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Proximate analysis of coal by micro-TG method

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ABSTRACT

The presented paper examines the feasibility of the application of micro-TG for the sake of proximate analysis of coal. It is aimed to develop a reliable and versatile procedure which allows to determine the content of each coal constituent during one experimental run. Among several investigated factors (i.e. temperature, heating rate, residence time, etc.), a special focus is given to the procedure of purging the TG furnace, which is claimed to be a possible source of erroneous moisture content determination. Analysis performed for nine samples indicates that the proposed method provides results close to these given by standardized approach, while discrepancies in the amount of measured moisture, volatile matter, fixed carbon and ash are not higher than 0.2%, 0.6%, 1.0% and 1.0% respectively.

1. Introduction

Proximate analysis is the simplest and most common form of coal evaluation, applied to determine fuel structure, its properties and energy value. It covers the determination of moisture *M*, volatile matter *V*, ash *A*, and the calculation of fixed carbon content *FC*. Traditionally, standards for proximate analysis are developed by several institutions, including the International Organisation for Standardisation (ISO), the American Society for Testing and Materials (ASTM), the German Institute for Standardisation (DIN) and the British Standards Institution (BSI). Despite the multiplicity of different standards for proximate analysis, the principle and procedure of measurement seems to be quite similar. In general, coal components are determined gravimetrically, after heating a sample under specified temperature, time and atmosphere conditions. Regardless of some differences in the measurement procedure, it may be stated that, for coals, moisture is determined at 104–110 °C [1–4], volatiles at 850–1050 °C [5–8] and ash at 700–950 °C [8–10].

The standard proximate analysis has some advantages, such as simple and inexpensive equipment required, however it is also limited due to the need to measure each component separately, a time-consuming procedure and reliance on operator's skills. Moreover, the standard method requires a significant amount of a sample, which may vary, depending on the results quality and complexity, from a few to a dozen grams. In the case of industrial application, it will not cause a problem, however, in research it may, especially when samples to be characterized are collected from microreactors.

Among several available laboratory techniques [11–13], thermogravimetric analysis (TG) is considered a promising alternative allowing to perform the proximate analysis for a slight specimen size. The technique requires samples about 1000 times smaller than the standard approach, with a mass of about several micrograms.

The application of TG for coal analysis dates back almost as far as the techniques themselves, the first attempt to investigate the volatile matter yield of coals was presented in 1930 [14]. The direct comparison of proximate analysis results, obtained using standard and TG approaches, is presented in [15]. The thermogravimetric procedure comprises the determination of moisture at 110 °C (hold time one minute), volatiles at 900 °C (at an inert atmosphere, hold time one minute) and fixed carbon at 900 °C (at an oxidizing atmosphere). The results of both methods, compared on dry basis, are quite similar. Some differences in ash content are attributed to the different temperature of ash determination, the TG method heats the sample 85 °C above the temperature used in the standard approach. As explained in the paper, the presentation of results in a moisture-free form eliminates the problem with variability in moisture content, however, on the other hand, it impedes evaluation of the quality of TG moisture determination.

The experimental procedure presented in paper [16] is similar to those applied in [15], except that the hold time for moisture determination is extended to 9.5 min and, in some cases, the temperature of volatile determination is increased to 950 °C. The results obtained using the TG approach correspond to data given by the standard proximate analysis. Unfortunately, as in the case of [15], TG data, obtained for coals, are presented on dry basis and thus the quality of thermogravimetric moisture determination cannot be investigated. Admittedly, for biomass, TG results are given on as received conditions, but results obtained using the standard approach are missing. Noteworthy is that, unlike the observations presented in [15], the ash results determined by

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both methods are in agreement, although the TG temperature of ash determination is higher by about 150–200 °C than the temperature applied in the standard approach.

Paper [17] provides information about proximate analysis, performed using TG, in as received conditions. The procedure is similar to [16], except the hold time for moisture and volatiles determinations are six and five minutes respectively. As stated in the work, the volatile matter, fixed carbon and ash results follow the expected trend, while the moisture content appears to be lower than expected. The explanation indicates that samples may have been intentionally or unintentionally dried by the supplier before shipment to the customer or during grinding in mortar and pestle, due to frictional heat.

The results presented in [18] confirms that moisture content determined using TG and the standard approach might differ significantly. Similarly to the observation presented in [17], for two investigated RDF samples, the TG method provides lower values than the traditional measurement. Moreover, the standard deviation for the thermogravimetric approach is significant, equal to 0.5% and 0.7% for samples containing 3.5% and 4.0% of moisture, respectively. The observed discrepancies are attributed to the fluctuations of room humidity and moisture pick up by the sample. Beside the moisture issue, it is interesting to note that, volatiles determined at 800 °C (TG procedure) and 950 °C (ASTM standard) are in good agreement.

The authors of [19] suggest differentiating the temperatures of volatiles and fixed carbon measurements. In their work, volatile matter is determined at 950 °C, after holding the specimen at high temperature for seven minutes, while fixed carbon is determined at 750 °C, until the sample weight became constant. The results obtained for 24 samples of Turkish lignites indicate some differences between values obtained using thermogravimetry and ASTM standards. The mean difference in the volatile matter content is 1.5%, while the maximum discrepancy reaches even 4.6%. It was suggested that, the higher volatile content determined by TG than ASTM is caused by the nitrogen flow through the thermogravimetric analyser, improving the mass transfer between the gas and solid phases. Differences in moisture and ash content are less significant, mean differences are 0.38% and 0.68%, respectively. However, for selected samples, TG values vary from the standard ones by about 1.3% and 1.8% respectively.

In all articles cited above, moisture is determined at 110 °C, following up the temperature applied in standard procedures. A different attempt is presented in [20], where moisture is measured at 200 °C. The obtained results of moisture value are satisfactory, nevertheless the application of such a high temperature seems to be questionable. According to [21,22], for coals, in this range of temperatures, not only is the release of inherent and surface moisture visible, but also the decomposition of, e.g. carboxylic acid may occur. Considering volatiles and fixed carbon content, the applied thermogravimetric procedure, leads to errors reaching more than 2%.

An interesting attempt at proximate analysis by means of TG is presented in [23], where three different approaches are compared. The first investigated procedure is based on [20]. The second one is an adaptation of a method originally presented in [24], where after devolatilization, a sample is cooled down to room temperature and afterwards heated again in an air atmosphere. The third method comprises the optimization procedure, aimed to find a set of parameters that ensure: minimal difference of volatile matter content determined by means of TG and the standard method, short run time and low flow rate. The variables include heating rate, final temperature, holding time, flow rate and sample mass. The application of the first method provides weight curves for which it is not possible to find an exact point of the end of devolatilization. The second method is suitable only for two out of four investigated coals. For the other two samples, the differences between the thermogravimetric and standard approach are more than 15% (for volatiles), more than 12% (for fixed carbon) and ca. 3% (for ash). The third series of tests indicate that optimal experimental conditions should cover: heating rate of around 80 deg min^{-1}, final temperature of around 780 °C and high flow rate of a carrier gas. Nevertheless, after 50 trials, the values failed to converge in complete agreement with the ASTM characterization. The lack of success is attributed to different physicochemical properties of coals; for low reactive coals, TG approach underestimates volatile content, while for highly reactive coals TG values are higher than the ASTM ones. It is also worthwhile to mention that the high temperature and long oxidation time imply low ash percentages, which is attributed to the devolatilization of light inorganics and changes in mineral matter.

Another relationship between the quality of TG procedure and coal properties can be found in [21]. The applied method comprises the determination of moisture at 110 °C and volatiles/fixed carbon at 900 °C (similar to [15–17]), for holding times 30, 20 and 75 min respectively. It is noted, that for coals containing a low amount of volatiles, results obtained using TG and the standard approach are similar. A further increase in volatile content implies a growing difference between the obtained values. For coal having more than 40% of volatile matter, the TG method provides values about 5.9% lower than the standard approach. Moreover, the performed analyses indicate variations in moisture and ash values, where the mean difference are 2.9% and 2.5% respectively.

Beside the results published in research papers, there are also standards describing the methodology of performing proximate analysis by means of TG. Nevertheless, the ASTM D7582 [25] is designed for macro thermogravimetric analysis and, as stated in the scope, cannot be applicable to thermograwimetric analyzers using microgram size samples. On the other hand, the ASTM E1131 [26] provides a technique incorporating micro thermogravimetry to determine proximate analysis, but in the case of coals, the procedure of moisture content determination is not tested. As mentioned in the text, coals are investigated on a dry basis therefore the highly volatile component (moisture) cannot be measured.

As shown above, despite many works in the literature, the need for the development of a universal and reliable TG procedure is still unresolved. Several cited works indicated difficulties in the application of TG in moisture determination, attributing them to different sources of errors. Other papers reported divergences between ash, volatiles and fixed carbon values determined by the standard and thermogravimetric approach. Moreover, from the state-of-art [21,23], it can be concluded that even if the TG procedure is successfully applied in one type of fuels (e.g. low-volatile hard coals), it cannot by applied in others (e.g. high-volatile hard coals).

The aim of this paper is to develop a reliable and versatile micro-TG procedure which allows to determine the content of moisture, volatiles, fixed carbon and ash during one experimental run. A special attention is devoted to the explanation of the possible sources of an erroneous moisture content determination. Moreover, the impact of holding time, maximum temperature and heating rate is discussed in the context of determining particular fuel components. In contrast to many works presented above, the measuring procedure developed in this paper, is not fast, however it does provide results similar to those given by the standard approach.

2. Experimental

Nine coals were analysed, including six samples from South Africa provided by ESKOM (specimens A1–A6), one sample provided by EDF Polska S.A. (E1) and two samples provided by Polish mines (E2 and E3). The fuels are selected due to their availability, suitability for combustion and future potential for use in industrial boilers. The samples are air dried, pulverized to a size below 200 μm and homogenized. Moisture content is determined according to [4] (at 110 °C), volatile matter according to [7] (at 900 °C) and ash according to [9] (at 815 °C). The obtained results are reported in Table 1.

Table 1 illustrates differences between the physicochemical properties of the investigated coals. The samples contain from 18.5% to