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Effect of mineral matter on the burning profile of lignites

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Abstract

In this study, the effect of the mineral species and of the total mineral matter content on the burning profile of twenty-five lignite samples originating from different parts of Turkey was investigated by thermogravimetry.

The burn-out times, DTG maximum peak temperatures and weight loss rates of the samples were correlated with the CaO, MgO, Na_2O and K_2O contents of the lignite samples. The results have shown that these mineral species catalytically influence the combustion phenomena of the lignite samples. Their catalytic effects are more pronounced at higher temperatures.

Keywords: Coal; Mineral matter; DTG; Lignite

1. Introduction

The combustion efficiency and reactivity of coal depends on a number of factors, some related to the operating conditions, others to the coal properties and composition. The amount and composition of the mineral matter can significantly influence the combustion characteristics of coal; this is important in the design of coal-fired boilers.

In the design of industrial coal-fired furnaces, it is of importance to have an assessment of the reactivity of the intended fuel. Alternatively, if it is proposed to change the fuel supply for an existing installation, it is advantageous to have a test which enables the burning characteristics of the candidate fuels to be compared with the original in terms of reactivity or burning rate [1].

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Non-isothermal thermogravimetry has been widely used for evaluating the burning properties of coals and chars [2–8]. A plot of the rate of weight loss against temperature while burning a sample in air has been referred to as a "burning profile" [2].

Mineral matter is generally considered to be the sum of all inorganic minerals and elements that are present in coal. Thus, all elements in coal except organically combined C, H, N, O and S are classified by this definition as mineral matter [9].

In this study attention has been directed to the effect of the mineral matter content on the combustion characteristics using the DTG curves of 25 lignite samples derived from TG applications.

2. Experimental

In the experiments, twenty-five lignite samples originating from different areas of Turkey were used. Samples were ground and sieved into a powder with a particle size of 250 μm.

Thermogravimetric analysis was carried out using a Shimadzu TG 41 thermal analyser. 40-mg lignite samples were spread uniformly on the bottom of the crucible made of alumina. The temperature was raised with a heating rate of 40 K min^{-1} to 1273 K and held at this temperature after the weight was constant. During the studies, the flow rate of the air was fixed at 40 cm^3 min^{-1}. The chart speed was selected as 5 mm min^{-1}.

The proximate analyses of the lignite samples were performed according to ASTM standards [10]. Chemical analyses of the ash produced from the lignite samples were determined according to the ASTM standards [11]. Determination of the total mineral matter content of the lignite samples was carried out according to the ISO-602 standard [12].

The DTG curves of the samples were derived using the TG curves obtained under the conditions mentioned above.

3. Results and Discussion

The proximate analysis of the lignite samples is given in Table 1. The moisture content of the lignite samples varied between 2.0 and 48.0%; the ash content between 6.2 and 40.6%; the volatile matter content between 22.2 and 46.4% and the fixed carbon content between 11.8 and 53.4%.

The chemical composition of the lignite ash and the total mineral matter content of the lignite samples are given in Table 2. As shown, the mineral matter content of 25 lignite samples used in this study varied between 7.68 and 47.97% on dry basis.

The TG curves of the lignite samples contain an initial weight loss due to the moisture released up to about 473 K; after that, a second step occurs which is represented by either a slight loss of weight or a horizontal plateau. The rate of weight loss starts to increase in the temperature range 473–573 K; the rapid increase in the weight loss ends in the temperature range of 773–873 K and the weight loss continues

Table 1
Proximate analysis of the lignite samples

Sample Code	Moisture/%	Volatile matter/%	Fixed carbon/%	Ash/%
L 01	10.5	32.2	25.1	32.2
L 02	4.4	22.2	32.8	40.6
L 03	15.7	36.1	16.4	31.8
L 04	9.6	39.2	40.2	11.0
L 05	10.5	36.8	40.6	12.1
L 06	19.9	30.3	35.8	14.0
L 07	27.6	39.8	22.8	9.8
L 08	24.2	38.4	31.2	6.2
L 09	2.0	32.0	51.6	14.4
L 10	14.0	36.1	23.3	26.6
L 11	7.2	46.4	39.1	7.3
L 12	25.3	28.7	16.7	29.3
L 13	16.2	40.9	10.3	32.6
L 14	15.9	41.0	36.4	6.7
L 15	35.4	32.2	23.4	9.0
L 16	12.5	32.3	32.3	22.9
L 17	17.9	37.3	26.1	18.7
L 18	27.0	34.4	18.0	20.6
L 19	14.1	33.4	39.8	12.7
L 20	13.9	24.6	22.3	39.2
L 21	40.4	32.1	12.3	15.2
L 22	6.4	28.6	37.4	27.6
L 23	5.9	31.8	53.4	8.9
L 24	27.5	34.4	24.0	14.1
L 25	48.0	28.2	11.8	12.0

up to about 1273 K. Lignite samples were kept at 1273 K after the weight was constant and it was observed that the weight loss was almost complete in the first 15 min.

The DTG curves showing weight loss rates versus temperature are derived from the curves obtained through TG analysis of the lignite samples. The DTG curves generally have the shape of a curve with two maxima corresponding to water release followed by progressive combustion (Fig. 1).

During the TG studies, the temperature was raised with a heating rate of 40 K min^{-1} to 1273 K and held at this temperature until the weight loss was constant. It was found that the time required to complete the combustion of the lignite samples varied between 25 and 43 min. Since volatile matter evolution and combustion occured within a few seconds, the total combustion time of the samples was strongly affected by their fixed carbon content (Fig. 2). On the TG curves, the time interval between the beginning and the end ($dm/dt = 0$) of the weight loss is called as the burn-out time. The correlation coefficient of the relationship between the burn-out time obtained from the TG curve and the fixed carbon content (dry basis) of the lignite samples is calculated as 0.8163. As can be seen from Fig. 2, there is a strong correlation between the burn-out time and the fixed carbon content of the lignite samples.

Table 2
The mineral matter content of the lignite samples (dry basis) and the composition of the ash

Sample code	SiO_2/%	Al_2O_3/%	Fe_2O_3/%	CaO/%	MgO/%	Na_2O/%	K_2O/%	Mineral matter/%
L01	49.70	27.77	7.28	2.90	0.92	9.94	0.97	41.90
L02	54.40	21.20	12.49	4.12	2.15	1.67	1.99	44.37
L03	37.40	33.36	12.02	11.75	0.74	0.40	1.96	46.22
L04	12.02	30.41	45.05	5.42	1.89	4.05	0.44	11.92
L05	30.17	35.23	24.63	7.76	0.30	0.97	0.12	16.51
L06	28.30	30.79	16.08	15.88	4.04	2.93	0.44	16.42
L07	33.28	29.74	12.36	15.77	2.12	1.31	0.44	12.30
L08	29.40	34.40	10.62	15.86	1.64	0.55	0.39	7.68
L09	33.05	33.46	23.11	7.24	0.51	0.30	1.42	17.04
L10	33.59	28.62	21.19	8.79	2.85	0.52	3.21	34.72
L11	16.08	38.69	34.48	6.51	1.22	0.77	1.15	12.46
L12	41.18	22.91	13.68	7.40	1.74	10.70	2.46	38.34
L13	19.39	20.44	20.36	23.54	1.04	0.37	1.12	44.14
L14	13.25	24.52	18.79	23.62	12.37	0.25	0.18	13.67
L15	27.84	20.46	26.02	11.89	7.84	0.96	0.46	15.27
L16	48.61	35.60	9.64	2.92	0.70	0.51	1.24	27.66
L17	23.67	20.44	22.14	15.63	3.26	0.92	0.70	28.88
L18	35.22	24.79	13.42	13.68	2.06	0.81	1.30	26.80
L19	32.57	27.72	18.16	9.03	4.74	2.32	0.89	15.14
L20	60.14	17.38	14.01	0.86	4.56	0.35	1.19	47.97
L21	30.00	19.44	20.30	15.26	3.38	0.40	1.14	35.60
L22	54.48	28.58	8.03	1.08	0.98	0.71	2.32	33.94
L23	29.20	28.00	30.41	9.01	0.31	0.29	0.91	8.84
L24	28.46	22.59	25.54	13.08	2.04	1.47	0.60	27.62
L25	18.50	17.59	13.18	22.64	6.64	1.11	1.09	30.24

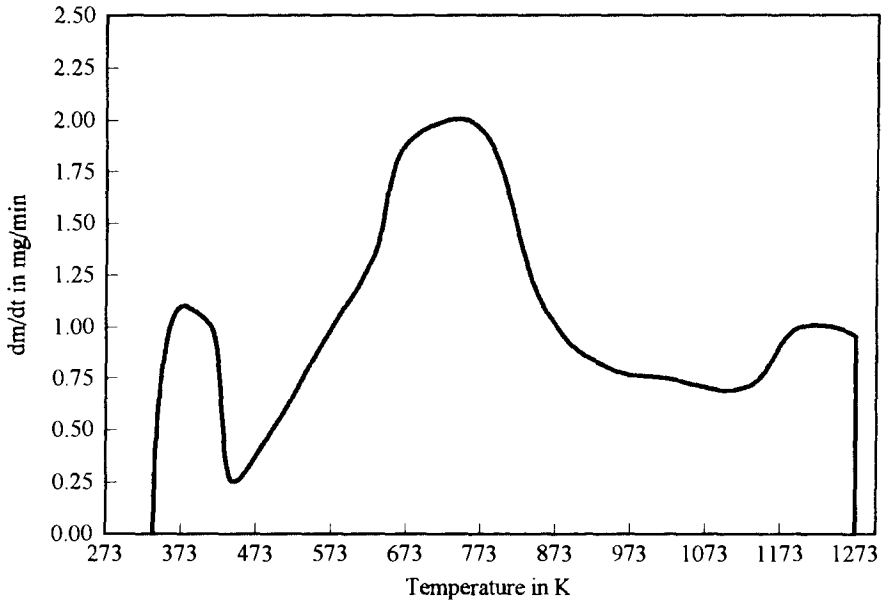

Fig. 1. The DTG curve of lignite sample L11.

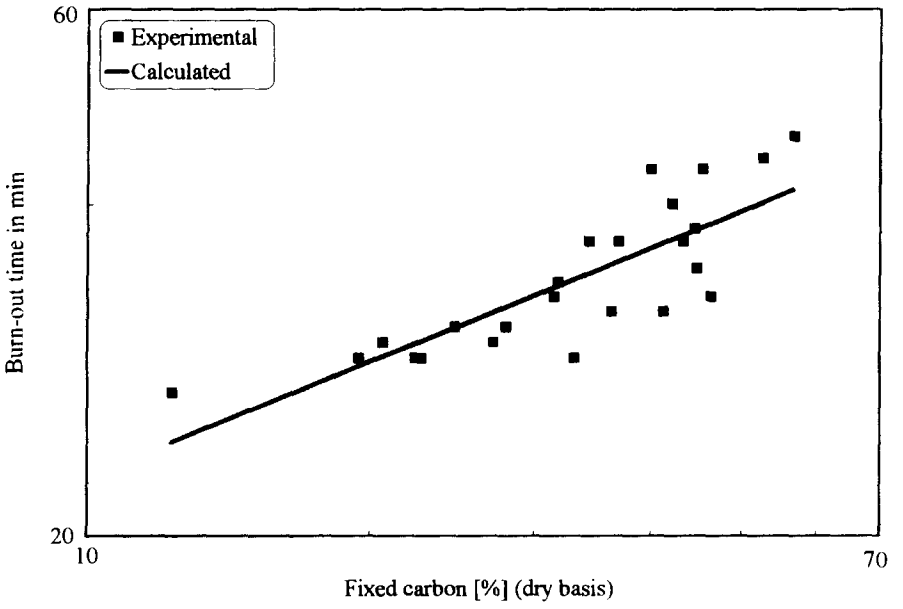

Fig. 2. The relationship between burn-out time and fixed carbon content of the lignite samples.

Also the relationships between the mineral species and the total mineral matter content of the lignite samples with their burn-out times were investigated. As can be seen from Figs. 3–6, an increase in the CaO, CaO + Na_2O, CaO + Na_2O + K_2O and CaO + Na_2O + K_2O + MgO content of the lignite samples causes a decrease in the burn-out time. The high correlation coefficients of the relationships show that these mineral species significantly affected the burn-out times. The correlation coefficients of the relationships shown in Figs. 3–6 are 0.7770, 0.8388, 0.8343 and 0.8333, respectively. The correlation coefficients of the relationship between burn-out time and mineral species of the lignite samples have approximately the same magnitude as of the relationship between the burn-out time and the fixed carbon content. These results have shown that the examined mineral species significantly influence the rate of coal combustion by catalytically increasing the rate.

The relationship of the burn-out time with the total mineral matter content of the lignite samples is weaker than that with the mineral species. The correlation coefficient of the relationship is 0.5035.

The peak temperature at which the rate of weight loss due to combustion of the lignite samples is a maximum is called as the "DTG maximum peak temperature (DTG-MPT)"; the rate of weight loss at DTG maximum peak temperature is called the "maximum weight loss rate".

The maximum weight loss rate is proportional to the volatile matter content of the samples. The correlation coefficient of the relationship shown in Fig. 7 is 0.7504. Due to the rapid evolution of volatile matter and its high combustion rate, there is a close

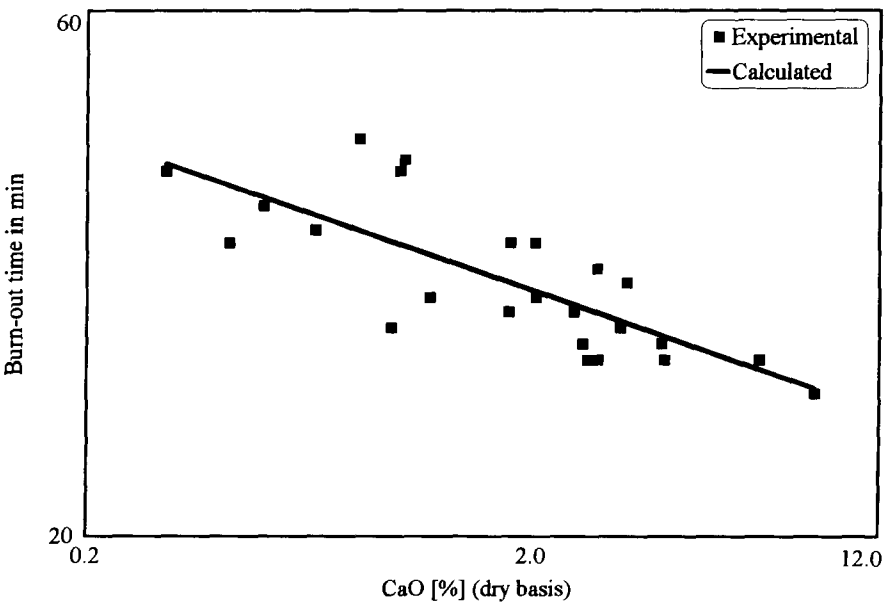

Fig. 3. The relationship between burn-out time and CaO content of the lignite samples.

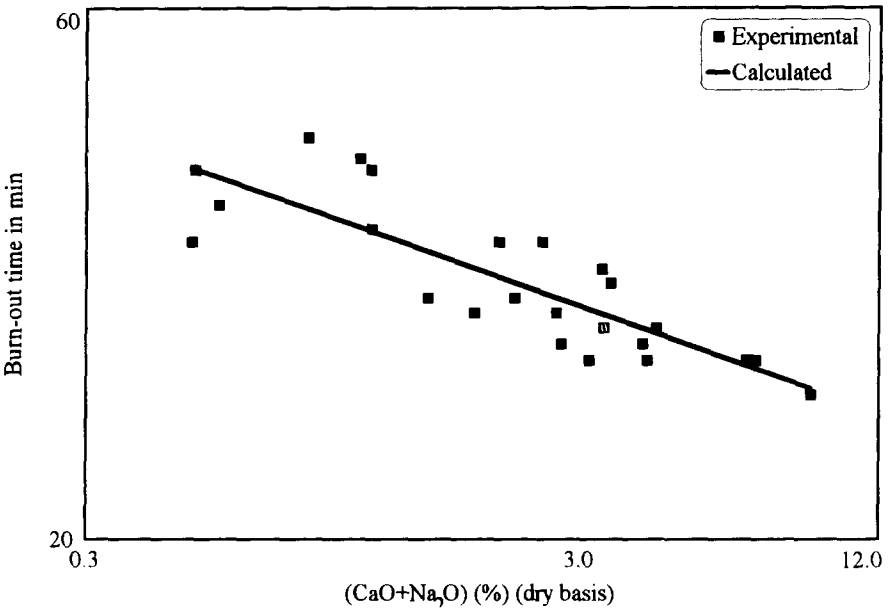

Fig. 4. The relationship between burn-out time and the sum of the CaO and Na_2O content of the lignite samples.

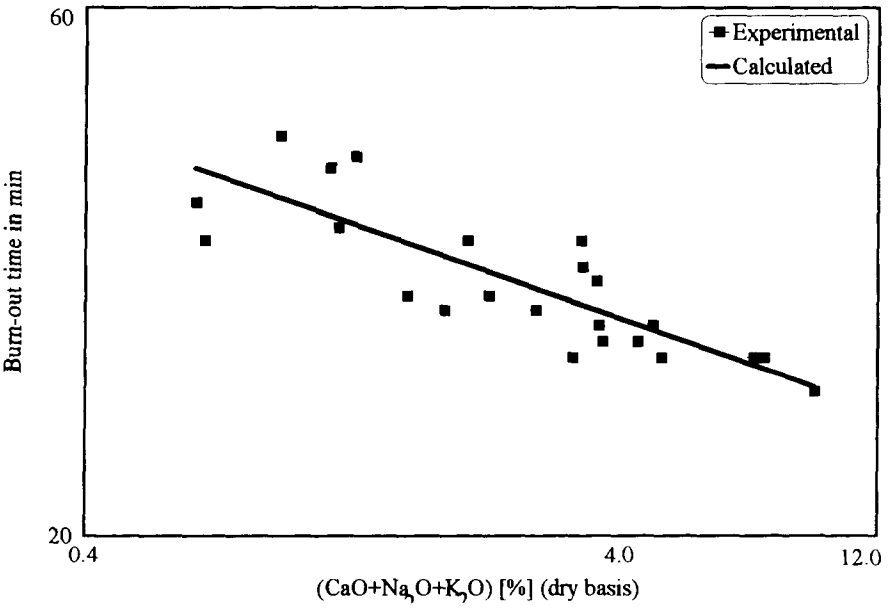

Fig. 5. The relationship between burn-out time and the sum of the CaO, Na_2O and K_2O content of the lignite samples.

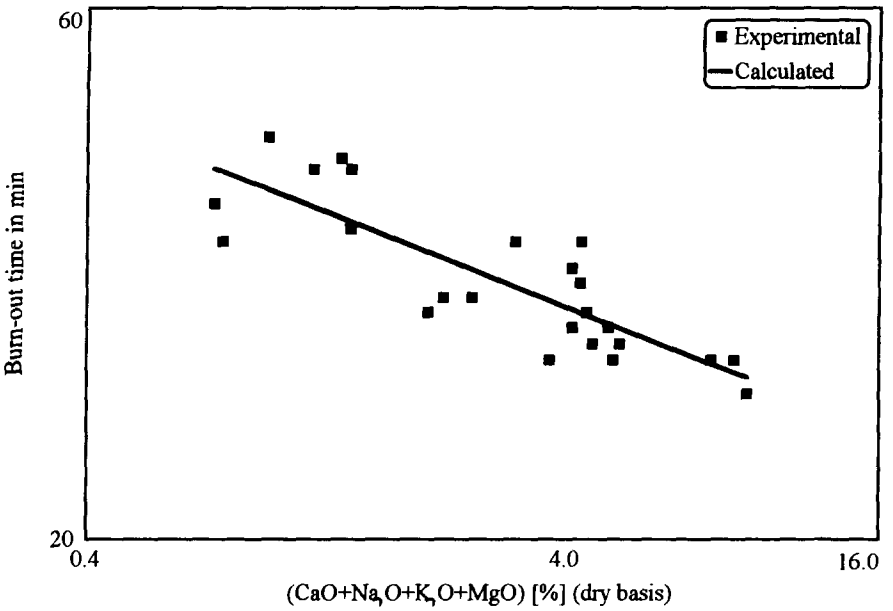

Fig. 6. The relationship between burn-out time and the sum of the CaO, Na_2O, K_2O and MgO content of the lignite samples.

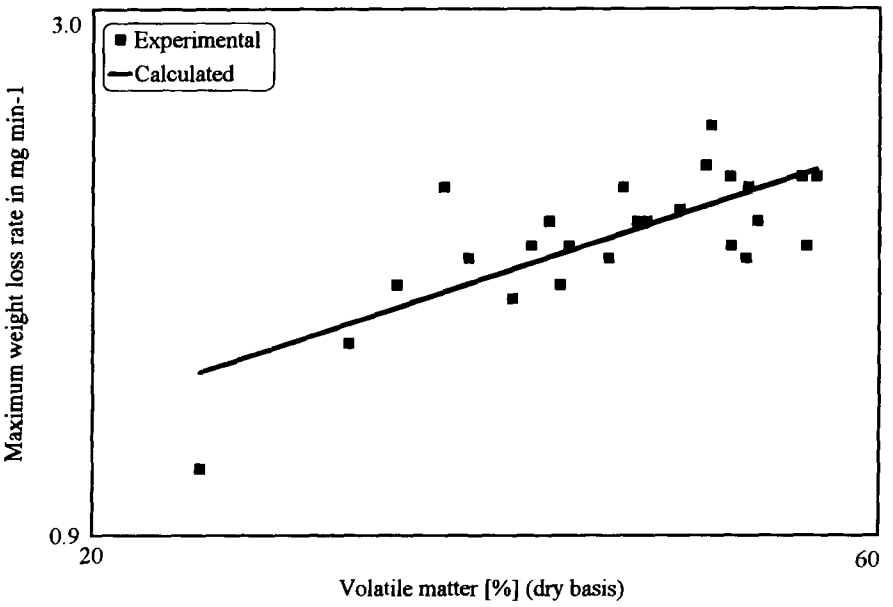

Fig. 7. The relationship between the maximum weight loss rate and volatile matter content of the lignite samples.

relationship between the volatile matter content and the maximum weight loss rate of the lignite samples.

The maximum peak temperature of the lignite samples varies between 530 and 810 K. It has been observed that the maximum peak temperatures of the lignite samples with high volatile matter content occurred at lower temperatures (Fig. 8). The samples with high volatile matter content showed a rapid weight loss at relatively low temperatures. The correlation coefficient of the relationship between the volatile matter content and DTG maximum peak temperature of the lignites is determined as 0.6289. The burning profiles of three partially devolatilized coals were obtained by Rostam–Abadi et al. [13] using a thermogravimetric analyser. They have reported that the devolatilization process shifted the burning profiles to higher temperatures.

DTG maximum peak temperature is taken as a measure of the combustibility or reactivity of a coal: the lower the maximum peak temperature, the more reactive a coal may be considered [1, 14].

There is a good correlation between the DTG maximum peak temperature and the mineral species of the samples (Figs. 9, 10). It has been observed that an increase in the CaO, CaO + Na_2O, CaO + Na_2O + K_2O and CaO + Na_2O + K_2O + MgO content of the lignite samples causes a significant decrease in the maximum peak temperature of the DTG curves; the correlation coefficients of the relationships were calculated as 0.8503, 0.8525, 0.8407 and 0.8014, respectively.

Two models have been proposed to explain the effect of catalyst on the combustion phenomena of coal. The first is the oxygen transfer model: the catalyst enhances

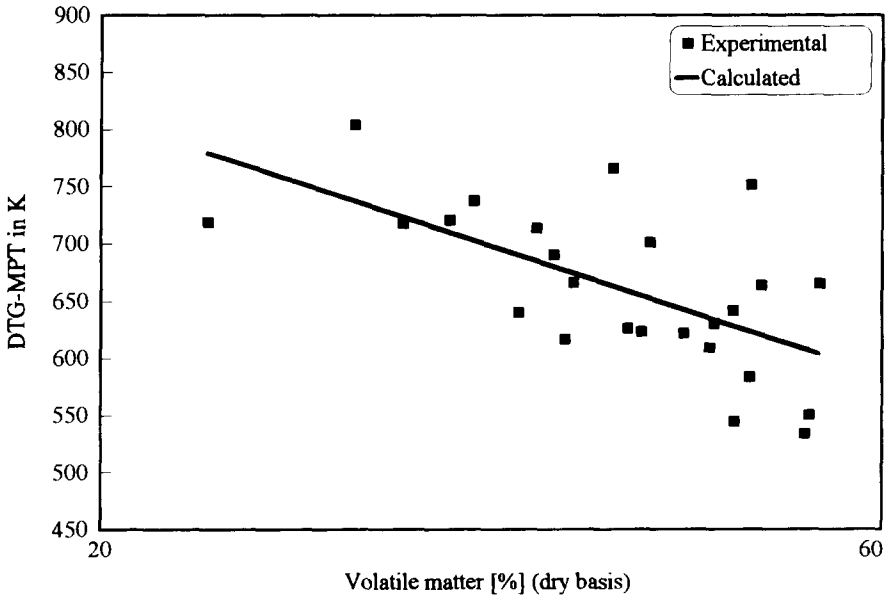

Fig. 8. The relationship between the maximum peak temperature of the DTG curves and volatile matter content of the lignite samples.

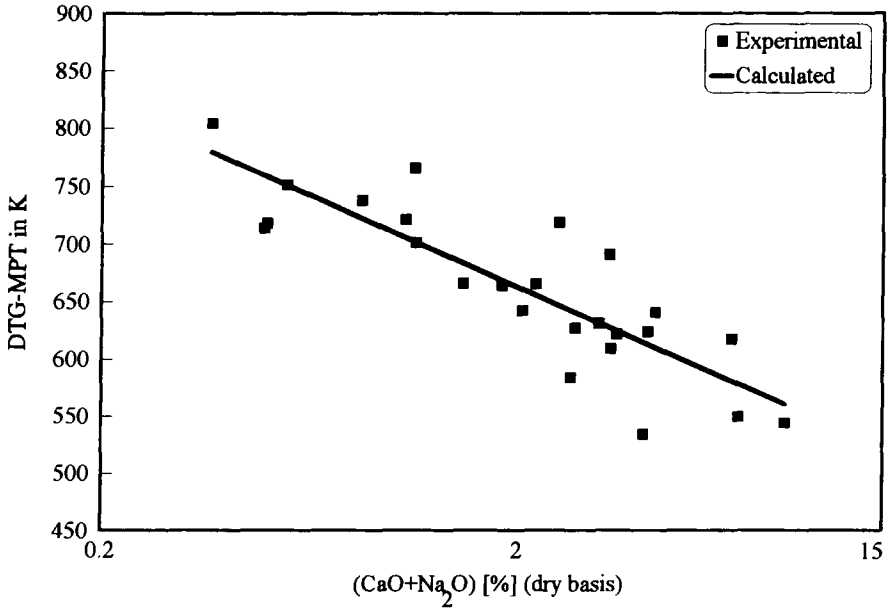

Fig. 9. The relationship between the maximum peak temperature of the DTG curves and the sum of the CaO and Na_2O content of the lignite samples.

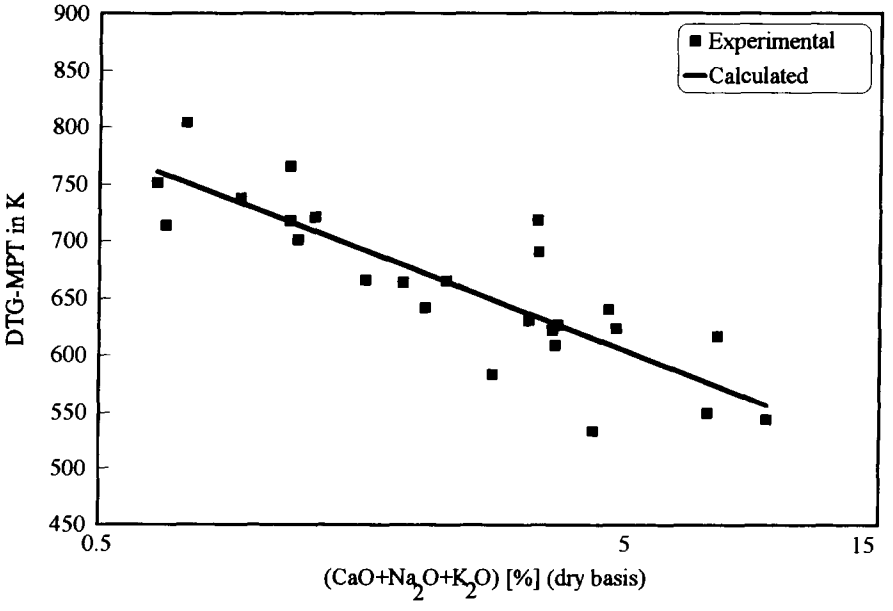

Fig. 10. The relationship between the maximum peak temperature of the DTG curves and the sum of the CaO, Na_2O and K_2O content of the lignite samples.

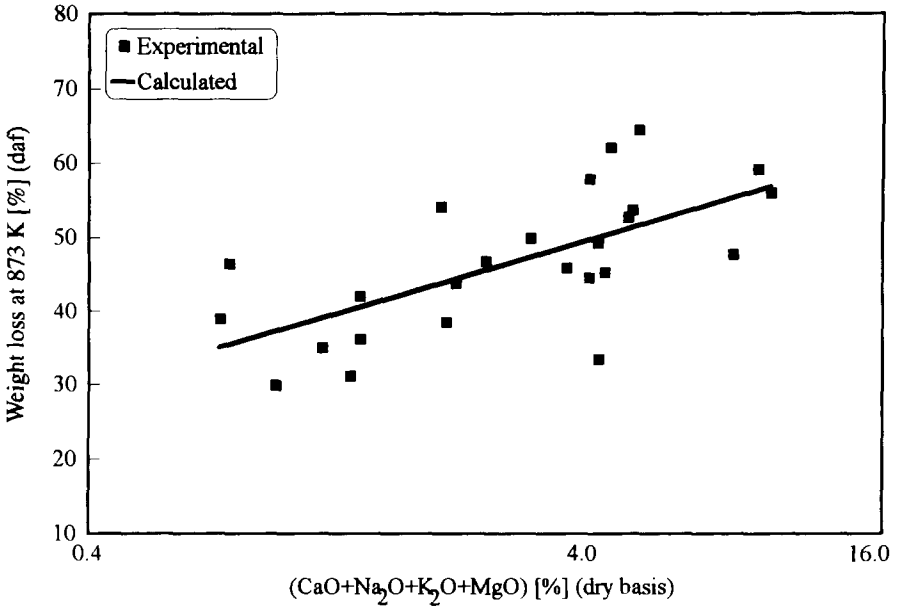

Fig. 11. The relationship between the weight loss percentage at 873 K and the sum of the CaO, MgO, Na_2O and K_2O content of the lignite samples.

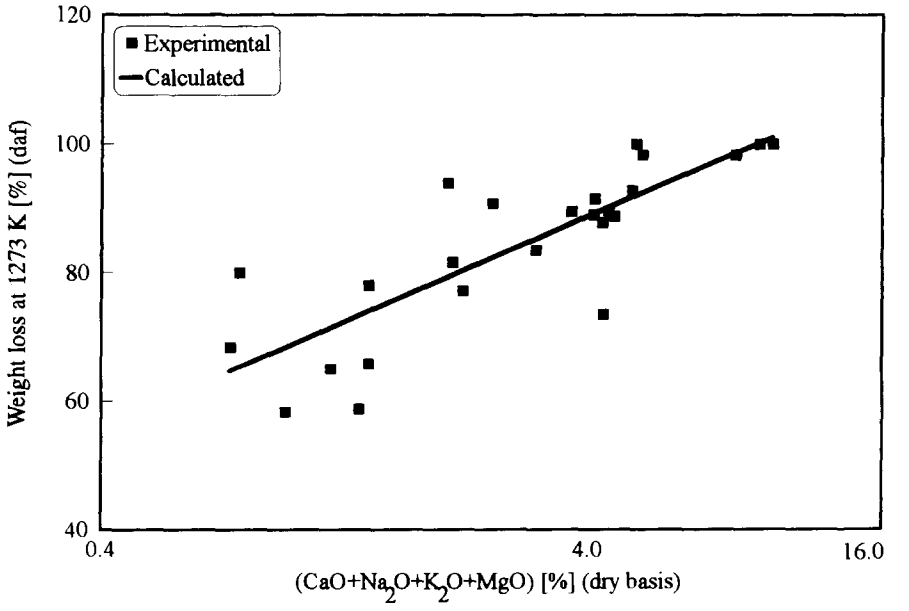

Fig. 12. The relationship between the weight loss percentage at 1273 K and the sum of the CaO, MgO, Na_2O and K_2O content of the lignite samples.

dissociation of the adsorbed oxygen, and the oxygen atoms so formed are then substantially more reactive than the molecular form [15]. The second model is the electron-transfer mechanism that originated with Long and Sykes [16]. It requires electronic binding between the adsorbed oxygen atoms and the carbon atoms. It is then assumed, however, that the presence of a catalyst modifies the electronic binding in such as way that the C=O bond is strengthened and any C–C bonds are weakened. The first model emphasizes the catalyst–gas interaction; the second emphasizes the catalyst–carbon interaction.

Data indicated that the catalytic effects of the mineral species on the combustion characteristics are more pronounced at higher temperatures. Effects of the mineral species on the weight loss percentages (calculated on dry, ash-free basis) at 873 K and at 1273 K were investigated (Figs. 11 and 12). The correlation coefficients of the relationships between the CaO, $CaO + Na_2O$, $CaO + Na_2O + K_2O$, $CaO + Na_2O + K_2O + MgO$ content of the lignite samples and their weight loss percentages at 873 K are 0.6570, 0.6601, 0.6640, 0.6598, respectively and at 1273 K are 0.7125, 0.7719, 0.7849 and 0.8154, respectively. These results clearly show that increasing the temperature from 873 K to 1273 K caused an increase in the catalytic effect of mineral species on the combustion phenomena of the lignite samples.

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