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# The application of thermal analysis to the study of ignition processes of solid fuels [1]

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## Abstract

The present literature survey deals with the application of thermal analysis and associated coupled techniques to the study of the self-ignition processes of solid fuels. These techniques make possible the assessment of the antioxidative action of inorganic and organic inhibitors which prevent the coals self-igniting. Thermal analysis is regarded as a method for investigating oil-dispersed fuel suspensions as fossil fuel substitutes.

## INTRODUCTION

It was at the end of the last century that was established that most of the fires in coal stores resulted from self-ignition processes. German statistics of that period note that 155 ships carrying coal sank from 1889 to 1896, 40 of which were destroyed by fire due to the self-ignition of the transported fuel [1]. Recent investigations show without doubt that the self-ignition of coal is the main reason for the occurrence of 85% of the fires in coal mines. This is the reason why this phenomenon has attracted the diverse interests of laboratory, industrial and theoretical researchers. Many scientfic works are carried out with the aim of investigating ignition processes in various solid fuels.

Thermal analysis has been broadly applied in the last few years for studying the self-ignition of solid fuels. Martli [2] and Golesteamm [3] have investigated these processes for wood, for peat after oxidation at 200°C and for coal powder. Falyushin [4, 5] has used the same method to study the

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self-ignition of peat. He has found that the endothermic effect registered on the DTA curves of the initial lowland peat is missing from that of the sample after self-ignition. Marinov [6] has applied thermal analysis quite successfully to the study of the self-ignition of Bulgarian coal and anthracite in the temperature range 330–360°C. He has established that these processes mainly affect the non-aromatic structures of coals.

Rustschev [7] has performed thermal analysis of peat and brown and black coals before and after oxidation as a result of storage under laboratory conditions for 4 years. The character of the DTA curves (Fig. 1, curves a, a′, b, b′, c, and c′) demonstrates the insignificant changes which have occurred in gas and black coal during their storage. However, the DTA curves of the coking and brown coals (Fig. 1, curves d, d′, e, e′, f, f′, g, and g′) show that they have undergone essential changes as a result of oxidation during their time in storage. Applying this method, Markova and Rustschev [8] have studied the changes which occur in Bulgarian coking coals from the Balkan basin after their storage for 4 months. They have established that both the surface of the exothermic effect and its maximum temperature (330°C) change as the temperature rises.

With the help of special equipment constructed for thermal analysis, Choi and Güntermann [9, 10] carried out versatile research on the self-ignition of coal when gas is released during underground work.

Most of the laboratory methods developed to study self-ignition processes are based on determining the temperature at which the spontaneous heating of coal commences, the so called "initial temperature". This is the temperature at which the self-ignition of solid fuels takes place in air, oxygen or in the presence of different solid oxidants ($NaNO_2$, $AgNO_3$, etc.). For details of these methods, which were widely used in the past, refer to the works of Erdmann [11], Kreulen [12] and Veselovskii and Orleanskaya [13]. Later, Guel [14] proposed that the heating Leitz microscope could be successfully applied for direct visual or photometric registration of the self-ignition of a briquette from the investigated solid fuel. Terpogosova [15] was the first to use the apparatus for DTA analysis to determine the susceptibility of coal to self-ignition.

By means of DTA, Rustschev and Filipova [16] have determined the self-ignition temperature of various types of Bulgarian peats and brown and black coals. The DTA curves of the latter that are mixed with 20% $NaNO_2$ show that the ignition temperature for peats varies between 275 and 285°C, for lignite and brown coals from 275 to 330°C and for black coals from 300 to 355°C (Figs. 2–4). Using the same method, Atanasov [17] determined that the ignition temperature of peat is 240°C, of lignite coals is 280–285°C, of gas coals is 280–285°C and of coking coals is 330–340°C.

Rustschev and Khetcheva-Markova [18] and Markova [19] have successfully used thermal analysis to determine the ignition temperature of low rank petrographic lithotypes. With the help of this method Rustschev [20]

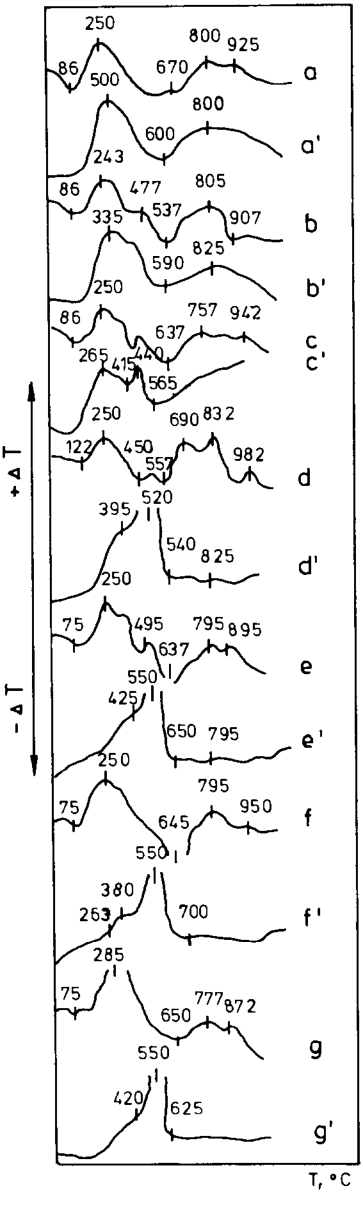

Fig. 1. DTA curves of black coals before (a, b, c, d, e, f, g) and after 4 years' storage (a', b', c', d', e', f', g') under laboratory conditions.

has made an attempt to evaluate the ignition temperature of some of the components in lignite and brown coals. The DTA curves of lignite coals which are mixed with 20% $NaNO_2$ before and after the consecutive separation of bitumens and humic acids are presented in Fig. 5. It can be seen that the isolation of the bitumens (4.5% to 11.0%) reduces the ignition temperature by 20–45°C. It has also been reported that the ignition

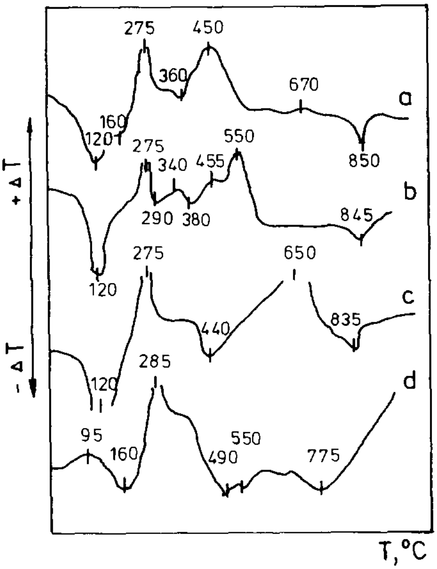

Fig. 2. DTA curves of mixtures containing 20% $NaNO_2$ and 80% peat from the following deposits: (a) Lagit, (b) Sukhoto ezero, (c) Baikal and (d) Razdelna.

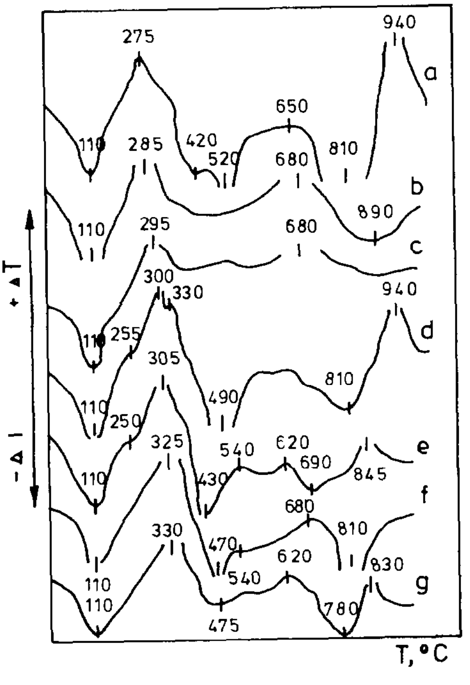

Fig. 3. DTA curves of mixtures containing 20% $NaNO_2$ and 80% lignite and brown coals: (a) lignite coals from "Chukurovo" mine; (b) lignite coals from "Matitsa Zapad" mine; (c) brown coals from "Pernik" mine; (d) brown coals from "Bobov Dol" mine; (e) brown coals from "Burgas" mine; (f) brown coals from "Pirin" mine; (g) lignite coals from "Bolshevik" mine.

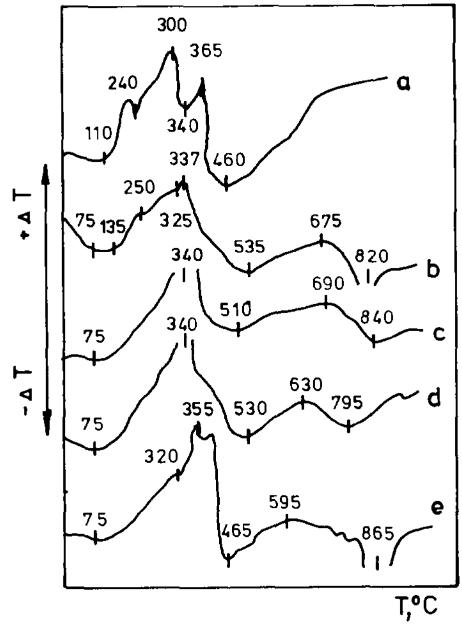

Fig. 4. DTA curves of mixtures of 20% $NaNO_2$ and 80% black coals from the Balkan coal basin: (a) "Koks" mine; (b) "Divina" mine; (c) "Gramadliva" mine; (d) "nadezhda Yug" mine; (e) "Kachulka" mine.

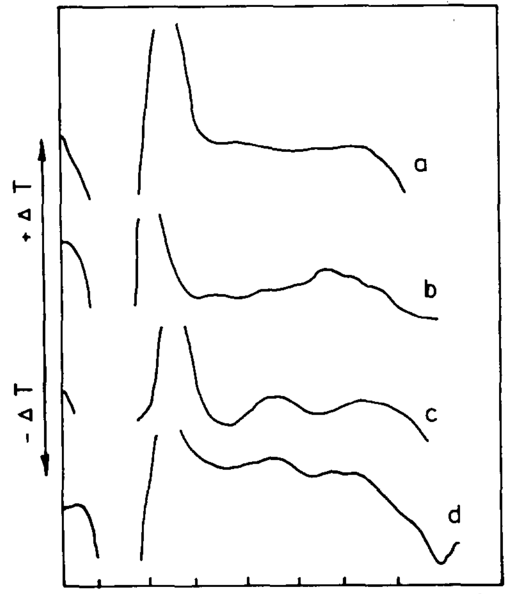

Fig. 5. DTA curves of mixtures of 20% $NaNO_2$ and 80% lignite coals from "Aldomirovtsi" mine: (a) initial coals; (b) after separation of the bitumens; (c) after separation of humic acids; (d) of isolated humic acids.

temperature of the isolated humic acids is 20–35°C lower than that of the original coal.

Rustschev and Toschkova [21] have used DTA to determine the ignition temperature of semi-coke, and of middle-temperature and high-temperature cokes. On the basis of the DTA curves of the solid residues of gas coals with 20% $NaNO_2$ that have been heated at 400, 450, 550, 650, 750, 850 and 950°C, it has been found that this temperature varies from 300 to 365°C for coke, from 370 to 380°C for the middle-temperature coke and for the high-temperature coke it increases to 390°C (Fig. 6).

In order to assess the inhibitory effects of different organic and inorganic additives on the ignition of solid fuels, Rustschev and Markova [22] have proposed a thermal analysis where the inhibiting fuel is mixed with $NaNO_2$. The antioxidative efficiency is estimated by the temperature difference ($\Delta T = T - T_0$) between the maxima in the explosive exothermic effects

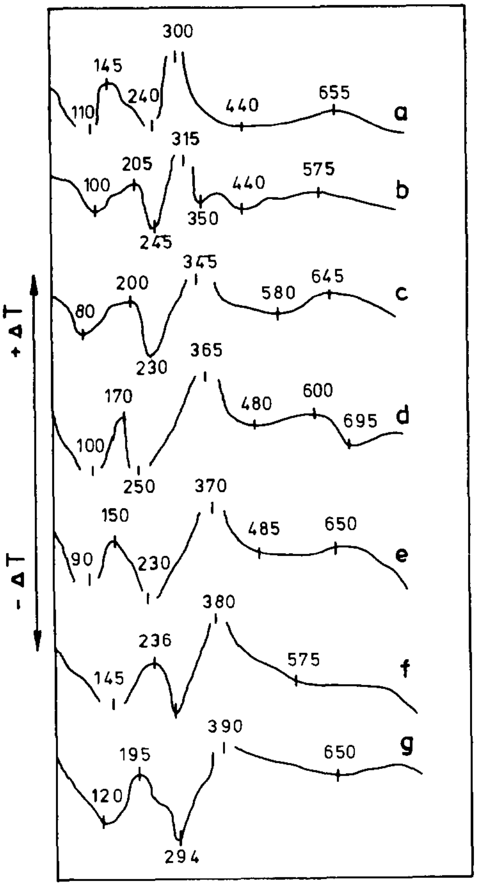

Fig. 6. DTA curves of mixtures of 20% $NaNO_2$ and 80% semi-coke (a, b, c, d), middle-temperature coke (e, f), and high-temperature coke (g).

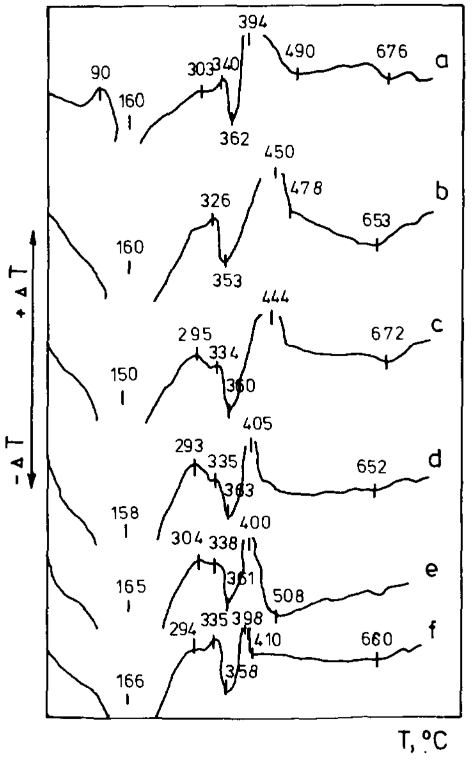

Fig. 7. DTA curves of brown coals: (a) without inhibitor; (b) in the presence of suspension of $MgCO_3$ and $CaCO_3$; (c) in the presence of 2.5% solution of $Na_2SO_3$; (d) with 1.0% solution of NaCl; (e) in the presence of 2.5% solution of $Na_2CO_3$; (f) with 2.5% solution of $(NH)_4CO_3$.

before and after inhibition. It has been shown that this difference $\Delta T$ for brown coals varies between 4 and 56°C, but it is essentially high (56 and 50°C, respectively) when using a suspension of $MgCO_3$ and $CaCO_3$ and 2.5% $Na_2SO_3$ (Fig. 7, curves b and c). The same authors proved that the carbonate mixture exerts a pronounced inhibitory effect on peat and lignite coals. Using DTA and TG analyses to determine the ignition temperature Rustschev and Markova [23–25], Rustschev et al. [26, 27] and Markova [19], have evaluated the antioxidant action of phenol, hydroquinone, pyrogallol, $\alpha$-naphthol, $\beta$-naphthol and aniline on peat and different types of Bulgarian solid fuels. They have shown that hydroquinone and pyrogallol are the best antioxidants with respect to the oxidation of peat, whereas the coals are most affected by phenol and aniline. The inhibitory effects of monohydroxyphenols are shown to be stronger than those of di- and trihydroxyphenols. In low-carbonized coal the inhibitory effect of phenol is stronger than that of aniline, whereas for high-carbonized coal the effects observed are similar.

On the basis of thermogravimetric analysis, Rustschev and Markova [28] proposed a method for determining the ignition temperature of solid fuels, and reported that this is 240°C for peat, from 245 to 250°C for lignite coal, from 260 to 270°C for brown coal, 305°C for black coal and 355°C for anthracite.

Recently, in many countries programmes have been developed for stabilization of coal–oil dispersed fuel systems which can successfully replace expensive fossil fuels.

The first DTA and TG analyses of these systems which contain 50–70% liquid petroleum products have been performed by Lin [29, 30]. Together with Dezhoug [31] he used the DTA curves to study the ignition of similar dispersed systems. Both researchers found an increase in burning time of the mixture with increasing concentration of the solid phase in it.

Using original thermal analysis in oxygen atmosphere, Rustschev [32] and Atanasov [17] have investigated the burning characteristics of dispersed systems, and thus have assessed the effectiveness of burning.

By following the influence of metamorphism of solid fuels, which are used as solid phase, on the burning dispersed fuel suspensions, some relationships have been established. From the DTA curves of peat, cracking black oil and their suspension (40% peat and 60% cracking black oil) in oxygen atmosphere, it has been found that the ignition temperature of the solid phase (peat, 240°C) is lower than the flame temperature of the dispersed medium (the black oil, 280°C). At the same time, the ignition temperature of the solid phase in the dispersed system (280°C) is considerably higher compared to that of the initial peat (240°C) (Fig. 8). The DTA and TG curves that have been obtained under oxygen atmosphere for anthracite, cracking black oil and their suspension (40% anthracite and 60% black oil) show that the ignition temperature of

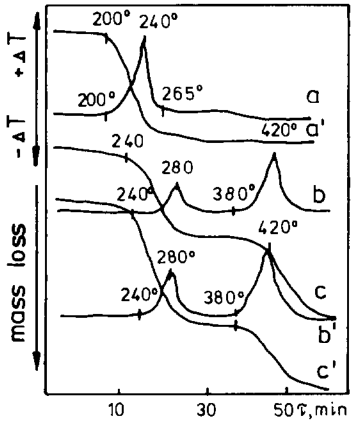

Fig. 8. DTA and TG curves of peat (a, a′), of cracking black oil (b, b′) and of suspension containing 40% peat and 60% black oil (c, c′) in oxygen atmosphere.

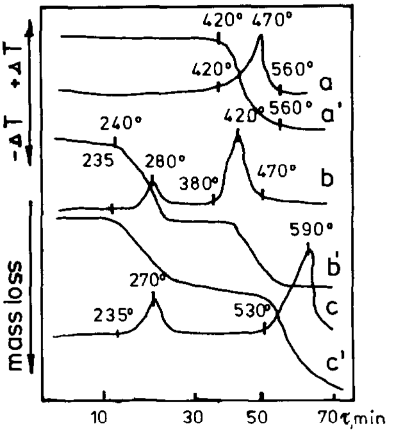

Fig. 9. DTA and TG curves of anthracite (a, a′), of cracking black oil (b, b′) and of suspension containing 40% anthracite and 60% black oil (c, c′) under oxygen atmosphere.

anthracite (470°C) is higher than that of the dispersed medium (the cracking black oil, 420°C). Figure 9 demonstrates that for the dispersed system, the temperature of the second exothermic effect is much higher (590°C) compared with that of the dispersed medium (420°C).

## CONCLUSIONS

Thermal analysis and associated coupled techniques have been extensively used to investigate the self-ignition processes of solid fuels both during their mining and on their storage. These methods make possible the assessment of the inhibitory action of different types of inorganic and organic additives, applied with the aim of preventing of endogenous fires in mines and fires during coal transportation and storage. The thermal methods could be quite perceptive for performing a profound research on dispersed fuel suspensions which can successfully replace the expensive and insufficient fossil fuels.

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