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Thermal analysis of oxidised coals

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Abstract

The study has been performed on samples of high sulphur content Spanish brown coal Mequinenza and Polish flame coal Czeczot. The samples of raw coals and the coals oxidised by four different oxidising agents have been subjected to derivative thermogravimetry analysis (DTG). The results have shown that demineralisation has no effect on the temperature range of the maximum mass loss. The Czeczot flame coal has been shown to be characterised by a narrower temperature range of the main devolatilisation peak (380–500 °C) than that of Mequinenza (320–500 °C). The most pronounced structural changes in coal have been found to occur as a result of its oxidation by 5% nitric acid. After such a process of oxidation a new peak of devolatilisation appears with a maximum at 265 °C, which can be assigned to the compounds having nitric groups in their structure.

Keywords: Coal; Oxidation; DTG

1. Introduction

The behaviour of coals in pyrolysis processes is of significant importance because coal processing usually proceeds at elevated temperatures (coking, gasification, liquefaction and combustion). The exposure to high temperatures results in decomposition of coal organic matter and formation of gas, solid and liquid products of decomposition, quantity and chemical composition of which depend on the structure of starting coal material and process conditions. Transformations proceeding in coal under the influence of temperature were the subject of many studies [1–6]. The effect of mineral and organic matter, grain size and demineralisation on thermal properties of coal has been determined in the above studies. However, the mechanism of coal transformations has not been explicitly determined yet and the complex structure of solid fuels makes the interpretation of phenomena occurring during heating more difficult.

Recently, growing interest in sulphur compounds present in coal is observed due to increased mining of sulphur-rich coals. The utilisation of bastard coal in industry is accompanied by a number of technological and environmental problems. In the presence of oxygen at high temperature of coal combustion, sulphur compounds undergo oxidation to sulphur oxides which can react with ozone, hydrogen peroxide and water vapour present in the atmosphere to form sulphuric acid and the latter is one of the main contributors to acid rain. They cause unfavourable changes in water, soil and air by acidifying them and are toxic for humans [7]. Moreover, sulphur present in coal affects quality of products of technological processes in undesirable way. It deteriorates parameters of iron blast furnaces and properties of pig iron and in cupola coke it reduces castability of cast iron. Sulphur compounds deactivate catalysts used in petrochemical industry and in processes of coal liquefaction.

Chemical methods of desulphurisation [8–10] are the most promising and effective way of sulphur removal from coal. One of experimental methods is coal oxidation by using different oxidising agents [8,11–13]. As a result of the oxidation, physico-chemical properties of coal undergo changes and the latter are often characterised by thermogravimetric methods.

According to Markova et al. [14,15] the effect of oxidisers on solid fuels depends on their origin, petrographic and chemical components, coal structure and degree of coalification. On the basis of thermogravimetric analysis of oxidised coals Puente et al. [16] have proved that the maximum temperature of the volatile substances released can be used as a parameter describing the degree of coalification.

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Jakab et al. [17] by thermogravimetric method in combination with mass spectrometry (TG-MS) have reported that coals of lower degree of coalification are characterised by a wider range of the main devolatilisation temperature and are more susceptible to oxidation than those of a higher degree of coalification.

Yaman et al. [18,19] have proved that oxidation of lignites increases their thermal reactivity leading to a decrease in the ignition temperature and an increase in the combustion rate. According to Pis et al. [20] the process of oxidation leads to a decrease in the coal calorific value.

Using thermogravimetric methods Sapunov et al. [21] studied the kinetics and mechanism of oxidation of anthracites by nitric acid, while Aylmer and Rowe [22] determined the content of pyrites in coals.

Many authors have been interested in thermogravimetric study of coal but only a few have reported information on the effect of the sulphur compounds contained in coal on its thermal properties. In view of the above it seems interesting to study the structure of coal, and in particular, transformations of the sulphur compounds it contains taking place as a result of oxidation.

The main aim of this study was to determine the effect of oxidation by four different oxidising agents: nitric acid, peroxyacetic acid, gaseous oxygen dissolved in water solution of sodium carbonate and air, on the thermal properties of coals of a different degree of coalification and different content of sulphur.

2. Experimental

The measurements were performed for two types of coal characterised by different degree of coalification and different content of sulphur, that is the Spanish high-sulphur Mequinenza brown coal and the Polish Czeczot flame coal. Proximate analysis has been done according Polish Standard [23–25]. Results of the proximate analysis are given in Table 1. Most of the measurements were carried out on samples demineralised by the Radmacher method [26] by HCl and HF. The coals were subjected to oxidation by peroxyacetic acid (PAA), 5% of nitric acid and gaseous oxygen dissolved in a water solution of sodium carbonate (O_2/Na_2CO_3). Moreover all samples were oxidised by air at 125 °C. The preparation of coal and the procedure of their oxidation was described in detail in the previous study [11]. Table 2 presents the results of the elemental analysis and the contents of particular sulphur species in raw, demineralised and oxidised coal samples [11,27].

Table 1
Proximate analysis of raw coals (wt.%)

Coal	Moisture	Ash^d	VM^{daf}
Mequinenza raw	8.6	21.9	51.0
Czeczot raw	5.4	7.5	43.6

Thermogravimetric analysis of the coal samples and the products of their oxidation was performed on an SETSYS 12 made by Setaram. The samples (10 mg, particle size below 0.06 mm) were heated at the rate 10 °C/min, in the helium atmosphere. Analysis lasted for 6 h and the temperature during the decomposition varied from 20 to 1100 °C.

3. Results and discussion

The results presented in Table 2 prove that the most effective oxidisers are HNO_3 and PAA, causing the greatest structural changes in the coal samples studied. The main sulphur species in the samples studied is organic sulphur,

Table 2
Elemental analysis of raw, demineralised and oxidised coals (wt.%) [11,25]

Coal	Ash^d	C^{daf}	H^{daf}	N^{daf}	S^{daf}_{org}	$O^{daf\ a}_{diff}$	Types of sulphur species^b			
							S^d_t	$S^d_{SO_4}$	S^d_p	S_{org}
Mequinenza										
Raw	21.9	62.3	5.5	0.6	9.8	21.8	9.67	0.81	1.22	7.64
Demineralised	1.2	65.1	5.2	0.8	10.4	18.5	11.60	0.03	1.29	10.28
Ox. O_2/Na_2CO_3	0.9	63.9	5.1	0.9	10.3	19.8	11.14	0.00	0.94	10.20
Ox. PAA	1.7	61.1	6.2	0.8	7.1	24.8	7.40	0.00	0.40	7.00
Ox. 5% HNO_3	0.6	57.0	3.9	4.0	7.6	27.5	7.45	0.00	0.02	7.43
Ox. air/125 °C	1.0	59.2	4.2	0.8	10.2	25.6	10.13	0.05	0.16	9.92
Czeczot										
Raw	7.5	74.7	5.2	1.1	1.0	18.0	1.65	0.05	0.64	0.96
Demineralised	1.5	75.4	5.2	1.0	1.4	17.0	1.92	0.00	0.59	1.33
Ox. O_2/Na_2CO_3	0.7	73.8	4.9	1.0	1.4	18.9	1.60	0.00	0.18	1.42
Ox. PAA	0.6	68.5	4.5	1.0	1.1	24.9	1.09	0.00	0.00	1.09
Ox. 5% HNO_3	0.5	64.1	3.8	3.8	1.0	27.3	1.00	0.00	0.01	0.99
Ox. air/125 °C	1.0	70.7	4.4	1.0	1.5	22.4	1.61	0.06	0.08	1.47

[a] By difference.

[b] S^d_t, S_{SO_4}, S^d_p, S_{org} are total content of sulphur and S in sulphates, pyritic or organic S compounds, respectively.

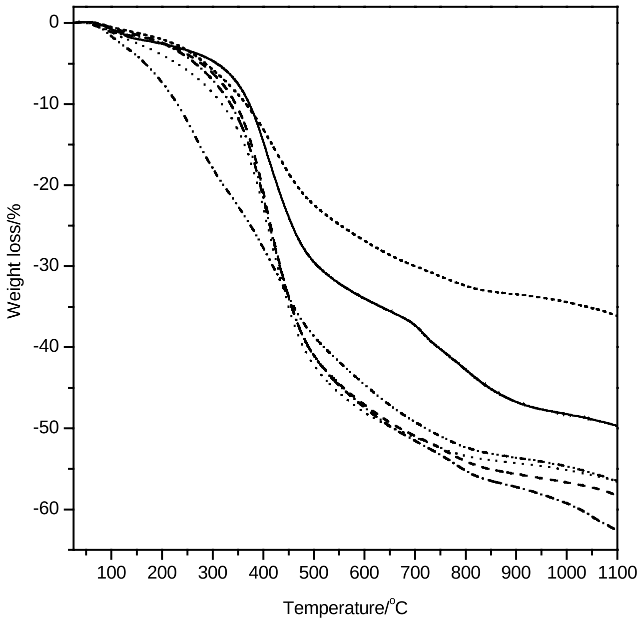

Fig. 1. TG curves of Mequinenza raw, demineralised and oxidised coals (—) raw coal, (– – –) demineralised coal, (. . .) oxidised by oxygen/Na_2CO_3, (–· –· –·) oxidised by peroxyacetic acid, (– · – · – ·) oxidised by nitric acid and (- - -) oxidised by air oxygen.

moreover, Czeczot is characterised by a greater contribution of pyritic sulphur than Mequinenza. Nitric and peroxyacetic acids are also the most effective in removing sulphur from the coals studied. The effect of oxidation on the coals structure and the particular species of sulphur they contain has been presented in detail in [11,27,28].

In order to characterise the behaviour of the oxidised coal samples at elevated temperatures they were subjected to thermogravimetric measurements. The results obtained for all the samples are shown in Figs. 1–4 in the form of TG and DTG curves. All of the curves are presented on the same scale of the percent of mass loss per minute.

The peak at 60–100 °C, present in all DTG curves (Figs. 2 and 4) for the two types of coal: Mequinenza and Czeczot is assigned to elimination of the adsorbed water.

The DTG curve obtained for the sample of raw Mequinenza coal (Fig. 2a) reveals two peaks corresponding to the loss of mass on heating, with maxima at 400 °C and at about 700 °C. According to the data of [16], the one at 400–450 °C can be assigned to the process of primary devolatilisation at which the volatile substances and tar components are released. The peak at about 700 °C is assigned to the process of secondary devolatilisation in which hydrogen and methane are released from the sample under decomposition. Analysis of the temperatures of the maximum mass loss of the raw (Fig. 2a) and demineralised (Fig. 2b) coal samples indicates that demineralisation has no effect on the position of the peak assigned to the primary devolatilisation but is responsible for a shift of the peak assigned to the secondary devolatilisation towards higher temperatures.

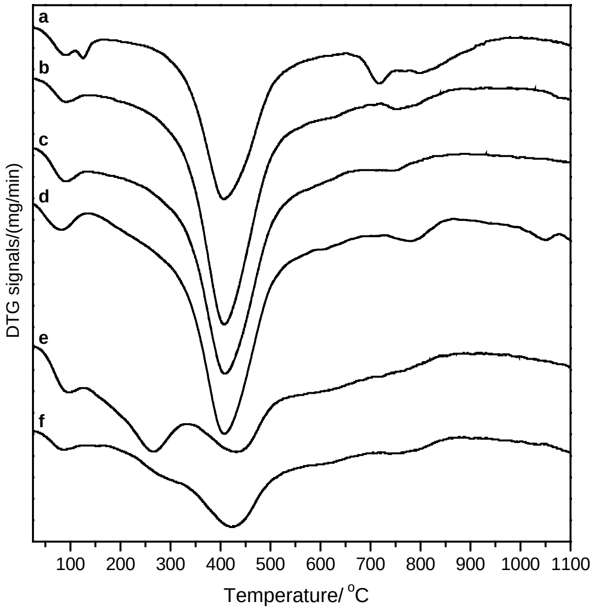

Fig. 2. DTG curves of Mequinenza raw, demineralised and oxidised coals (a) raw coal (b) demineralised coal (c) oxidised by oxygen/Na_2CO_3 (d) oxidised by peroxyacetic acid (e) oxidised by nitric acid and (f) oxidised by air oxygen.

The oxidation of the demineralised coal samples by PAA (Fig. 2d) and O_2/Na_2CO_3 (Fig. 2c) has practically no effect on the shape of the DTG curves. Greater changes are observed in the curve obtained for the sample oxidised by air at 125 °C (Fig. 2f). In this curve the peak assigned to the primary devolatilisation is significantly decreased and

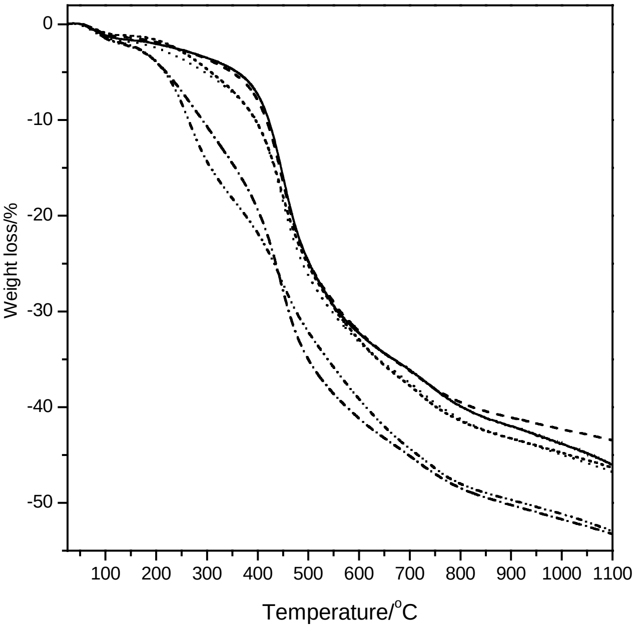

Fig. 3. TG curves of Czeczot raw, demineralised and oxidised coals (—) raw coal, (– – –) demineralised coal, (. . .) oxidised by oxygen/Na_2CO_3, (–· –· –·) oxidised by peroxyacetic acid, (– · – · – ·) oxidised by nitric acid and (- - - -) oxidised by air oxygen.

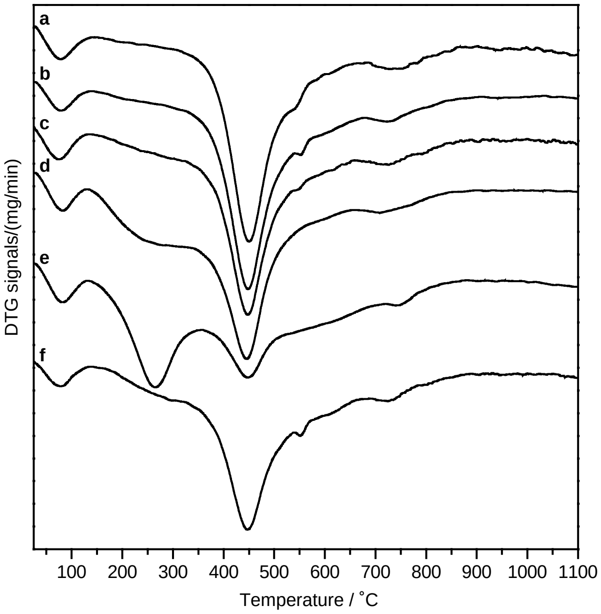

Fig. 4. DTG curves of Czeczot raw, demineralised and oxidised coals (a) raw coal (b) demineralised coal (c) oxidised by oxygen/Na_2CO_3 (d) oxidised by peroxyacetic acid (e) oxidised by nitric acid and (f) oxidised by air oxygen.

its maximum is shifted towards higher temperatures. The greatest changes are induced by the coal oxidation by a 5% nitric acid (Fig. 2e). As follows from the DTG curve, the area of the peak corresponding to the process of released of the volatile substances and tar components has been much reduced and the peak's maximum has been significantly shifted towards higher temperatures. As a result of oxidation by nitric acid the peak assigned to the secondary devolatilisation has disappeared completely and a new peak with a maximum at about 265 °C has appeared. The reduction of the peak corresponding to the primary devolatilisation and disappearance of the peak corresponding to the secondary devolatilisation in the curves obtained for the coal samples oxidised with nitric acid and air at 125 °C, is a result of removal of the less stable groups in the coal structure and a decrease in the content of hydrogen, which is confirmed by the analytical data on H^{daf} shown in Table 2. According to [16] a decrease in the mass loss at about 400–500 °C is a result of the lack of availability of the amount of hydrogen needed to saturate free radicals formed upon heating of the samples.

The new peak appearing as a result of oxidation by 5% HNO_3 with a maximum at about 265 °C can be assigned to release of nitrogen compounds rather unstable in high temperatures. This assignment is supported by [29,30] proving that upon the effect on nitric acid not only oxidation but also nitrification of coal occurs so in oxidised samples the content of nitrogen is elevated, see the content of N^{daf} in Table 2.

Fig. 4 presents the DTG curves obtained for the Czeczot coal. The mass loss upon heating is manifested by three peaks. Apart from those also present in the curves recorded for Mequinenza coal (Fig. 2), assigned to primary and secondary devolatilisation, the Czeczot coal curve shows a small peak assigned to decomposition of pyrite sulphur [31] with a maximum at 560 °C. This peak has not been observed on the DTG curves obtained for the Mequinenza coal because pyritic sulphur contained in this coal, because of its high reactivity [11,28], most probably undergoes decomposition in temperatures lower than it happens in Czeczot coal. As follows from the temperatures of the maxima of the mass loss peaks, similarly as for the Mequinenza samples, the process of demineralisation has no effect on their positions (Fig. 4a and b).

The oxidation of the demineralised Czeczot coal samples does not cause a shift of the peak assigned to the primary devolatilisation towards higher temperatures, in contrast to the observation for the Mequinenza samples. The DTG curves obtained for the oxidised samples indicate that the most effective oxidising agent, causing the greatest changes in the coal structure, is 5% HNO_3, similarly as for the Mequinenza coal samples. The other oxidising agents used in the study do not cause significant changes in the Czeczot coal that would be detectable by thermogravimetric measurements.

The disappear of the peak with a maximum at 560 °C confirms the analytical data shown in Table 2, that is the fact that nitric acid and (Fig. 4e) and PAA (Fig. 4d) are the most effective in removal of sulphur, mainly pyritic one.

For the Czeczot coal samples the temperature range of the primary degassing 380–500 °C is narrower than for the Mequinenza samples 320–500 °C.

Comparison of the peaks corresponding to mass loss obtained for all samples studied has confirmed the data of [17] indicating that with increasing degree of coalification the maxima assigned to the primary devolatilisation are shifted towards higher temperatures.

4. Conclusions

The effect of oxidation on the sulphur and oxygen compounds and on the content of the other elements is different and depends on the oxidation method used and on the degree of coalification of a given coal. Demineralisation of the coals has no effect on the temperature ranges of the mass loss maxima. The study has shown that the temperature range of the primary devolatilisation peak for the Mequinenza brown coal is wider than for the Czeczot flame coal. With increasing degree of coalification the temperature of the primary devolatilisation maximum increases. The greatest changes in the coal structure are caused by the oxidation with 5% nitric acid. These changes are manifested by the appearance of a new peak with a maximum at 265 °C, which can be assigned to liberation of compounds containing nitric group in their structure.

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