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INFLUENCE OF THE MINERAL MATTER CONTENT ON THE RATE OF HEAT RELEASE FROM TURKISH LIGNITES

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Abstract

In this study, combustion curves of twenty-five original and demineralized Turkish lignite samples were obtained through use of a differential thermal analyser. The lignite samples were demineralized by treatment with hydrochloric and hydrofluoric acids. Samples of 20 mg were heated up to 1074 K at a constant rate of 10 K min^{-1} in a 40 cm^3 min^{-1} flow of dry air. The rates of heat release from the original and demineralized samples were compared and are discussed.

Keywords: DTA, lignite, mineral matter

Introduction

The amount and composition of the mineral matter content can influence the combustion characteristics of coal, which are important in the design of coal-fired boilers. All coals except anthracites, and all coal components other than macerals of the inertite group, are extremely sensitive to oxygen, and even a small oxygen addition can have serious effects on the coal properties [1].

When a coal particle is heated progressively in an oxygen-rich atmosphere, the events that lead to combustion can be divided into three stages [1–3]:

1. Release of the volatile matter resulting from heating of the coal and then carbonization.
2. Burning of the volatile matter in the gas phase.
3. At sufficiently high temperatures and only if sufficient oxygen can reach the particle surface, ignition and burning of the residual solid particle (char).

The relationship between these stages depend on particle size, heating rate and char porosity [1]. Very few details are known about the combustion of volatile matter, although it influences length and stability of the flame. The variables affecting the stage of char burning are very important because this is the

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slowest stage. The time period required for char burning is ten times higher than that for the release of the volatile matter. Investigations concerning improvement of the efficiency of coal combustion are therefore focussed on the burning of char. Coal is a porous solid, which is why an increase in the fixed carbon content causes a decrease in its surface area. It can therefore be concluded that char burn-out is critically influenced by porosity and surface area [4].

Although noteworthy investigations have been made on the combustion of coal, the details are not known definitely. Knowledge relating to the effects of the mineral matter on the combustion characteristics is not clear. Since Turkish lignites contain large amounts of mineral matter and a great number of species [5], this subject is extremely important for Turkey.

The mineral matter content is generally considered to be the sum total of all the organic minerals and elements that are present in the coal. Thus, all elements in coal except organically combined C, H, O, N and S are classified by this definition as mineral matter. This definition adequately classifies most inorganic elements present in coals, including those that are structurally bound within various minerals, but some other elements are also combined in the organic matter [6]. Carbon is present in carbonates of calcium, magnesium and iron; hydrogen in free water and water of hydration; oxygen in oxides, water, sulfates and silicates; and sulfur in sulfides and sulfates [2].

The purpose of the present study was to investigate how the mineral matter present in 25 lignite samples taken from different parts of Turkey influences the rate of heat release.

Experimental

DTA was carried out with a Shimadzu DTC 40 analyser. 20 mg of original and previously demineralized lignite samples which had been ground to pass through a 0.25 mm sieve were spread uniformly on the bottom of a crucible made of alumina. During the studies, the rate of flow of dry air was fixed at 40 cm^3 min^{-1}. The chart speed was selected as 2.5 mm min^{-1}. The furnace was heated up to 1074 K at a constant rate of 10 K min^{-1}.

The proximate analyses and the calorific value measurements were carried out according to the ASTM standards [7–10].

The mineral matter contents of the samples were determined according to the ISO-602 standards [11].

The chemical analyses of the ashes prepared from the lignite samples were carried out as in ASTM standards [12].

Results and discussion

The range of the calorific value of the lignite samples was found to be 11.6–28.9 MJ kg^{-1} (Table 1).

Table 1 The calorific values of the lignite samples [MJ kg^{-1}]

Sample code	Gross calorific values	Net calorific values
L01	11.6	10.47
L02	15.3	14.45
L03	12.9	11.40
L04	23.1	21.68
L05	22.1	20.75
L06	18.6	16.95
L07	18.8	16.87
L08	19.2	17.23
L09	28.2	27.08
L10	15.5	14.23
L11	27.4	26.01
L12	13.2	11.59
L13	13.6	12.13
L14	21.6	20.01
L15	15.5	13.38
L16	20.5	19.24
L17	17.6	16.10
L18	16.5	14.64
L19	21.1	19.68
L20	13.4	12.13
L21	14.8	12.80
L22	20.1	19.02
L23	28.9	27.68
L24	13.8	12.26
L25	12.4	10.27

The results of proximate analyses of the lignite samples are shown in Table 2. 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 10.3 and 53.4%.

The chemical analysis data on the ashes produced from the lignite samples and the mineral matter content can be seen in Table 3. The mineral matter content of the 25 lignite samples used in this study varied in the interval 7.68–47.97%.

The DTA method involves a technique in which the temperature difference between a substance and a thermally inert material is recorded when the two substances undergo identical temperature changes within an environment which is heated and cooled at a controlled rate [13].

Table 2 Proximate analyses of the lignite samples

Sample code	Moisture/%	Volatile matter/%	Fixed carbon/%	Ash/%
L01	10.5	32.2	25.1	32.2
L02	4.4	22.2	32.8	40.6
L03	15.7	36.1	16.4	31.8
L04	9.6	39.2	40.2	11.0
L05	10.5	36.8	40.6	12.1
L06	19.9	30.3	35.8	14.0
L07	27.6	39.8	22.8	9.8
L08	24.2	38.4	31.2	6.2
L09	2.0	32.0	51.6	14.4
L10	14.0	36.1	23.3	26.6
L11	7.2	46.4	39.1	7.3
L12	25.3	28.7	16.7	29.3
L13	16.2	40.9	10.3	32.6
L14	15.9	41.0	36.4	6.7
L15	35.4	32.2	23.4	9.0
L16	12.5	32.3	32.3	22.9
L17	17.9	37.3	26.1	18.7
L18	27.0	34.4	18.0	20.6
L19	14.1	33.4	39.8	12.7
L20	13.9	24.6	22.3	39.2
L21	40.4	32.1	12.3	15.2
L22	6.4	28.6	37.4	27.6
L23	5.9	31.8	53.4	8.9
L24	27.5	34.4	24.0	14.1
L25	48.0	28.2	11.8	12.0

The DTA curves obtained for coal in the presence of air are 'combustion curves'. They provide information on combustion characteristics such as ignition temperature, heat release rate, heat of combustion, etc. [14].

The combustion curves of the lignite samples obtained before and after mineral matter removal exhibited significant differences. The combustion curves of the original lignite samples initially displayed an endothermic peak relating to the release of moisture, and one or two combined exothermic maxima due to the combustion of the volatile matter released on heating, followed by burning of the char. An endothermic peak relating to moisture release was also observed in the DTA curves of the demineralized lignites; however, this decrease was rather small compared with that for the raw samples, due to the drying process applied after demineralization. The combustion curves of all demineralized lignite samples contained two exothermic peaks due to combustion of the volatile matter and the char.

The area under the exothermic peak of the combustion curve is proportional to the heat released. It can therefore be used to determine the rate of release of the combustion heat of coal [13–15]. For this purpose, the temperature (T_{50}) up to which 50% of the calorific value of the lignite sample released was determined. Since initially volatile matter release and combustion occur, with an increase in the volatile matter content of the lignite sample, the percentage of the calorific value released at low temperatures increases. The relationship between

Table 3 The mineral matter content of the lignite samples (dry basis) and the composition of the ashes

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

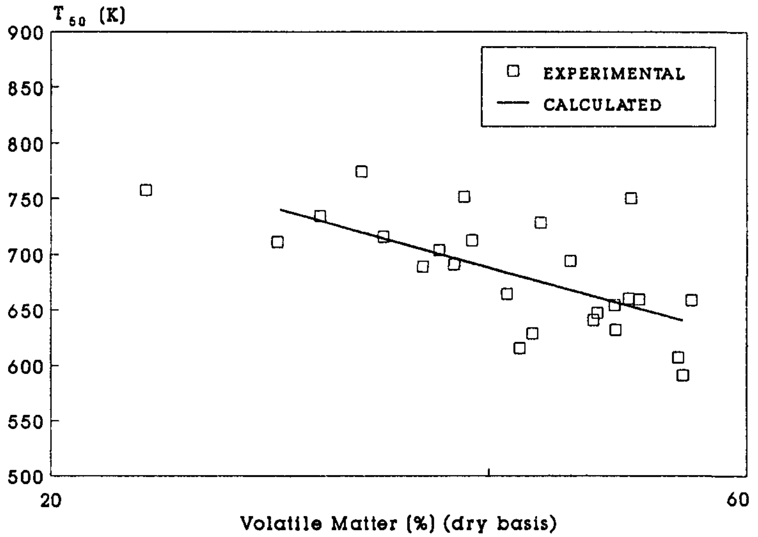

Fig. 1 The relation between T_{50} and the volatile matter content of the lignite samples

T_{50} and the volatile matter content of the lignite sample is shown in Fig. 1. The regression coefficient of the relation was calculated to be 0.6756.

An increase in the CaO, CaO+Na_2O, CaO+Na_2O+K_2O or CaO+MgO+Na_2O+K_2O contents of the lignite samples appears to cause a decrease in T_{50}. The relationships of the sum of the mineral components and the volatile matter content of the lignite samples with T_{50} are shown in Figs 2–5; the regression co-

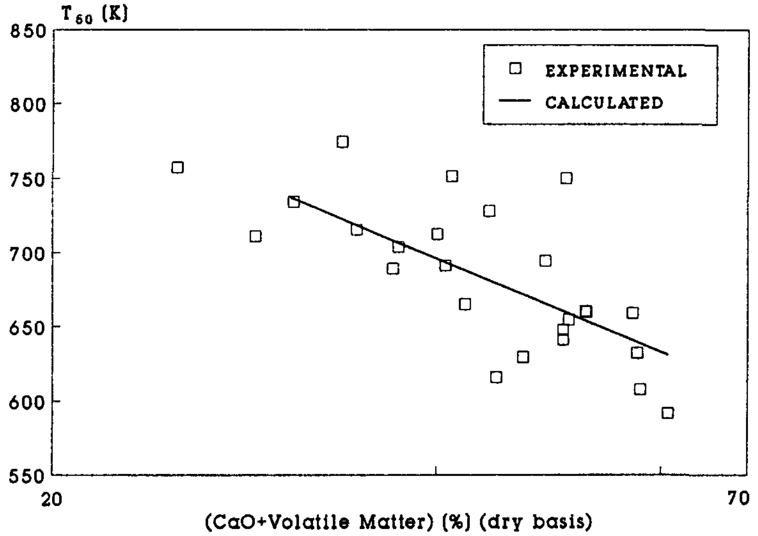

Fig. 2 The relation between T_{50} and the (CaO+volatile matter) content of the lignite samples

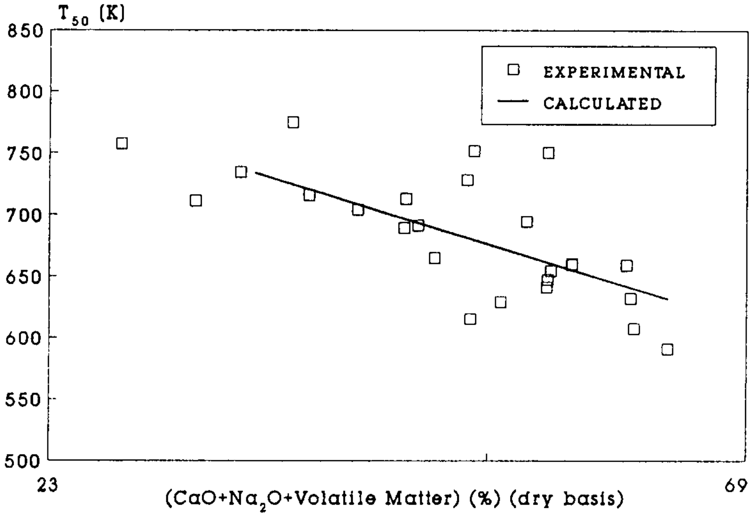

Fig. 3 The relation between T_{50} and the (CaO + Na_2O + volatile matter) content of the lignite samples

efficients for these relations were calculated to be 0.7192, 0.7036, 0.7087 and 0.7202, respectively.

It is obvious that the rate of release of combustion heat from the lignite samples was strongly affected by the mineral components.

The rate of release of combustion heat from coal is very important for coal-fired combustion systems. The rate of heat release from the lignite samples was

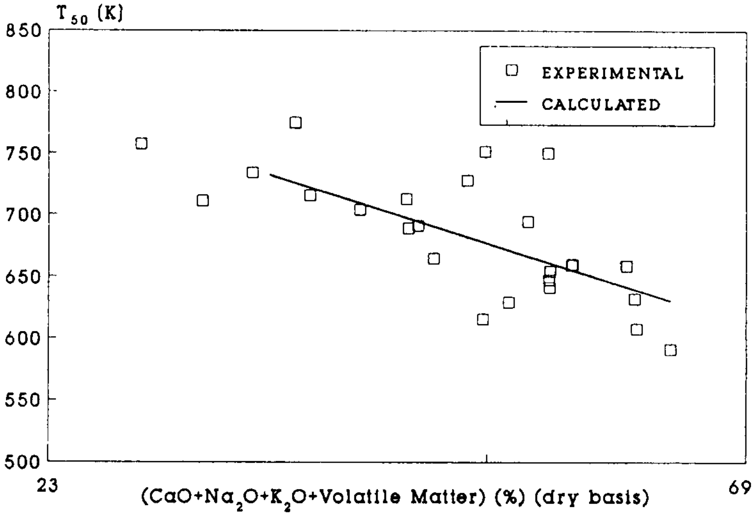

Fig. 4 The relation between T_{50} and the (CaO + Na_2O + K_2O + volatile matter) content of the lignite samples

determined by measuring the area under the exothermic peak of the combustion curve. Its dependence on temperature was examined. The demineralization process dramatically influenced the rate of heat release from the lignite samples. The rates of heat release from the demineralized lignite samples and their dependence on temperature are considerably different from those for the original lignite samples. The heat release rate curves for four lignite samples (L14,

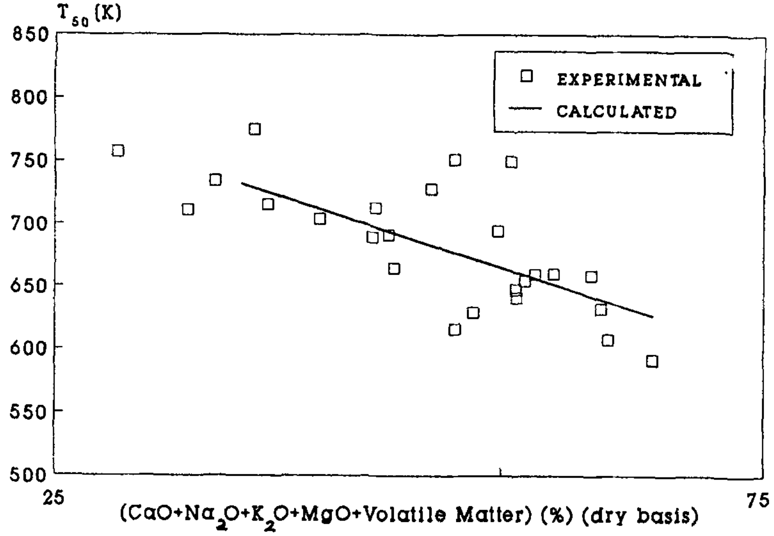

Fig. 5 The relation between T_{50} and the ($CaO+Na_2O+K_2O+MgO$+volatile matter) content of the lignite samples

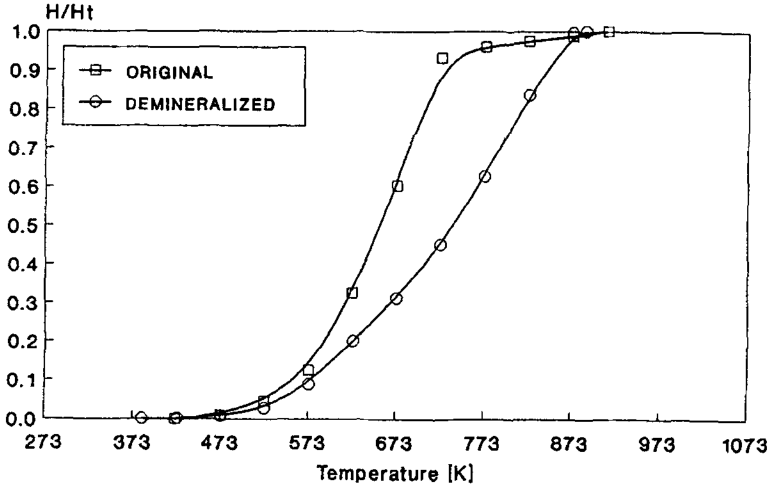

Fig. 6 Effect of temperature on the heat release rate of the original and demineralized lignite samples L14 (Ht=net calorific value; H=heat released up to temperature T)

L15, L18 and L25) before and after mineral matter removal can be seen in Figs 6–9. The original lignite sample L14 loses 70% of its calorific value up to 690 K, but after demineralization this occurs up to about 790 K (Fig. 6). Lignite sample L15 loses 70 and 100% of its calorific value up to 690 and 790 K, respectively, before demineralization, but the corresponding temperatures after demineralization are about 790 and 915 K, respectively (Fig. 7). Lignite sample L18 loses 70% of its calorific value up to 680 K, and 100% of its calorific value up to 800 K; after mineral matter removal, the corresponding tempera-

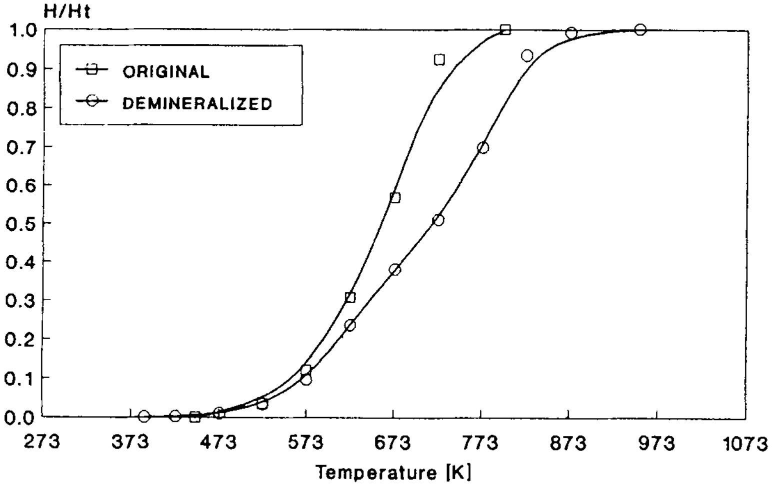

Fig. 7 Effect of temperature on the heat release rate of the original and demineralized lignite sample L15

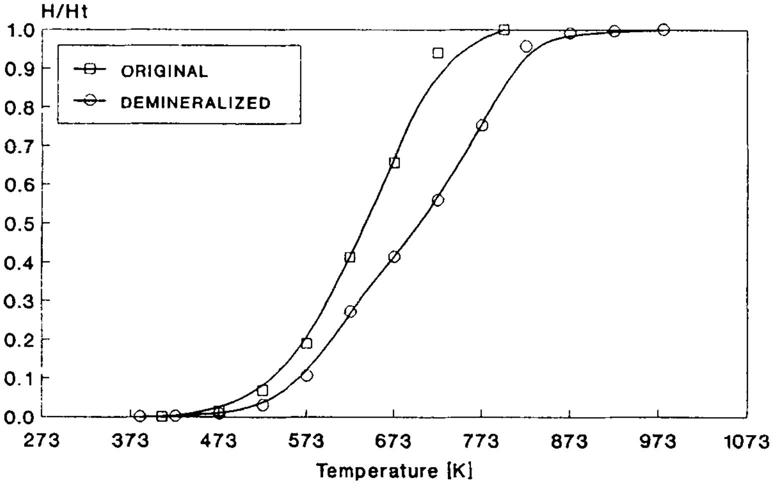

Fig. 8 Effect of temperature on the heat release rate of the original and demineralized lignite sample L18

tures are 800 and 930 K, respectively (Fig. 8). The original lignite sample L25 loses 70% of its calorific value up to 640 K, but this occurs up to about 740 K after demineralization (Fig. 9).

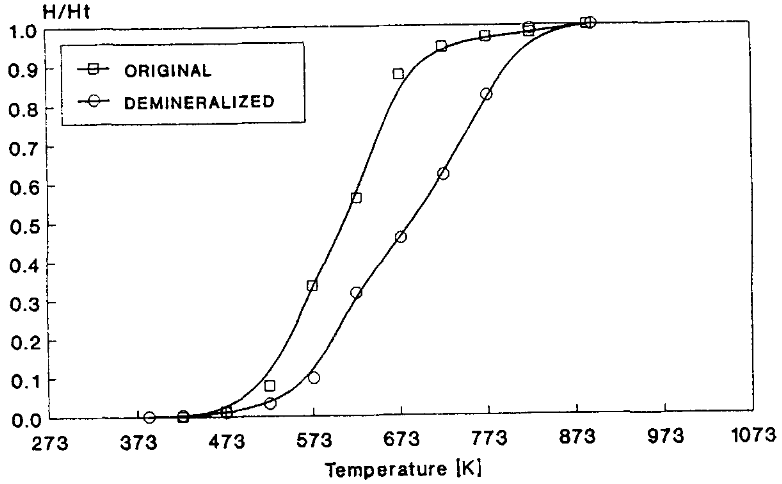

Fig. 9 Effect of temperature on the heat release rate of the original and demineralized lignite sample L25

This investigation of the rate of heat release from the original and demineralized lignite samples permits the conclusion that no significant change occurred up to about 600 K, but at higher temperatures it was observed that the difference between the heat release rates increases as the temperature rises. This situation clearly demonstrates that the catalytic effect of the mineral matter content of the lignite samples is extremely important at high temperatures.

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