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TEMPERATURE-CONTROLLED COMBUSTION AND KINETICS OF DIFFERENT RANK COAL SAMPLES

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Differential scanning calorimetry (DSC) and thermogravimetry (TG/DTG) has been used to obtain information on the temperature-controlled combustion characteristics of seventeen coals of different origin from Thrace basin of Turkey. Experiments were performed in air atmosphere up to 600°C at a heating rate of 10°C min^{-1}. The DSC/TG curves clearly demonstrate distinct transitional stages in the entire coal samples studied. Reaction intervals, peak and burn-out temperatures of the coal samples are also determined. Two different kinetic methods known as, Arrhenius and Coats–Redfern, were used to analyze the kinetic data and the results are discussed.

Keywords: *coal, differential scanning calorimetry, lignite, reaction kinetics, thermal analysis, thermogravimetry*

Introduction

Much attention has been focused in recent years on coal. Obviously an understanding of the physical and chemical processes occurring in coal while it is being heated will help in better design and optimization of practical conversion systems. Thermoanalytical tools such as differential scanning calorimetry (DSC), thermogravimetry (TG) and differential thermal analysis (DTA) can play an important role in this regard. The use of thermal methods for characterization of coal is certainly not new. Much work has been carried out to study the combustion and pyrolysis processes taking place in fossil fuels.

Alula *et al.* [1] used thermogravimetry and differential scanning calorimetry to characterise low- and high-temperature coal tar and petroleum pitches and their fractions, thermal methods to the characterization of pyrolysis coal products. Markova and Rustchev [2] studied the changes which occur in peat and coal with different degrees of carbonization when these are oxidised in the temperature range 150–300°C, and demonstrated that interaction of the coal with atmospheric oxygen results in the formation of unstable structures. Smith *et al.* [3] investigated the burning process of sixty-six coal samples, from lignite to black coal, and found that the burning temperature for half of these coal types is linearly dependent on their concentration. Smith and Neavel [4] carried out coal combustion experiments in the temperature range 25–900°C using air at atmospheric pressure in a derivative thermogravimetric analysis system. Calculated apparent activation energies were of the correct orders of magnitude to describe combustion regions corresponding to chemical-reaction-controlled as well as diffusion-controlled processes. Morgan and Robertson [5] determined coal-burning profiles by thermogravimetric analysis. They have claimed that kinetic parameters from Arrhenius plots of the profiles cannot readily be related to any specific stage of combustion. Patel *et al.* [6] measured the rate of combustion of lignite char using TG over a range of oxygen concentrations (5–20%) and at temperatures between 325–650°C. The activation energy in the chemical rate-controlled zone was 120 kJ mol^{-1} and the transition to film diffusion control occurred at 430°C. Iordanidis *et al.* [7] carried out thermogravimetry (TG/DTA) experiments for lignite samples. Different thermal effects were distinguished and a good correlation between the results of proximate and calorimetry analyses and the DTA and TG data is noticed. Alonso *et al.* [8] investigated the pyrolysis and combustion behavior of a set of eleven coals with different ranks and maceral composition by thermogravimetry (TG/DTG). Results showed that the pyrolysis curves of the coals do not match at all with any specific feature of the corresponding combustion profiles, and that the temperature of initiation of both processes are very different in the low-rank end, to become similar only for coal ranks of similar vitrinite reflectance and above. Várhegyi *et al.* [9] developed least squares criteria for the kinetic evaluation of thermal analysis experiments. They discussed several evaluation techniques for the handling of the non-statistical errors during the least squares evaluation of experimental series. The methods are

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illustrated by the evaluation of oxidative thermogravimetric experiments of lignite. Ozbas *et al.* [10] determined the combustion behavior and kinetic analysis of raw and cleaned coal samples of different size fractions by differential scanning calorimetry (DSC). Two different reaction regions were observed on DSC curves. Kinetic parameters of the coal samples were determined and the results are discussed. Kizgut *et al.* [11] characterized a set of seven bituminous coal chars by IR spectroscopy and thermogravimetry (TG) and elemental analysis. The reactivity of these samples was also studied and correlated with the coal parameters of mean vitrinite reflectance, fuel ratio and H/C ratio. The data suggest that reactivity as determined can be correlated with the mean vitrinite reflectance, fuel ratio and H/C ratio.

Experimental

In this research, differential scanning calorimetry (DSC) and thermogravimetry (TG/DTG) experiments were performed with a *Du Pont 9900* thermal analysis system. The seventeen coal samples studied in this research were from the Thrace basin (Turkey) and prepared (<60 mesh) according to ASTM Standards (ASTM D 2013-72). It is assumed that for such a small particle size the effect of temperature distribution within the sample particle is eliminated. It was also essential to calibrate the thermobalance for buoyancy effects in order to allow quantitative estimation of mass changes. The DSC and TG/DTG curves were obtained using the following experimental conditions: atmosphere. Air; flow rate: 50 mL min^{-1}; sample size: 10 mg; heating rate: 10^{o}C min^{-1}, and temperature range: 20–600^{o}C. All the experiments were performed twice for reproducibility. Properties of the coal samples are given in Table 1.

Results and discussion

The combustion process is exceedingly complex and many competing processes contribute to the thermal analysis curves. Theoretically, the combustion of fuel can be initiated whenever oxygen comes into contact with fuel. However, the temperature and composition of the fuel and air supply dictate the nature of the reactions. In all the samples studied (DSC experiments), in the temperature range of 30 and 115^{o}C coals start to loose small amount of pyrolysis water from decomposing phenolic structures, and oxides of carbon from carboxylic and carbonyl groups. At around 310^{o}C primary carbonization starts initially with the release of carbon dioxide and hydrogen (Figs 1, 2). Methane and other lower aliphatic are evolved together with hydrogen, carbon monoxide and alkyl aromatics with an increase in temperature [12]. These two temperature regions of evident chemical reactivity, elimination of water and primary carbonisation presumably forming CO_2 and CO are evident in all coal samples studied (Table 2). The TG/DTG curves of coals showed one main reactivity region. Oxidation reactions started around 300^{o}C and reached a maximum. The shoulder, that is seen in some of the samples, on the high temperature side of the reaction region, was attributed to the possible swelling of the sample, resulting in an impermeable mass that reduced the oxygen accessibility, causing a decrease in the reaction rate and thus a delay in burn-out temperature (Figs 3, 4). Reaction intervals, peak and burn-out temperatures of the coal samples are given in Table 3. It was observed that the reaction intervals of the coal samples studied are varied between 265–500^{o}C depending on the properties. On the other hand peak and burn-out temperatures are varied in the temperature range of 360–450 and 450–555^{o}C, respectively.

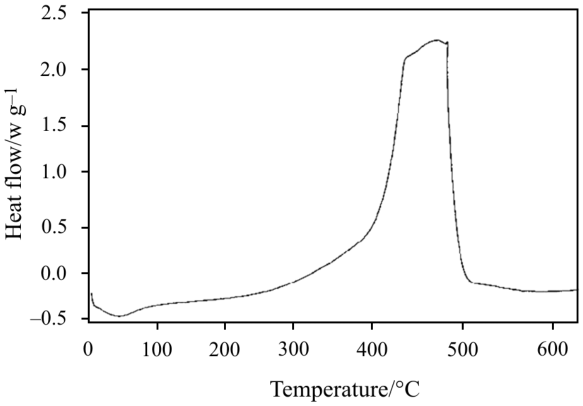

Fig. 1 DSC curve of the coal sample-3

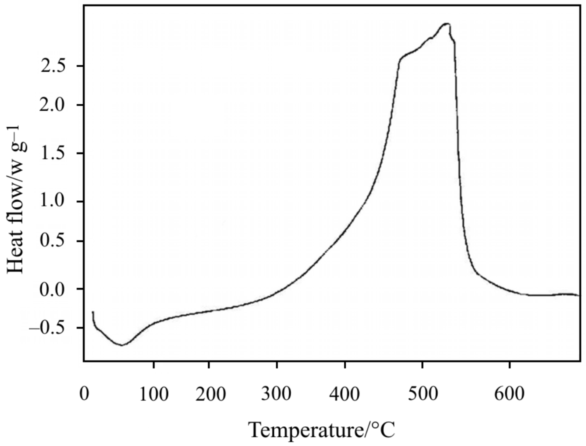

Fig. 2 DSC curve of the coal sample-4

Table 1 Properties of coal samples [11]

Sample	Moistrue content/%	Ash content/%	Volatire matter/%	Fixed carbon/%	Organic sulphur/%	Inorgan. sulphur/%	Total sulphur/%	Calorific value*/ kJ kg^{-1}	Calorific value**/ kJ kg^{-1}
01	20.39	30.03	22.89	26.69	2.50	0.56	3.06	12040	13120
02	27.84	14.73	23.61	33.82	1.24	0.26	1.50	14998	16320
03	28.31	15.07	24.35	34.15	1.36	0.28	1.64	15450	16538
04	27.05	14.15	23.15	33.24	1.20	0.22	1.42	14968	16328
05	31.95	19.05	23.42	25.58	0.79	0.64	1.43	11966	13300
06	28.36	16.82	27.43	27.39	1.04	0.40	1.44	14118	15460
07	27.56	25.29	23.49	23.66	0.82	0.22	1.04	11234	12464
08	27.17	17.67	25.70	29.46	1.30	0.22	1.52	13586	14875
09	28.32	16.45	26.92	26.25	1.14	0.42	1.56	11828	12770
10	34.96	12.53	24.85	27.66	1.41	0.77	2.18	12702	14155
11	15.96	12.70	30.26	41.08	0.65	0.35	1.00	19464	20670
12	22.45	14.70	23.25	21.56	1.15	0.28	1.43	14068	15500
13	24.10	15.07	25.15	22.41	0.95	0.31	1.26	14946	16370
14	19.70	13.68	27.45	28.10	0.78	0.27	1.05	15742	16642
15	16.75	12.47	31.56	39.22	0.61	0.22	0.83	18346	19565
16	19.60	21.42	26.35	31.75	1.10	0.47	1.57	16160	17165
17	16.40	14.35	30.15	39.05	0.76	0.42	1.18	16390	17982

*Low heating value: heat transfer with vapour H_2O in the products (kJ kg^{-1})
**High heatin value: heat transfer with liquid H_2O in the products (kJ kg^{-1})

Table 2 Reaction intervals and peak temperatures of coal samples (DSC)

Sample	React. regi. I/°C	Peak temp. I/°C	React. regi. II/°C	Peak temp. II/°C
01	30–110	70	310–500	430
02	30–110	68	335–500	426
03	30–100	64	335–485	410
04	30–115	66	330–505	395
05	30–110	74	330–490	408
06	30–115	65	310–505	406
07	30–105	68	310–515	420
08	30–105	67	310–490	415
09	30–110	70	315–500	418
10	30–110	72	310–495	422
11	30–115	75	310–490	416
12	30–110	66	320–485	410
13	30–105	68	315–495	385
14	30–105	68	310–505	413
15	30–115	65	325–500	415
16	30–110	70	310–490	388
17	30–110	72	315–495	420

Kinetic analysis

The non-isothermal kinetic study of mass loss during a combustion process is extremely complex, because of the presence of numerous components and their parallel and consecutive reactions. In this study, two different methods, all based on the Arrhenius theory were used for the kinetic analysis of TG/DTG data using a computer program developed for this purpose. During

Table 3 Reaction intervals, peak and burn-out temperatures of coal samples (TG/DTG)

Sample	Reaction interval/°C	Peak temperature/°C	Burn-out temp./°C
01	350–500	450	515
02	320–380	350	450
03	300–385	370	460
04	275–480	415	525
05	285–370	360	490
06	250–450	375	475
07	320–450	380	490
08	280–500	385	510
09	315–475	420	505
10	285–500	385	510
11	275–480	420	555
12	300–465	400	500
13	265–430	405	500
14	265–455	400	495
15	270–455	410	505
16	300–430	372	505
17	275–450	370	525

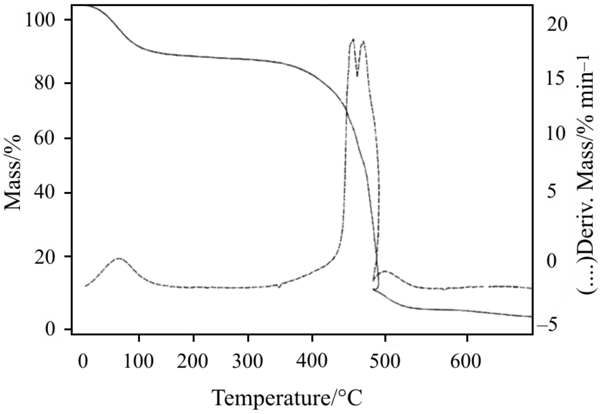

Fig. 3 TG/DTG curve of coal sample-3

recent years, several methods have been developed to allow the kinetic analysis of TG/DTG data.

The calculation of kinetic data is based on the formal kinetic equation:

$$d\alpha/dt = k\,\alpha^n \tag{1}$$

where, α is the amount of sample undergoing reaction, n is the order of reaction and k is the specific rate constant.

In Arrhenius method [13–14], since the measured rate of mass loss accounts for gross changes in the system, the reaction model assumes that the rate of mass loss of the total sample is dependent only on the rate constant, the mass of sample remaining (W) and the temperature.

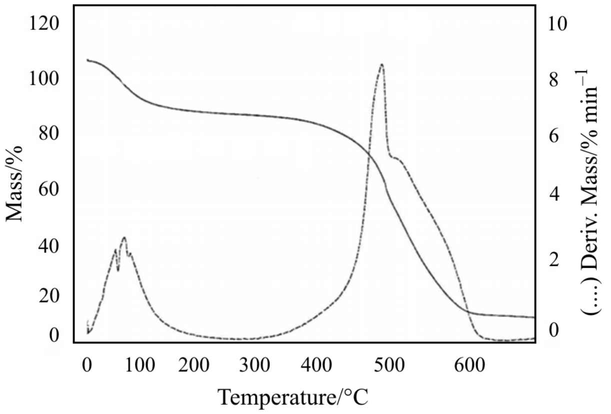

Fig. 4 TG/DTG curve of coal sample-4

$$dW/dt = k\,W^n \tag{2}$$

The temperature dependence of k is expressed by the following Arrhenius equation:

$$k = A_r \exp(-E/RT) \tag{3}$$

Assuming first-order kinetics,

$$dW/dt = A_r \exp(-E/RT)W \tag{4}$$

$$[(dW/dt)1/W] = A_r \exp(-E/RT) \tag{5}$$

taking the logarithm of both sides,

$$\log[(dW/dt)1/W] = \log A_r - E/2.303\,RT \tag{6}$$

where dW/dt is the rate of mass change, E is the activation energy, T is the temperature, A_r is Arrhenius constant and n is the reaction order. When log $[(dW/dt)1/W]$ is plotted *vs.* $1/T$, a straight line is obtained which will have a slope equal to $E/2.303R$ and from the intercept the Arrhenius constant can be estimated.

Coats and Redfern [15] developed an integral method, which can be applied to TG/DTG data, assuming the order of reactions. The correct order is presumed to lead to the best linear plot, from which the activation energy is determined. In this method, the rate of disappearance of sample may be expressed by:

$$d\alpha/dt = k\,(1-\alpha)^n \tag{7}$$

For a linear heating rate, say, deg β min^{-1}.

$$\beta = dT/dt \tag{8}$$

The extent of conversion, or fraction of material combusted, can be defined by the following expression;

$$\alpha = (w_o - w_t)/(w_o - w_f) \tag{9}$$

where, w_o is the initial mass loss, w_t is the mass after time t and w_f is the mass left after complete combustion. The final form of the equation which is used for the analysis is:

$$\ln\left[1-(1-\alpha)^{1-n} / (T_x^2(1-n))\right] = \\ = \ln\left[(AR/(\beta E))(1-2RT/E)\right] - \left[E/(RT)\right] \quad (10)$$

Thus a plot of ln $[1-(1-\alpha)^{1-n}/(T_x^2(1-n))]$ *vs*. $1/T$ should result in a straight line of slope equals $-E/R$ for the reaction order (n) of 1 (Figs 5, 6). A regression analysis with the least square method was used to determine the best straight line. Linear least square correlation coefficients for the identified rectilinear portions varied from 0.94 to 0.99 for both kinetic models. The activation energies of the coal samples are determined using two different kinetic methods as mentioned above are given in Table 4. It was observed that the activation energies of the samples are varied in the range of 66.5–92.0 kJ mol^{-1} in Arrhenius and 54.0–88.0 kJ mol^{-1} in Coats and Redfern methods respectively. The obtained activation energies were in consistency in two different methods. It was concluded that, depending on the mineral matter contents, different coal samples showed slight changes in activation energy values.

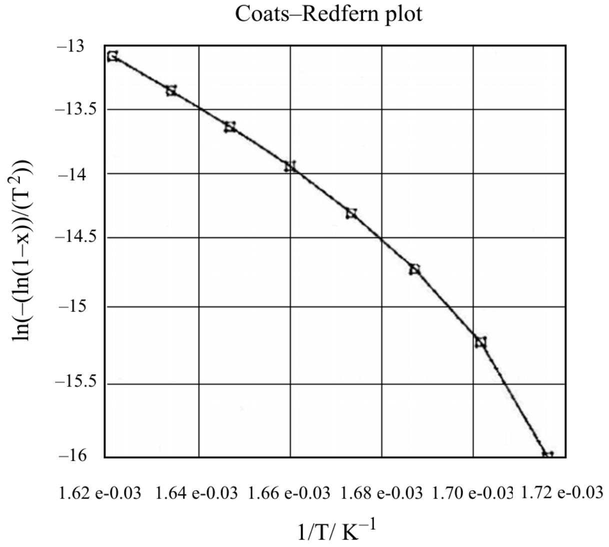

Fig. 5 Arrhenius curves of coal sample-3

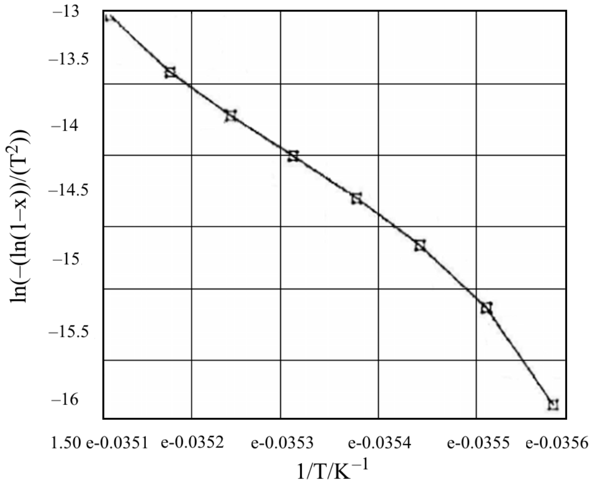

Fig. 6 Arrhenius curves of coal sample-4

Table 4 Activation energies (kJ mol^{-1}) of coal samples (TG/DTG)

Sample	Activation energy/kJ mol^{-1}	
	Model I	Model II
01	79.0	70.5
02	66.5	59.0
03	74.0	68.5
04	90.0	81.5
05	60.5	54.0
06	80.5	72.0
07	84.0	77.0
08	67.5	64.0
09	91.5	88.0
10	62.0	58.5
11	73.0	71.0
12	92.0	85.5
13	83.5	76.5
14	66.5	62.5
15	77.0	73.0
16	74.0	70.0
17	81.0	76.0

Conclusions

In this research, differential scanning calorimetry (DSC) and thermogravimetry (TG/DTG) has been used to obtain information on the temperature-controlled combustion characteristics of coals of different rank. The results showed that:

- Two temperature regions of evident chemical reactivity, elimination of water and primary carbonization are evident in all of the coal samples studied.
- It was observed that the activation energies of the samples are varied in the range of 54–92 kJ mol^{-1} in.

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