

*Special Review*

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**THE APPLICATION OF THERMAL ANALYSIS TO THE STUDY OF THE OXIDATION OF SOLID FUELS**

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Thermal analysis and associated coupled techniques have been broadly applied in the last years for studying interaction of different kinds of solid fuels (peat, lignite, brown and bituminous coals, antracite, bituminous shales and etc.) with air, with other gas, liquid and hard oxidizers. References showed that these analysis were important not only theoretical but practical point of view.

**Intoduction**

The interaction of the different types of solid fuels (peat, lignite, brown, black and anthracite coal, and bituminous rocks) with the oxygen in the air and with other oxidants ( $O_3$ ,  $H_2O_2$ ,  $KMnO_4$ ,  $K_2Cr_2O_7$ ,  $HNO_3$ ,  $H_2SO_4$ , etc.) depends on their origin, their petrographic and chemical composition, their structure and the degree of carbonization. The natural and artificial oxidation of solid fuels can be used successfully to study their molecular structures and to obtain commercially valuable chemical products. Of exceptional importance for practical purposes are the auto-oxidative processes taking place during the preservation of solid fuels, resulting in changes in their properties such as particle size, burning temperature, capacity for concentration and coking capacity.

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Many thermal analysis techniques are being increasingly used to study the oxidative processes taking place in solid fuels on the action of oxygen [1, 2]. These techniques make it possible to verify the existence of auto-oxidation, to identify the chemical reactions occurring between the solid fuels and the various oxidants, and to study the final stage in the oxidative process (self-ignition and burning). DTA is also used successfully to determine the inhibitory effects of different types of organic and inorganic additives in the solid fuels, applied with the aim of preventing or delaying undesirable auto-oxidative processes.

The different conditions under which the thermal analysis is conducted result in considerable fluctuations in the results obtained. For example, Berkowitz [3] reported major changes both in the temperature at which the auto-oxidation takes place and in the value and sign of thermal effects registered. Berger and Whitehead [4] verified that significant differences appear in the interval 150–500°C and especially in regions where a stronger or weaker exothermic effect is registered (120–300°C) for coal analysed in air atmosphere. Some researchers associate this exothermic effect with the physico-chemical transformations taking place in the coal on the action of oxygen [5, 6].

A detailed analysis of the DTA curves obtained from Bulgarian coal types shows that the low-temperature exothermic effect observed at 150–300°C is most probably due to oxidative processes [7, 8]. In their systematic studies of this effect, Marinov and Angelova [9] concluded that it is a result of the oxidation of the coal, and it can therefore serve as an indicator in a determination of the capacity of the coal to interact with the oxygen in the air. The same authors proved that, when the coal is heated in an inert nitrogen atmosphere, this exothermic effect is replaced by an endothermic effect. Smothers and Chiang [10] found that an oxidative atmosphere causes the appearance of a characteristic exothermic effect for xylite, similar to the effect observed for wood. The thermal effects before and after the oxidation of bituminous shales and organic fractions are qualitatively similar to those established for coal [11].

Weltner and Marinov [12, 13] and Dobrovolskiy *et al.* [14] expressed the opinion that DTA is an excellent method for monitoring the changes resulting from oxidation. Weltner [12] concluded that the thermal maximum of decomposition occurring at low temperatures is due primarily to the breaking of functional groups containing oxygen, formed in the course of oxidation. Hence, the less carbonized types of coal are more easily oxidized.

Kessler and Romovackova [15] observed a shift of the temperature maximum of the low-temperature exothermic effect towards higher temperatures

in the following sequence: brown, black and anthracitic coal. Thus, this thermal effect is suggested as a classification parameter.

Markova and Rustshev [10] studied the changes which occur in Bulgarian peat and coal with different degrees of carbonization when these are oxidized in the temperature range 150–300°C for 45 and 60 h, and demonstrated that the interaction of the coal with atmospheric oxygen results in the formation of unstable structures. The maximum of the low-temperature exothermic effect increases, but its surface is reduced in the following carbonization sequence: peat, brown coal, black coal.

Metheson and Rogers [17] studied the low-temperature oxidation of New Zealand coal. The sharp exothermic effect observed at room temperature increases with temperature increase until ignition commences at 200°C. The mechanism of the low-temperature oxidation of coal was also examined and the major exothermic effect was proposed as a parameter of the reactivity of the coal. Although temperature has a considerable effect on the properties of the coal surface, and hence on the porosity of the coal during oxidation, according to Adama *et al.* [18] the (temperature *vs.* time) dependence is poorly manifested for coal, because the access of oxygen to a new surface is limited by slow diffusion. According to Marinov [19], TG and DTA curves can be used to identify the existence of three regions of oxygen diffusion in granulated coal samples. Under thermal analysis conditions, the radical mechanism is possible only on a coal surface whose redox potential is higher than +0.4 V.

Using thermal analysis, several Soviet authors [20–23] made successful attempts to prove the mechanism of the auto-oxidative processes taking place in the initial and advanced stages of coal oxidation. These processes have also been studied in the 20–100°C range [24]. The exothermic effect at 230–330°C was proved to be due to thermal oxidation [25]. On increase of the degree of oxidation, the mass loss at 350°C also increases [26]. Using thermal analysis, Sdobnikov and Grigorieva [27] found that breaking of the lateral structures and oxidation of the aromatic nuclei occur above 380°C. Bombalov *et al.* [28] believe that at 400–500°C there is decomposition of the noncondensed oxyaromatic and oxygen structures of peat, whereby the peat is enriched with heterocyclic structures, which supports the notion of the humus-forming character of the oxidative process.

Mayumdar [29] studied the interaction of coal with oxygen in the air at 30–400°C and specified the initial stage in which the peroxide groups are formed. For Colorado bituminous rocks, Lee *et al.* [30] observed two exothermic effects in the DTA curve registered in oxygen atmosphere, and proposed that the position of the first peak is determined by the oxidation of

the easily volatile fractions, whereas the second and more intensive peak correlates with the burning of the carbon residue formed. The maximum of the latter effect occurs at higher temperatures with increase in the carbon content of the rocks.

Krypina *et al.* [31] successfully applied thermal analysis to study the thermo-oxidative destruction of a concentrate of Leningrad bituminous shales. They reported two maxima in the DTA curves: the first at 270°C, corresponding to the low-temperature oxidation and leading to destruction of the aliphatic structures, and the second at 450°C, due to the hydrogen-depleted organic content. Calahorra *et al.* [32] studied oxygen chemisorption in anthracite and the absorbents obtained from it.

Klose and Hahn [33] used thermogravimetric analysis to study the low-temperature oxidation (150–270°C) of the so-called high-temperature coke obtained from brown coal.

Marinov and Angelova [9] reported that Weltner [9], improving the experiments of Scott and Bauer [34] had studied the oxidation of coal under nonadiabatic conditions, using higher heating rates, and had quantitatively distinguished several phases in this process. The onset of the exothermic reaction for the low- and medium-temperature oxidation was found via the point of intersection of the differential curve with the 'zero line' which corresponds to the coal sample, the furnace and the gas released at identical temperatures. This experimental set-up was used by Sebastian and Mayers [35] to establish the constant of the surface oxidation reaction ( $K_s$ ), which is necessary for calculation of the activation energy of the oxidative processes with the Arrhenius equation.

Ablaeva and Kulev [36] used thermogravimetric analysis and an oxidative medium to determine the temperatures at which coal begins to react intensively, and specified the maximum rate of mass decrease. Using original thermogravimetric methods, Sapunov *et al.* [37] studied the kinetics and the mechanism of the gaseous-phase oxidation of anthracite with nitric acid, while Rodkin *et al.* [38] investigated the kinetics of coke oxidation under iso- and non-isothermal conditions, using a MOM derivatograph.

Markova *et al.* [39] performed TG and DTA studies on some gages from Bulgaria and later studied their oxidation with molecular oxygen in pressure gauge equipment [40]. From the kinetic curves obtained, they calculated the induction period, the maximum and stationary rates of the oxidative process and the activation energy.

Rustschev [41] performed thermal analysis on samples of peat, lignite, brown and black coal stored under laboratory conditions for 4 years, and found that the oxidized solid fuels are characterized by a strong exothermic

effect. Similar conclusions were reached by Butuzova, who studied brown coal stored for 2 years [42]. Vadona and Bristoti [43] described the changes which occur as a result of auto-oxidation taking place during the storage of Brazilian coal with poor caking properties. The low-temperature exothermic effect observed in the curves was associated with a reduced intensity.

When Bulgarian black coal was stored for 4 months, Markova and Rustschev [16] found that the maximum of the low-temperature exothermic effect increased by 30 deg. The insignificant changes in the character of the DTA and TG curves were indicative of the low rates of the auto-oxidative processes taking place during the storage period. DTA was used by Chrisanfova and Suchodrovskaya [44] to determine the degree of resistance of brown coal to oxidation. Depending on the changes in the TG and DTA curves, these authors proposed the following three stages of auto-oxidation: (a) separation of the moisture (endothermic effect at 150–155°C); (b) onset of the destruction of the lateral bonds (endothermic effect at 320–330°C); (c) splitting of the phenolic hydroxy and the –C–C– bonds (endothermic effect at 580°C). The third stage had been observed earlier by Weltner [45].

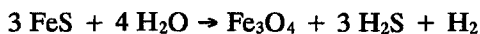
Dobrovolskiy *et al.* [46] proposed from the DTA curves that the activity of brown coal with respect to oxygen in the air may be assessed. DTA is a reliable method for characterizing the degree of oxidation of coal [47, 48]. Chrisanfova *et al.* [49] carried out experiments to assess the degree of oxidation of coal from the oxidation zone on the basis of the character of the thermal effects obtained. An exothermic effect is observed at low temperatures (32–125°C), which is absent for nonoxidized coal. The depth of the oxidized zone is determined on the basis of this fact and it is differentiated from the oxidized zone. When the peroxide compounds and the intermediate oxides are decomposed, nonoxidized coal is characterized by two exothermic effects (at 160° and around 290°C), together with an endothermic effect at around 400°C, marking the transition to a plastic state for long-flame coal, gas coal, metabituminous and coking types of coal, or partial softening of the grains of different grades of dry-caking and dry coal. Matyjaszyk and Przeliorz [50] and Merrill [48] studied the susceptibility of coal to oxidation.

Earnest [51] proposed the ratio between the organic and the mineral components, specified on the basis of thermogravimetric studies, as a criterion for the degree of oxidation of the bituminous rocks from the deposits in Green River (USA) and Glen Davis (Australia). DTA was considered to be a reliable method for determining the susceptibility of coal to oxidation both by Butuzova [47] and Merrill [48]. The same method can be used for a comparative evaluation of the reactivity of brown coal and the related products of thermal and chemical processing with respect to the

oxygen in the air [52]. Thermogravimetric analysis was used successfully by Mitra and Raja [53] to determine the reactivity of some Indian coals. Rodkin and Zorin [54] investigated the principal reactions in the gasification process. Using the DTA, DTG and TG curves, Maryganova and Falyushina [55] explored the thermal stability of coke obtained from peat, separated from the zone of intensive self-heating (74–78°C). It was reported that the same coke was associated with a higher thermal stability, because, after heating to 700 K, twice the quantity of volatile substances was released as compared with the coke obtained from the non-oxidized peat used as initial material. It is also believed that after self-heating of the peat, oxygen-containing structures with increased thermal stability are formed. Aylmer and Rowe [56] determined the pyrite content of coal by combining thermogravimetric and thermomagnetogravimetric analysis and by performing such analysis in an atmosphere of oxidative gases.

Pong and Harris [57] used the DTA curves to study the catalytic action of additives of different inorganic compounds of Fe, Ca, Mg, Ni and Cu on the combustion of low-calorie brown coal from Morville. These authors found that Cu ions cause the greatest acceleration of the oxidation. Using DTA, Earnest [58] obtained the oxidative thermal curves of pyrite, marcasite, low-temperature coal ashes and synthetic mixtures. Seiageldin and Pan [59] studied the action of alkali metals on the decomposition of coal in atmospheres of nitrogen, CO<sub>2</sub> and air, whereas Condina *et al.* [60] studied the behaviour of Bulgarian kombat nickel concentrate and collie coal in oxygen and air atmospheres.

Using a computer-controlled TG system, Levy and White [61] proved that the interaction between pyrite and water vapour in the temperature range 560–760°C results in a slow decrease of mass, which is a consequence of oxidation occurring according to the reaction



Using DTA, it is possible to determine the lowest temperature at which coal interacts with atmospheric oxygen, also referred to as the 'initial temperature of self-ignition', which is determined under nonadiabatic conditions and at low heating rate. The ignition temperatures vary from 100° to 180°C, and are a function of the coal metamorphism. The inconsistency of attempts to judge the susceptibility of coal to self-ignition via auto-oxidative processes under nonadiabatic conditions led to parallel studies using adiabatic conditions, whereby the coal was not heated. These conditions are similar to those relating to self-ignition in the layers or during

storage [62]. When there is minimal scattering of the heat resulting from the oxidation of the coal, the process is found to be self-inducing, since, in the course of a certain period of time (a week or a month), the temperature of the coal rises suddenly. A similar method was used by Peters, Münzner and Rustschev [63] to study the auto-oxidation and the self-ignition of coal used in the Kremikovtsi Coke Chemical Plant.

Neshin *et al.* [64] claim the existence of two temperature regions associated with the self-ignition of coal in the presence of oxygen: the first is registered around room temperature, and the second from room temperature to 180°C.

**Table 1** Ignition temperatures [69] of various Bulgarian solid fuels

Fuel type	Deposit	DTA / °C	TG / °C
Peat	Lagut, Smolyan	275	-
	Suhoto Ezero, Rila	275	-
	Baykal	250-275	240
	Razdelna	285	-
Lignite coal	Aldomirovtsi	250	-
	Maritsa-Iztok	265	245
	Chukurovo	260-275	250
	Maritsa-Zapad	285	-
	Bolshevik	330	-
Brown coal	Cherno More, Burgas	290-305	270
	Bobov Dol	270-300	260
	Pernik	295	-
	Pirin	325	-
Black coal	Balkanbas		
	-Koks mine	300	-
	-Divina mine	337	-
	-Gramadliva mine	340	-
	-Nadezhda mine	340	-
	-Kachulka mine	325-355	305
Anthracite	Svoqe	420	355

The DTA method is beginning to be used in parallel with the classical methods of determining the temperature of self-ignition of coal [65, 66]. Terpogosoova [67] determined this temperature by using the equipment designed by Kurnakov. Finely-ground coal was mixed with 20% solid oxidizer ( $\text{AgNO}_3$ ,  $\text{NaNO}_2$  or  $\text{KNO}_3$ ). The maximum temperature of the strongly explosive thermal reaction was assumed to be the temperature of self-ignition, which is a necessary parameter for assessing the auto-oxidation and self-ignition capacity of the coal [68] (Table 1). According to Rustschev and Filipova [69], the ignition temperatures of Bulgarian peat types vary from 275°C to 285°C, of brown coal from 275° to 330°C, and of black coal from 300° to 355°C. These authors found that the ignition temperature decreases with increasing yield of volatile matter. Atanasov [70] determined the ignition temperature of peat (240°C), lignite coal (280–285°C), gas coal (280–285°C) coking coal (330–340°C), semi-anthracite (360°C) and anthracite (410–470°C) from the DTA curves, and compared the data with the curves obtained in the presence of  $\text{NaNO}_2$ . A substantial difference was found only for anthracite (480 and 410°C, respectively).

Rustschev and Markova [71, 72] used the same method to determine the ignition temperature of the petrographic ingredients of low-carbonized types of coal. Rustschev [73] proved that, after the separation of the bitumens 'A' from lignite and brown coal, the ignition temperature was decreased by 20–40 deg. It was also reported that the humic acids isolated from the coal exhibited an ignition temperature 20–35 deg lower than that of the original coal.

The process of self-ignition was studied for peat and wood with a particle diameter between 10 and 13 mm, oxidized to 200°C, and for coal powder [74, 75]. The ignition temperature of low-temperature and high-temperature coke ranged from 350° to 370°C and from 380° to 400°C, respectively [76].

Joe-Ou Choi and Guntermann [77, 78] constructed a special thermal analysis system for a comprehensive study of the self-ignition of coal when gas is released during underground work, and for determination of some thermal parameters connected with the oxidation of different solid fuels.

Falyushin [79, 80] studied peat before and after its self-ignition and found that the endothermic effect of lowland peats is not associated with self-ignition. During this process, the mineral components of peat undergo considerable changes [81]. Kashinskaya *et al.* [82] suggested that the composition of the ash residue obtained at 400–450°C can serve as an indicator of the depth of the exchange processes that had taken place.

With respect to the self-ignition of Bulgarian coal and anthracite in the temperature range 300–360°C, Marinov [83] verified that oxygen affects the



non-aromatic part of the coal. We also attempted to explain the mechanism of the self-ignition processes at low temperatures.

On the basis of thermogravimetric analysis, Rustschev and Markova [84] proposed a method for determining the ignition temperature, and reported that this is 240°C for peat, 245–250°C for lignite coal, 260–270°C for brown coal, 305°C for black coal and 355°C for anthracite.

Rustschev and Markova-Jetschewa [85] assessed the inhibitory effects of organic and inorganic additives in lowering the ignition temperature. Using DTA and TG methods to determine the ignition temperatures of solid fuels, the same authors [86] determined the inhibitory effects of phenol, hydroquinone, pyrogallol,  $\alpha$ -naphthene and aniline for Bulgarian peat [87], lignite coal [88], brown coal [89], black coal [90] and anthracite coal [90] (Table 2). They showed that hydroquinone and pyrogallol have the strongest inhibitory effects on peat, whereas lignite, brown, black and anthracite coals are most affected by phenol and aniline. In all cases, the ignition temperature increased by 5 to 25 deg. The effects of monohydroxyphenols were shown to be stronger than those of di- and trihydroxyphenols. Phenol was a stronger antioxidant than naphthene. In low-carbonized coal, the inhibitory effect of phenol was stronger than that of aniline, whereas for high-carbonized coal, the effects were equivalent.

By means of DTA and TG analysis, Carter *et al.* [91] studied the inhibitory effects of boric oxides on the solid residues of the carbonization of Australian coal. On the basis of the DTA curves of coal, Zamislov *et al.* [92] studied both the inhibition of the processes taking place during heating and oxidation with air, and their stabilization. With DTA, it is possible to analyse the final stage of the oxidative or burning process [93]. For example, in determining the ignition temperature in air to assess the reactivity of 14 coal types from New Zealand, Scott and Bauer [34] found two exothermic effects (at 300–500°C and 500–850°C), which are characteristic of the burning process.

Mickelson and Walas [94] investigated the heating and the oxidative chemisorption of carbonaceous char. The latter process was also studied by Charsley *et al.* [95].

Weltner [96] reported the appearance of two maxima in the DTA curves when coal is heated. The first peak is due to the volatile matter released at low temperatures, and corresponds to the burning of the coals, whereas the second peak is registered at higher temperatures, and corresponds to the burning of coke.

Stewart *et al.* [97] investigated the burning process of 66 coal samples, from lignite to black coal, and found that the burning temperature for half

of these coal types is linearly dependent on their oxygen and carbon contents.

**Table 2** Effect of various inhibitors on peat and coal [85]

Type of solid fuel and inhibitor	Maximum of exothermic effect /C°		
	Without inhibitor, $T_0$	With inhibitor, $T$	$\Delta T = T - T_0$
1. Peat from the Baykal deposit	304	-	-
5% $\beta$ -C <sub>10</sub> H <sub>7</sub> OH solution	-	418	114
MgCO <sub>3</sub> and CaCO <sub>3</sub> suspension	-	408	104
CaCO <sub>3</sub> suspension	-	395	91
1.0% NaCl solution	-	347	70
2.5% Na <sub>2</sub> SO <sub>4</sub> solution	-	347	70
0.01% Na <sub>2</sub> S solution	-	350	46
2.0% C <sub>6</sub> H <sub>5</sub> OH solution	-	348	44
2. Lignite coal from Maritsa-Iztok	387	-	-
MgCO <sub>3</sub> and CaCO <sub>3</sub> suspension	-	414	27
2.0% C <sub>6</sub> H <sub>5</sub> OH solution	-	403	16
CaCO <sub>3</sub> suspension	-	403	16
2.5% Na <sub>2</sub> SO <sub>4</sub> solution	-	397	10
3. Brown coal from the Chernomore mine	394	-	-
MgCO <sub>3</sub> and CaCO <sub>3</sub> suspension	-	450	56
2.5% Na <sub>2</sub> SO <sub>3</sub> solution	-	444	50
1.0% NaCl solution	-	405	11
2.5% Na <sub>2</sub> CO <sub>3</sub> solution	-	400	6
2.5 % (NH <sub>4</sub> ) <sub>2</sub> CO <sub>3</sub> solution	-	398	4
4. Gas coal	456	-	-
5% $\beta$ -C <sub>10</sub> H <sub>7</sub> OH solution	-	517	61
CaCO <sub>3</sub> suspension	-	473	17
0.01% Na <sub>2</sub> S solution	-	470	14
5. Metabittuminous coal	496	-	-
2.5 % NaHSO <sub>3</sub> solution	-	532	36
2.5% C <sub>6</sub> H <sub>5</sub> OH solution	-	510	14
1.0% NaCl solution	-	498	2

Table 2 (continued)

Type of solid fuel and inhibitor	Maximum of exothermic effect /C°		
	Without inhibitor, $T_0$	With inhibitor, $T$	$\Delta T = T - T_0$
6. Anthracite from the Svoge mine	497	-	-
5.0% $\beta$ -C <sub>10</sub> H <sub>7</sub> OH solution	-	571	74
2.5 % NaHSO <sub>3</sub> solution	-	516	19
2.0% C <sub>6</sub> H <sub>5</sub> OH solution	-	500	3
2.0% Na <sub>2</sub> SO <sub>4</sub> solution	-	500	3
CaCO <sub>3</sub> suspension	-	496	1

Ivanov *et al.* [98] demonstrated that the exothermic effect at 250–400°C corresponds to the burning of wood and that the complete disappearance of the exothermic effect at 500–600°C for the lignite coal from the lignite coal basin in the Southern Urals is due to the burning of the humic acids. It was further shown that clays contain considerable amounts of coal-based substances, whose oxidation and burning are accompanied by the appearance of an intensive exothermic effect, commencing at around 250°C and terminating at from 550 to 900°C, depending on the amount of organic mass in the coal.

Smith *et al.* [99] investigated the burning process of brown and black coal containing 69–91% carbon. Popescu and Simion [93] studied the character of burning by using thermal analysis on the basis of soot and cellolignin. Royan *et al.* [100] used the position, height and the surface area of the thermal effect to obtain information about the reactivity and effective burning characteristics.

Recently, carbon-oil and hydrocarbon dispersed fuel systems have become typical and have been studied by means of various methods. The first DTA and TG analyses of carbon black oil mixtures were reported by Hao Lin [101, 102]. Later, together with Dezhoug, [103], we used thermogravimetric analysis to study the ignition of similar dispersed fuels and found an increase in burning time with increasing concentration of the solid phase.

Thermal analysis makes it possible to define the combustion processes of the dispersed systems of solid and liquid fuels, and to study the effectiveness of burning. From the DTA curves of these mixtures, it is possible to calculate the duration of the two exothermic processes characterizing the burning. This is 20 min for a dispersed system consisting of 40% peat and 60% black oil, and 35 min for the anthracite-black oil dispersed system [104].

Table 3 Ignition temperatures /°C [86]

Solid fuel Type	Deposit	Method	Initial sample	Sample inhibited by				
				Phenol	Hydroquinone	Pyrogallol	$\alpha$ -naphthene	$\beta$ -naphthene
Peat	Baykal	Gugel	205	230	230	230	225	230
		DTA	250	290	300	290	290	290
		TG	240	255	260	250	255	255
Lignite coal	Maritsa Iztok	Gugel	185	215	215	210	210	215
		DTA	265	280	270	270	270	265
		TG	245	255	255	250	250	255
		Gugel	190	225	220	220	220	215
		DTA	260	280	265	260	260	265
Brown coal	Chukurovo	TG	250	260	250	250	250	255
		Gugel	240	255	245	245	245	250
		DTA	290	285	290	290	290	290
		TG	270	275	270	270	270	275
		Gugel	230	235	235	235	235	235
Black coal	Bobov Dol	DTA	270	275	270	270	270	275
		TG	260	265	260	260	260	265
		Gugel	345	395	385	375	395	390
		DTA	325	345	325	330	345	345
		TG	305	320	305	305	320	320
Anthracite	Svoge	Gugel	435	460	450	455	460	455
		DTA	420	435	405	420	430	435
		TG	355	400	340	370	380	390

## Conclusions

In the past 10–15 years, thermal analysis and associated coupled techniques have been used extensively to elucidate the origin, structure, petrographic and chemical composition, degree of carbonization and different physico-chemical properties of peat, lignite, brown, black and anthracite coal types and bituminous shales [104]. The present literature survey shows that such techniques have been applied very successfully for studies of the interaction of these solid fuels with oxygen in the air and with other gaseous, liquid and solid oxidizers. Further, use of these techniques to investigate the oxidative processes taking place in these solid fuels is of considerable theoretical and practical significance in terms of the determination of the changes in their properties after prolonged storage and of the effective burning characteristics of these fuels for the generation of heat and electrical energy.

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**Zusammenfassung** — In den vergangenen Jahren fand die Thermoanalyse und die damit in Verbindung stehenden anderen Techniken eine breite Anwendung bei der Untersuchung der Wechselwirkungen zwischen verschiedenen festen Brennstoffen (Torf, Lignit, Braun- und bitumenhaltige Kohlen, Anthrazit, bitumenhaltige Schiefer usw.) und Luft, anderen Gasen, flüssigen und festen Oxidationsmitteln. Die Angaben zeigten, daß diese Analysen nicht nur theoretische, sondern auch praktische Bedeutung besitzen.