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Thermochimica Acta 342 (1999) 79–84

thermochimica acta

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Effect of mineral matter on the reactivity of lignite

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Received 23 April 1999; accepted 1 July 1999

Abstract

In this study, effects of total mineral matter content and of elements Ca, Mg, Na, K, Si and Al on the combustion reactivity of 25 lignite samples, originating from different areas of Turkey, was investigated. Non-isothermal thermogravimetry, where the sample was heated in air and the temperature of which increased at a linear rate of 40 K min^{-1} to 1273 K, has been used to investigate the combustion reactivities of the lignite samples. The calculated combustion activation energy values were related to the mineral impurities and definite correlations were observed. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Lignite; Mineral matter; Reactivity

1. Introduction

Coals are associated with mineral impurities that may affect several reactions occurring during the combustion process. Mineral matter is generally considered to be the sum of all inorganic minerals and elements that are present in coal [1]. The mineral matter of coal includes clays, sulphides, carbonates, sulphates, chlorides, silicates, oxides and hydroxides [2]. It occurs in many forms and sizes, which can be seen by the naked eye or occur in micron-sized particles that require an optical or electron microscope to observe [1]. Several investigators have suggested that the amount and composition of the mineral matter can influence the combustion characteristics of coal, which is important in the design of coal-fired boilers [3–8].

The objective of the research described in this study is to investigate the influence of the mineral matter on the reactivity of 25 Turkish lignite samples. Non-isothermal thermogravimety has been used to determine the combustion reactivities of the lignite samples.

2. Experimental

In the experiments, 25 lignite samples were used. Samples were ground and sieved into a powder with a particle size of 250 μm. The proximate analyses of the samples were performed according to ASTM standards. Chemical analyses of the ashes produced from the lignite samples were determined according to the ASTM standards. Determination of the total mineral matter content of the lignite samples was carried out according to the ISO-602 standard.

Thermogravimetric analysis was carried out using a Shimadzu TG41 thermal analyzer. 40 mg samples

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PII: S0040-6031(99)00209-9

were spread uniformly on the bottom of a crucible made of alumina. Dried air was selected as the oxidizing gas. The flow rate of air was fixed at 40 cc min^{-1}. The temperature was raised, with a heating rate of 40 K min^{-1}, to 1273 K and held for 30 min at this temperature.

3. Results and discussion

The analyses results of the lignite samples and the ashes are given in Tables 1 and 2.

Non-isothermal thermogravimetry, where the lignite sample was heated in air and the temperature of which increased at a linear rate (40 K min^{-1}), has been used to calculate the activation energy values of the lignite samples by the method of Coats–Redfern [9]. The best way to estimate the combustion reactivity of a coal sample is to determine its activation energy. The calculated activation energy values, by the method of Coats–Redfern, have ranged between 64 and 139 kJ mol^{-1} (Table 3). Since coal is a highly heterogeneous material, its activation energy may vary widely even within a given rank. The variation may arise from differences in the organic structure, mineral matter or physical structure of the lignite samples. As can be seen from Table 2, the mineral matter content and the chemical composition of the ashes changes in broad ranges. Ca, Mg, Na, Fe, Si and Al concentrations of the lignite samples were calculated using the ash analysis results.

Fig. 1 correlates the activation energy of the lignite samples with the total mineral matter content, calculated on dry basis. It is seen that the higher the total mineral matter content, the lower the activation energy, until the total mineral matter reaches about 20%. If the total mineral matter content exceeds this value, the activation energy increases with increasing total mineral matter content. Possible explanations of this result are as follows:

- For lignite samples with low total mineral matter content, the fractions of SiO_2 and Al_2O_3 of the mineral matter are small compared with the sum of

Table 1
Proximate analyses of the lignite samples

Sample code	Moisture (wt.%)	Volatile matter (wt.%)	Fixed carbon (wt.%)	Ash (wt.%)
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

Table 2
The mineral matter content of the lignite samples (dry basis) and the composition of the ashes (wt.%)

Sample code	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	Mineral matter
L 01	49.70	27.77	7.28	2.90	0.92	9.94	0.97	41.90
L 02	54.40	21.20	12.49	4.12	2.15	1.67	1.99	44.37
L 03	37.40	33.36	12.02	11.75	0.74	0.40	1.96	46.22
L 04	12.02	30.41	45.05	5.42	1.89	4.05	0.44	11.92
L 05	30.17	35.23	24.63	7.76	0.30	0.97	0.12	16.51
L 06	28.30	30.79	16.08	15.88	4.04	2.93	0.44	16.42
L 07	33.28	29.74	12.36	15.77	2.12	1.31	0.44	12.30
L 08	29.40	34.40	10.62	15.86	1.64	0.55	0.39	7.68
L 09	33.05	33.46	23.11	7.24	0.51	0.30	1.42	17.04
L 10	33.59	28.62	21.19	8.79	2.85	0.52	3.21	34.72
L 11	16.08	38.69	34.48	6.51	1.22	0.77	1.15	12.46
L 12	41.18	22.91	13.68	7.40	1.74	10.70	2.46	38.34
L 13	19.39	20.44	20.36	23.54	1.04	0.37	1.12	44.14
L 14	13.25	24.52	18.79	23.62	12.37	0.25	0.18	13.67
L 15	27.84	20.46	26.02	11.89	7.84	0.96	0.46	15.27
L 16	48.61	35.60	9.64	2.92	0.70	0.51	1.24	27.66
L 17	23.67	20.44	22.14	15.63	3.26	0.92	0.70	28.88
L 18	35.22	24.79	13.42	13.68	2.06	0.81	1.30	26.80
L 19	32.57	27.72	18.16	9.03	4.74	2.32	0.89	15.14
L 20	60.14	17.38	14.01	0.86	4.56	0.35	1.19	47.97
L 21	30.00	19.44	20.30	15.26	3.38	0.40	1.14	35.60
L 22	54.48	28.58	8.03	1.08	0.98	0.71	2.32	33.94
L 23	29.20	28.00	30.41	9.01	0.31	0.29	0.91	8.84
L 24	28.46	22.59	25.54	13.08	2.04	1.47	0.60	27.62
L 25	18.50	17.59	13.18	22.64	6.64	1.11	1.09	30.24

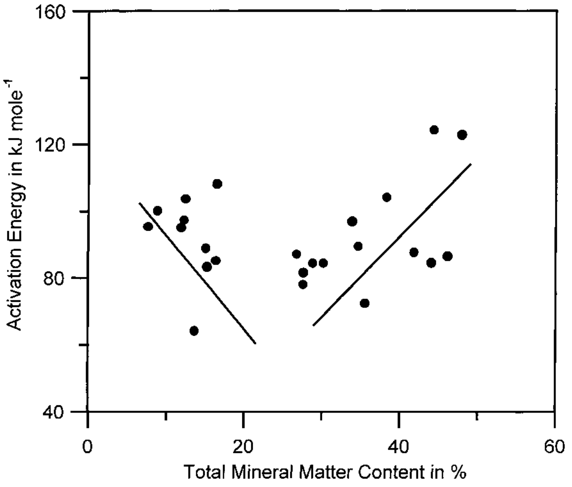

Fig. 1. Variation of activation energy with total mineral matter content (dry basis).

Fe_2O_3, CaO, MgO, Na_2O and K_2O fractions. For example, 3 lignite samples (L 08, L 23 and L 04) have the lowest total mineral matter content than the others. The sum of Fe_2O_3, CaO, MgO, Na_2O and K_2O fractions of these samples are 30.9, 44.1 and 58%, respectively. However, as far as the 3 lignite samples L 20, L 03 and L 02, which have the highest mineral matter content, are considered, the sum of the fractions of these species in the total mineral matter content is 20.4, 20.9 and 21.4%, respectively. Kaolinite and quartz have an inhibitory effect on the combustion process of coal because of their inert behavior.

- The distribution of the minerals in the coals is as important as their concentrations. Jenkins et al. [10] reported that if a catalyst is well distributed, then its apparent activity is enhanced; however, if it is concentrated in large agglomerates, its activity will be restricted. Mulcahy and Smith [11] concluded that if a catalytic impurity is well dispersed throughout the carbon, very little is required to produce a large effect. Pohl [12] has indicated that, to effectively catalyze the combustion rate of coal, the metal that accelerates the rate must be distributed on nearly the molecular level, and be

Table 3
Activation energy values of the lignite samples

Sample code	Activation energy (kJ mol^{-1})
L 01	87.65
L 02	124.14
L 03	86.39
L 04	95.02
L 05	108.14
L 06	84.99
L 07	97.33
L 08	95.40
L 09	138.47
L 10	89.44
L 11	103.69
L 12	104.16
L 13	87.49
L 14	64.18
L 15	83.19
L 16	81.51
L 17	84.32
L 18	87.06
L 19	88.86
L 20	122.82
L 21	72.40
L 22	96.88
L 23	100.12
L 24	78.05
L 25	84.35

present in sufficient concentration to accelerate the rate. The fraction of inherent mineral matter of coals with low total mineral matter content is high. Inherent mineral matter generally originates from plants, and is rich in Fe, P, Ca, K and Mg [13]. Inherent mineral matter is closely associated with the organic part of coal and has a uniform distribution.

- The third possibility can be expressed as follows: as the mineral matter content of the lignite sample increases, the combustion activation energy decreases as a result of the catalytic effect; however, when the available surface is covered by catalyst atoms, the excess amount causes a decrease in surface area and porosity, which results in an increase in the activation energy.

Fig. 2 represents the relationship between the activation energies and the Si content of the lignite samples. Fig. 3 represents the relationship of the activation energies with the sum of the Al and Si contents of the lignite samples. The variation of the activation energy with Si and/or Al contents of the lignite samples passes through a minimum and then increases as a result of the possible reasons mentioned above.

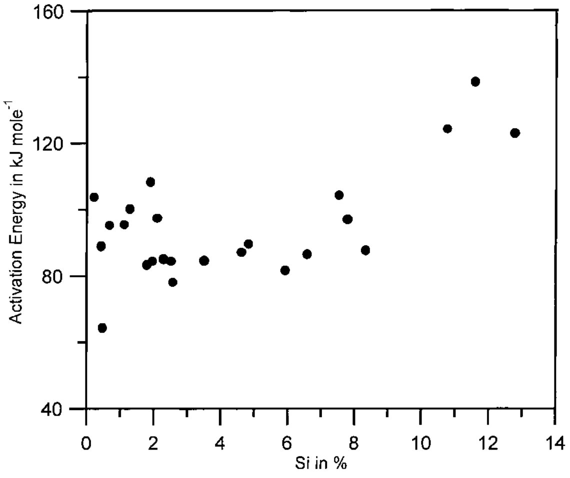

Fig. 2. Variation of activation energy with Si content (dry basis).

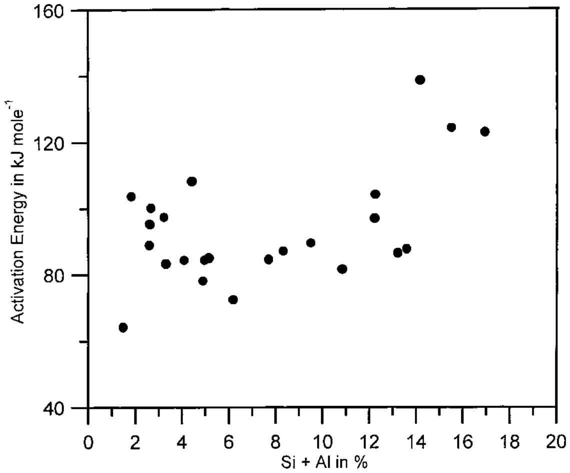

Fig. 3. Variation of activation energy with the sum of the Al and Si contents (dry basis).

Ca content of the lignite samples changes between 0.2 and 6.5%, and its effect on the combustion activation energy of the lignite samples is illustrated in Fig. 4. It is seen that the higher the Ca content, the lower the activation energy, until the Ca content reaches about 2%. It can be concluded that the catalytic effect

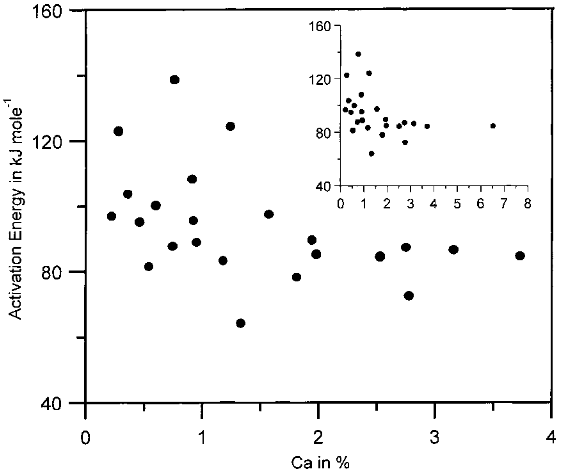

Fig. 4. Variation of activation energy with Ca content (dry basis).

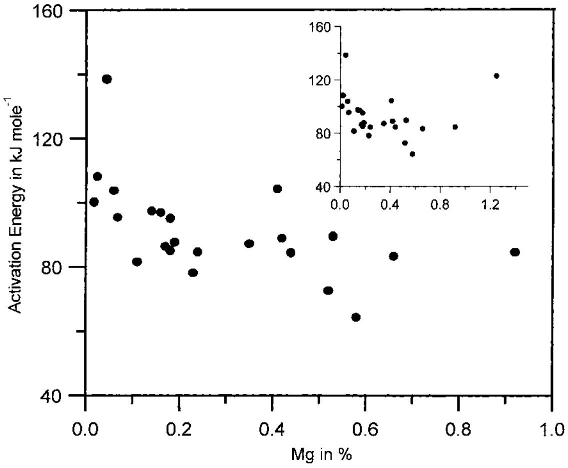

Fig. 5. Variation of activation energy with Mg content (dry basis).

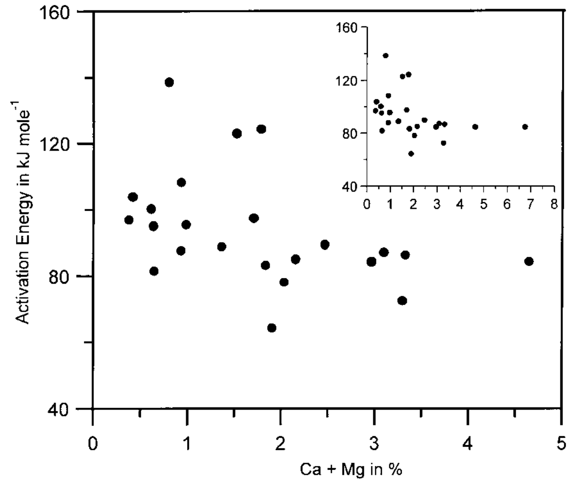

Fig. 6. Variation of activation energy with the sum of Ca and Mg content (dry basis).

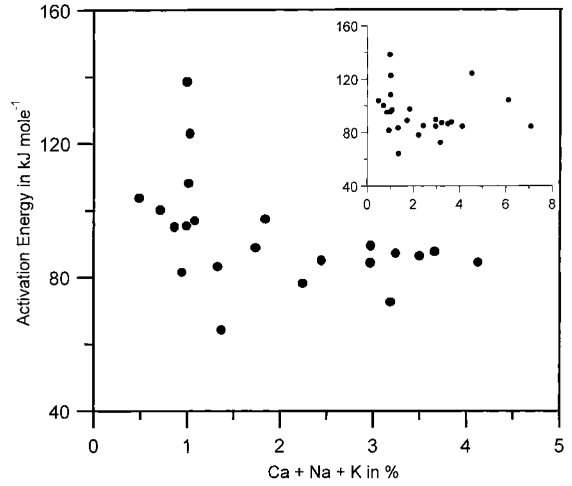

Fig. 7. Variation of activation energy with the sum of Ca, Na and K contents (dry basis).

of calcium increases with increasing amount until its concentration reaches about 2%. At that concentration, a saturation seems to occur.

Mg content of the lignite samples is relatively small, and ranges between 0.02 and 1.25%. However, its effect on the combustion activation energy is strong (Fig. 5).

Fig. 6 correlates the activation energy with the sum of the Ca and Mg contents of the lignite samples. It is apparent that the trend is similar to that of Ca content.

Fig. 7 represents the effect of the sum of Ca, Na and K contents of the samples on the activation energy. An increase in the concentration of these elements caused a corresponding decrease in the activation energy of the lignite sample until it reaches about 2%.

Sentorun and Küçükbayrak [6] investigated the relationships between the mineral species and burn-out times of the same lignite samples used in this study. They concluded that an increase in CaO, CaO + Na_2O, CaO + Na_2O + K_2O and CaO + Na_2O + K_2O + MgO contents of the lignite samples causes a decrease in the burn-out times. The high

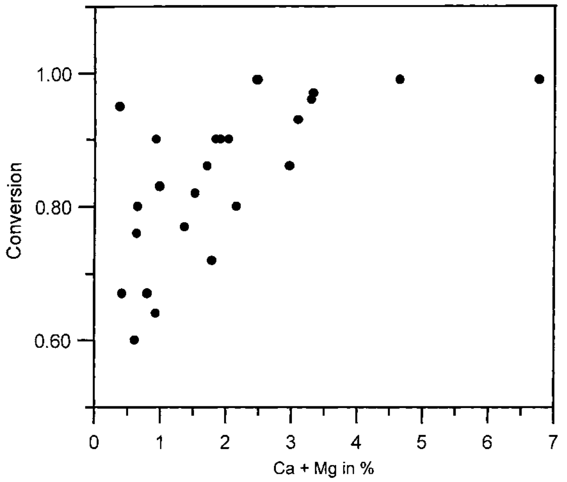

Fig. 8. The relationship between the conversion at 1273 K and the sum of Ca and Mg contents (dry basis).

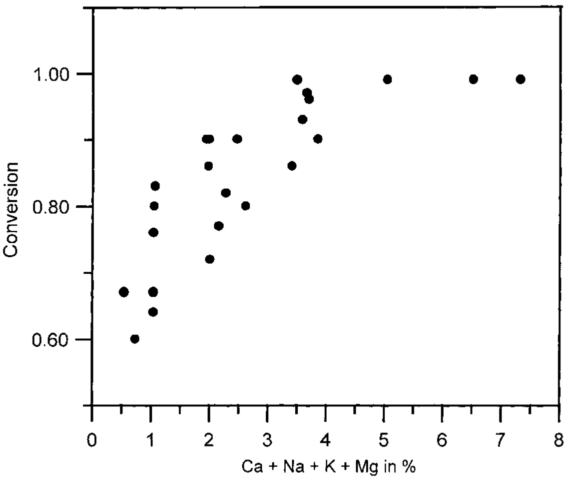

Fig. 9. The relationship between the conversion at 1273 K and the sum of Ca, Na, K and Mg contents (dry basis).

correlation coefficients of the relationships show that these mineral species significantly affected the burn-out times. The correlation coefficients of the relationships mentioned above are 0.7770, 0.8388, 0.8343 and 0.8333, respectively.

The conversion of the lignite samples during the heating in air atmosphere from room temperature to 1273 K was calculated and correlated with their Ca, Mg, Na and K contents. Figs. 8 and 9 indicate that an increase in the Ca + Mg content until it reaches about 3%, and an increase in the Ca + Na + K + Mg content until it reaches about 4% accelerate the conversion rates of the lignite samples at 1273 K. The results suggest that the Ca, Mg, Na and K fractions of the mineral impurities have strong effects on the conversion at 1273 K until their concentration in the lignite samples reach a saturation limit.

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