shales with $(CO_2)_M$ in the range of 1.0–41.5% by mass and Q_b between 0.079 and 25.900 MJ/kg were selected for this study.

2.2. Determination of the carbon dioxide content of undecomposed carbonates

The studied samples were combusted in the Parr 6300 calorimetric bomb. The mass of the weighted portion was 1.0–1.2 g. To fulfil the requirements of the standard methods a benzoic acid of qualification "for calorimetry" was added to the weighted portions of low-calorific oil shale samples to provide the temperature rise equal to that during calorimeter calibration. After combustion, the residues were transferred into weighing vessels and dried completely in a drying oven at 160 °C.

The determination of the carbon dioxide content of carbonates in the residues was carried out using a Vario Macro Cube SoliTIC module device. The test portions were acidified and heated to 50 °C. The amount of released carbon dioxide was quantified by a thermal conductivity detector. The obtained values ranged from 0.06 to 27% by mass.

3. Results and discussion

The relationship between the carbon dioxide content of carbonates present in the residue and the calorific value by the bomb was investigated. It can be seen from Figure 3 that there is a general reverse dependence between the calorific value and the amount of undecomposed carbonates in the residue. However, this correlation is not significant.

It is not possible to determine the degree of influence of the calorific value on the content of undecomposed carbonates in the residue since benzoic acid is added to the samples during analysis.

The dependence between the carbon dioxide content of carbonates in the residue and the carbon dioxide content of carbonates in oil shale is illustrated in Figure 4.

Figure 4 shows that the data points form two distinct groups based on their $(\text{CO}_2)_M$ value in oil shale. As the figure reveals, for oil shale samples with the carbon dioxide content of carbonates less than 23% mass, the latter has almost no influence on the content of undecomposed carbonates in the residue. On the other hand, for samples with the $(\text{CO}_2)_M$ mass percentage exceeding 23, this influence is significant and a linear correlation between the two parameters is observed. The R-squared value is 0.9654.

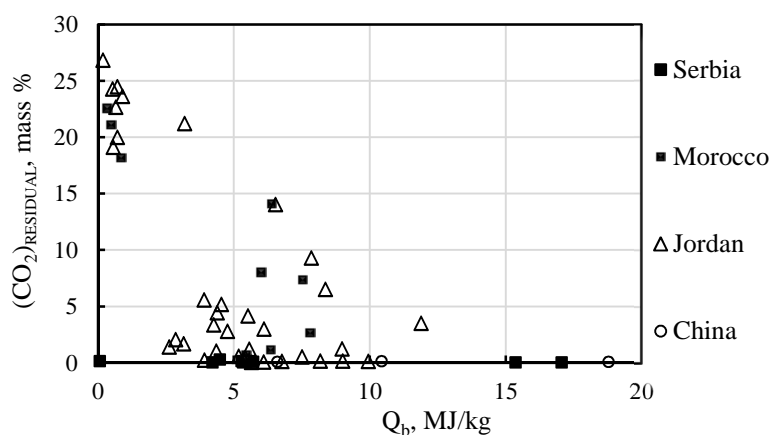


Fig. 3. The relationship between the carbon dioxide content of carbonates in the residue and the calorific value by the bomb.

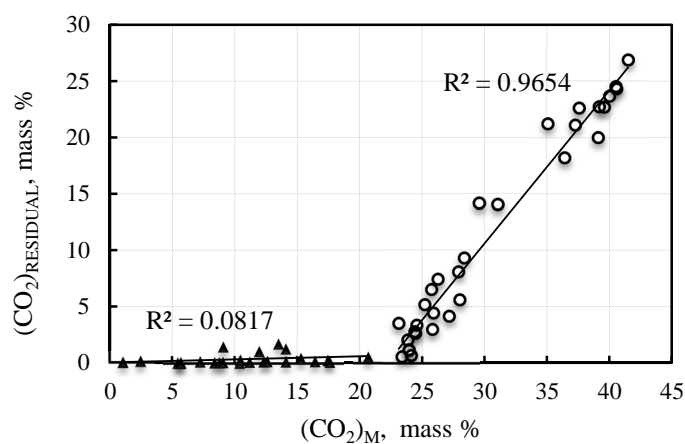


Fig. 4. The dependence of the carbon dioxide content of carbonates in the residue on the carbon dioxide content of carbonates in oil shale.

The obtained values of the carbon dioxide content of carbonates in the residue were recalculated as a mass percentage of the original oil shale sample, taking the yield of residue into account, for further calculations of correction to the gross calorific value.

To calculate the corrections to gross calorific value, the carbon dioxide content of carbonates in the residue, expressed as a mass percentage of the original oil shale sample, was multiplied by the constant ε . This constant takes into account the heat of the decomposition of carbonates and is equal to 40 kJ/kg per 1% of the CO_2 of carbonates. The obtained values are shown in Figure 5.

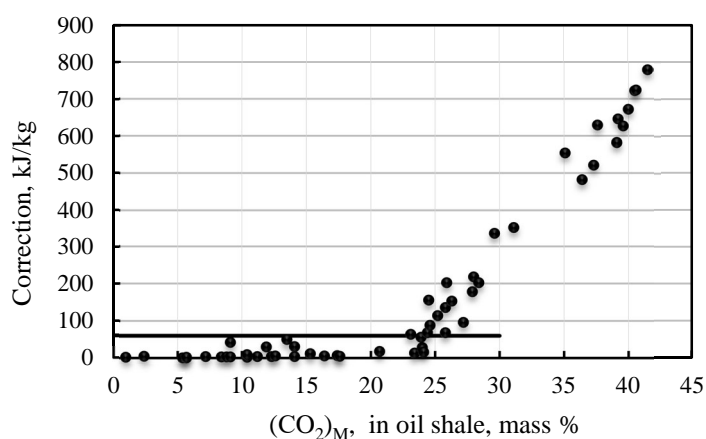


Fig. 5. The dependence of corrections to gross calorific value on the carbon dioxide content of carbonates in oil shale.

As can be seen from Figure 5, in case of oil shale samples with the carbon dioxide content of carbonates greater than 23% on mass basis, the value of the correction to the gross calorific value is higher than 60 kJ/kg, which is half the limit of the repeatability of the standard methods and therefore cannot be disregarded. As is clear from the figure, the correction to gross calorific value can reach 800 kJ/kg for some oil shales.

It should be noted that for Estonian oil shale, the correction needs to be applied only to samples with a calorific value lower than 5.440 MJ/kg since they contain more than 23% mass of the carbon dioxide of carbonates. This calorific value cannot be used as a criterion for oil shales from other deposits.

The results of this research were used when adapting ISO 1928-2009 as an Estonian national standard (EVS-ISO 1928-2016) [16].

4. Conclusions

A correction to gross calorific value for undecomposed carbonates is required for oil shales that contain more than 23% mass of the carbon dioxide of carbonates.

Currently both standard methods, ISO 1928-2009 and EVS-ISO 1928-2016, are valid. However, when dealing with solid fuels such as oil shale, it is more appropriate to use EVS-ISO 1928-2016 rather than ISO 1928-2009 because the requirements taking the specificities of oil shale analysis into consideration were included in this standard.

Since the net calorific value is calculated via gross calorific value, the correction to undecomposed carbonates will also have an influence on the net calorific value.

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