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DSC STUDY OF THE COMBUSTION PROPERTIES OF TURKISH COALS

K. E. Ozbas[1], *M. V. Kök*[2*] *and C. Hicyilmaz*[3]

[1]Department of Mining Engineering, Inönü University, Malatya, Turkey
[2]Department of Petroleum and Natural Gas Engineering, Middle East Technical University, 06531 Ankara, Turkey
[3]Department of Mining Engineering, Middle East Technical University, 06531, Ankara, Turkey

Abstract

In this research, differential scanning calorimetry (DSC) was used to determine the combustion behavior and kinetic analysis of raw and cleaned coal samples of different size fractions. DSC curves of the three coal samples (*Soma*, *Tuncbilek* and *Afsin Elbistan*) showed two reaction regions. The first reaction region was due to moisture loss (endothermic) and observed in the temperature range of ambient to 150°C. The second region was the exothermic region due to the combustion and observed in the temperature range of 150 to 600°C. Kinetic parameters of the samples were determined using Roger and Morris kinetic model and the results are discussed.

Keywords: coal, DSC, kinetic models, lignite, rank

Introduction

Coal is a physically heterogeneous and chemically complex mixture of organic and inorganic species, which undergoes appreciable physico-chemical changes when heated. The main studies of coal using thermal analysis techniques include characterization, high-pressure application to coal hydrogenation, catalytic effects due to inorganic substances, combustion, pyrolysis, and kinetic analysis.

Rosenvold *et al.* [1] analyzed twenty-one bituminous coal samples from Ohio by differential scanning calorimetry and non-isothermal thermogravimetry. Three regions of endothermic activity were distinguished in the DSC scans in an inert atmosphere. The first peak (25–150°C) corresponds to devolatilization of the organic matter and a partially resolved endotherm at temperatures above 550°C probably corresponds to cracking and coking processes subsequent to the pyrolysis step. Janikowski and Stenberg [2] analyzed the ten different coals in argon and hydrogen atmosphere; four lignite, four sub-bituminous and two bituminous coals. They have distinguished two temperature regions of increased chemical reactivity. Jayaweera *et al.* [3] studied the effect of particle size on the percentage mass loss of a low quality bituminous coal during combustion in air by ther-

* Author for correspondence: E-mail: kok@metu.edu.tr

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mal analysis. It was found that the method of sieving used to prepare the samples of different particle size have a significant effect on the results. Rajeshwar [4] applied differential scanning calorimetry and thermogravimetry to the study of coals, oil shales, and oil sands. Differential scanning calorimetry has been used to characterize twelve U.S. coals of varying rank from anthracite to lignite. Also, bituminous and lignite coals from four locations have been examined by TG over the temperature range 20–1000°C. Proximate analyses of coals were conveniently and rapidly carried out by TG technique, and either a combination of non-isothermal and isothermal TG or two consecutive non-isothermal experiments might be used for proximate analyses. Shah *et al.* [5] studied combustion of different sized coal samples. The results revealed that the effect of reduction in particle size of coal was advantageous insofar as a reduction in particle size caused a decrease in the ignition temperature. Durusoy *et al.* [6] reported pyrolytic behavior of raw and microbiologically treated lignite. Their experiments were carried out in a thermobalance apparatus at atmospheric pressure from 25 to 900°C at a heating rate of 20°C min^{-1}. The results indicated good behavior of the microbiologically treated lignite compared with raw lignite. They observed an increase in the activation energy after microbial removal of sulfur from coal.

Experimental

In this research, DSC experiments were performed with a DuPont 9900 thermal analysis system. The coal samples studied in this research were from, *Soma*, *Tuncbilek* and *Afsin Elbistan* regions. Before the experiments, representative samples were prepared from the coals obtained. Four different size fractions of these samples were prepared by applying closed circuit crushing and screening. These size fractions were –30+18 mm, –18+10 mm, –10+0.5 mm, and –0.5 mm. The size fractions were chosen depending on the feed sizes of household heating and the thermo-power plants of *Soma*, *Tuncbilek* and *Afsin Elbistan*. Since the fractions had different characteristics, the optimum separation density for each fraction was determined by using the criteria defined as degree of washability. The density, that gives the maximum degree of washability, was chosen as optimum separating density for that fraction. The degree of washability (DW) can be calculated as [7];

$$DW = \text{yield of clean coal } \{[\text{ash of raw coal} - \text{ash of clean coal}]/\text{ash of raw coal}\} \quad (1)$$

After the determination of optimum separating densities, final products were prepared by blending the clean coal products of each size fraction obtained at optimum separating densities with respect to their weight percentages.

The cleaned product and raw sample were ground and prepared for DSC experiments. The experimental procedure of the DSC includes placing 10 mg of sample, setting the heating and gas flow rates and commencing the experiments. All the experiments were carried out at a linear heating rate of 10°C min^{-1} within a temperature range of 20–600°C at an airflow rate of 50 mL min^{-1}. Prior to experiments, DSC instrument was calibrated for temperature readings, using indium as reference material.

The results of proximate and elemental analysis of the samples are given in Tables 1 and 2, respectively.

Table 1a Proximate analysis of the raw coal samples

Coal	Basis of analysis	Moisture/ %	Ash/%	Volatile matter/%	Fixed carbon/%	Calorific value/cal g^{-1}
Soma	air dried	4.47	39.34	36.26	19.93	9780
	dry	–	41.18	37.96	20.86	10240
	dry, ash free	–	–	64.53	35.47	17430
Tuncbilek	air dried	2.33	53.30	25.14	19.23	10070
	dry	–	54.57	25.74	19.69	10325
	dry, ash free	–	–	56.66	43.34	22740
Afsin-Elbistan	air dried	9.17	26.58	42.10	22.15	10450
	dry	–	29.26	46.35	24.39	11495
	dry, ash free	–	–	65.53	34.47	16262

Table 1b Proximate analysis of the cleaned coal samples

Coal	Basis of analysis	Moisture/ %	Ash/%	Volatile matter/%	Fixed carbon/%	Calorific value/cal g^{-1}
Soma	air dried	7.0	14.74	39.52	38.74	18220
	dry	–	15.85	42.50	41.65	19585
	dry, ash free	–	–	50.50	49.50	23280
Tuncbilek	air dried	3.58	21.29	32.89	42.24	20520
	dry	–	22.08	34.11	43.81	21275
	dry, ash free	–	–	43.78	56.22	27295
Afsin-Elbistan	air dried	11.39	19.70	42.70	26.21	13040
	dry	–	22.23	48.19	29.58	14710
	dry, ash free	–	–	61.96	38.04	18935

Table 2a Elemental analysis of the raw coal samples

Coal	Basis of analysis	Carbon/ %	Hydrogen/ %	Nitrogen/ %	Sulfur (combustible)/%	Oxygen/ %
Soma	air dried	32.80	2.20	0.79	0.57	19.83
	dry	34.33	2.30	0.83	0.60	20.76
	dry, ash free	58.37	3.92	1.41	1.01	35.29
Tuncbilek	air dried	29.86	2.41	1.27	0.70	10.13
	dry	30.57	2.47	1.30	0.72	10.37
	dry, ash free	67.30	5.43	2.86	1.58	22.83
Afsin-Elbistan	air dried	34.38	2.26	1.11	1.25	25.25
	dry	37.85	2.49	1.22	1.38	27.80
	dry, ash free	53.51	3.52	1.73	1.95	39.29

Table 2b Elemental analysis of the cleaned coal samples

Coal	Basis of analysis	Carbon/ %	Hydrogen/ %	Nitrogen/ %	Sulfur (combustible)/%	Oxygen/ %
Soma	air dried	53.17	3.45	1.20	1.06	19.38
	dry	57.17	3.71	1.29	1.14	20.84
	dry, ash free	67.94	4.41	1.53	1.35	24.77
Tuncbilek	air dried	55.72	3.96	2.26	1.39	11.80
	dry	57.79	4.11	2.34	1.44	12.24
	dry, ash free	74.16	5.27	3.01	1.85	15.71
Afsin-Elbistan	air dried	39.95	2.92	1.29	1.95	22.80
	dry	45.09	3.30	1.46	2.20	25.72
	dry, ash free	57.97	4.24	1.87	2.83	33.09

Results and discussion

In *Soma* coal sample, mainly two reaction regions were observed in raw and cleaned size fractions at different temperature intervals (Figs 1 and 2). The first region was the endothermic region where the heat flow rate was smaller and continued up to 150°C. In this region, moisture of the coal evaporates, and the physical adsorption and desorption to the particle surface continue. This region was observed in all size fractions. The second region was the most important region during the combustion of the coal where the heat flow was exothermic. This region observed in all size fractions, started around 150–200°C and continued up to the combustion of the sample completed. Decomposition temperatures of minerals mainly occurring in coals such as calcite, kaolinite is approximately 650–800°C, and the reaction are endothermic. Therefore, it can be said that the observed shoulders in DSC curves are not due to the mineral constituents of the samples. The reason of the shoulder of –0.5 mm fraction can be decomposed maceral or organic impurities. On the other hand, DSC curves of cleaned size fractions showed higher heat flow rates than raw samples, which can be explained by decreased mineral matter content and increased carbon concentration of these samples (Table 3).

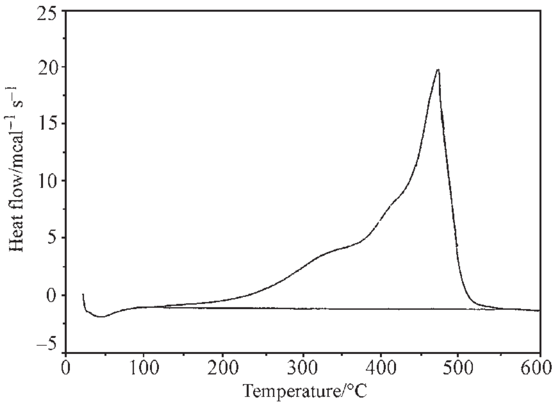

Fig. 1a DSC curve of *Soma* uncleaned sample (–30+18 mesh)

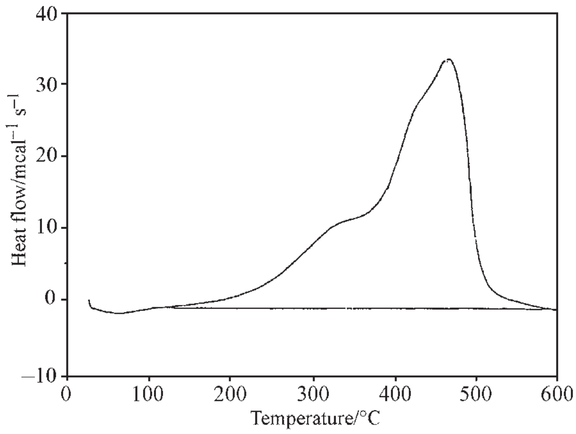

Fig. 1b DSC curve of *Soma* cleaned sample (–30+18 mesh)

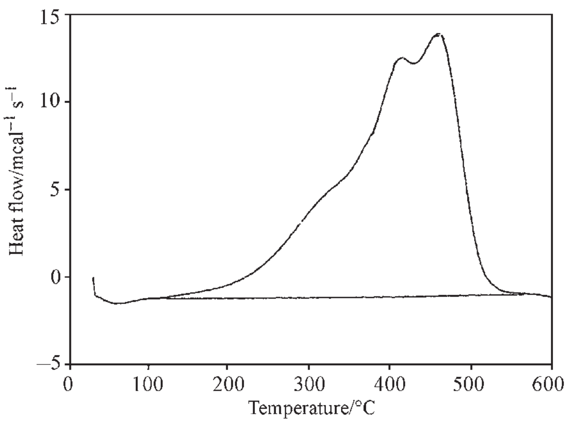

Fig. 2a DSC curve of *Soma* uncleaned sample (–0.5 mesh)

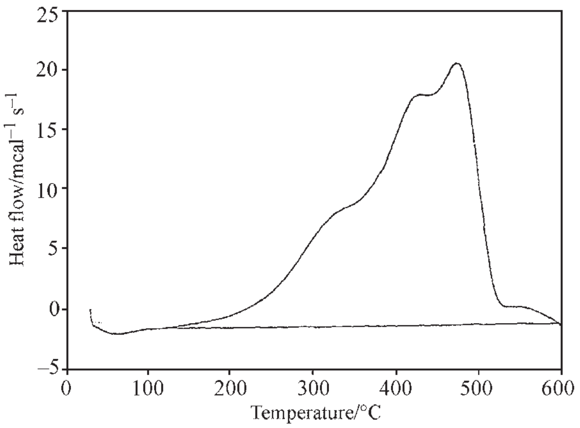

Fig. 2b DSC urve of *Soma* cleaned sample (–0.5 mesh)

Table 3 Heat flow rates of the samples (mcal s^{-1})

Coal sample	Mesh size/mm	Heat flow rate at peak maximum/mW s^{-1}
Soma	raw coal	18.1
	–30+18 uncleaned	20.5
	–30+18 cleaned	34.5
	–18+10 uncleaned	17.5
	–18+10 cleaned	27.0
	–10+0.5 uncleaned	22.0
	–10+0.5 cleaned	24.5
	–0.5 uncleaned	14.0
	–0.5 cleaned	21.0
	cleaned product	23.0
Tuncbilek	raw coal	1.2
	–30+18 uncleaned	1.40
	–30+18 cleaned	2.60
	–18+10 uncleaned	0.92
	–18+10 cleaned	2.90
	–10+0.5 uncleaned	2.10
	–10+0.5 cleaned	3.65
	–0.5 uncleaned	2.05
	–0.5 cleaned	2.25
	cleaned product	9.4
Afsin Elbistan	raw coal	5.4
	–30+18 uncleaned	5.6
	–30+18 cleaned	10.5
	–18+10 uncleaned	16.0
	–18+10 cleaned	21.5
	–10+0.5 uncleaned	9.4
	–10+0.5 cleaned	21.0
	–0.5 uncleaned	5.5
	–0.5 cleaned	11.5
	cleaned product	9.0

DSC curves showed that *Tuncbilek* coal has two-reaction region in raw and cleaned size fractions as in *Soma* coal. These regions were in the range of 25–200°C (endothermic) and 200–600°C (exothermic). Cleaned size fractions of *Tuncbilek* sample had higher heat flow rates than raw size fractions. Same reaction regions were also observed in *Afsin Elbistan* coal and generally, higher heat flow rates were observed for cleaned size fractions. In all the coals studied, at around 500°C and below more than half of the carbon in the samples burn to CO instead of CO_2 and caused huge effect on the magnitude of the DSC curves [8].

Kinetic analysis

A kinetic model developed by Roger and Morris [9] gives a means of estimation of activation energies from DSC curves. The recorded DSC data are in the form of distances between the curve and the baseline at the specified absolute temperature. This distance is proportional to the rate constant. The activation energy can be calculated from the following expression:

$$-E=R\ [(\ln D_1-\ln D_2)/(1/T_1-1/T_2)] \qquad (2)$$

where D_1 and D_2 are two distances from the baseline at the associated temperature T_1 and T_2. R is the gas constant (J mol^{-1} K^{-1}) and E is the activation energy (kJ mol^{-1}).

Kinetic data were also obtained from the main combustion region of the DSC curves, assuming a first order combustion reaction (*Soma* and *Tuncbilek* coals). The resulting form of the equation is [10]:

$$\log(\mathrm{d}h/\mathrm{d}t(1/h))=\log A-E/2.303RT \qquad (3)$$

where h is the fraction of the enthalpy yet to be released, R is the gas constant (J mol^{-1} K^{-1}) and E is the activation energy (kJ mol^{-1}) in terms of the usual Arrhenius equation.

Table 4a Activation energies of the samples by Roger and Morris method

Coal sample	Mesh size/mm	Activation energy/kJ mol^{-1}
Soma	raw coal	38.7
	–30+18 uncleaned	33.4
	–30+18 cleaned	29.1
	–18+10 uncleaned	38.7
	–18+10 cleaned	35.6
	–10+0.5 uncleaned	34.6
	–10+0.5 cleaned	27.9
	–0.5 uncleaned	30.5
	–0.5 cleaned	24.2
	cleaned product	23.6
Tuncbilek	raw coal	43.7
	–30+18 uncleaned	39.2
	–30+18 cleaned	34.3
	–18+10 uncleaned	34.8
	–18+10 cleaned	28.7
	–10+0.5 uncleaned	29.6
	–10+0.5 cleaned	25.0
	–0.5 uncleaned	43.2
	–0.5 cleaned	37.6
	cleaned product	36.3
Afsin Elbistan	raw coal	32.7
	–30+18 uncleaned	21.9
	–30+18 cleaned	20.3
	–18+10 uncleaned	32.0
	–18+10 cleaned	15.5
	–10+0.5 uncleaned	22.4
	–10+0.5 cleaned	17.6
	–0.5 uncleaned	26.0
	–0.5 cleaned	21.3
	cleaned product	25.8

Table 4b Activation energies of the samples by Arrhenius method

Coal sample	Mesh size/mm	Activation energy/kJ mol^{-1}
	raw coal	28.6
	–30+18 uncleaned	29.3
	–30+18 cleaned	25.6
	–18+10 uncleaned	29.8
Soma	–18+10 cleaned	25.8
	–10+0.5 uncleaned	30.0
	–10+0.5 cleaned	27.2
	–0.5 uncleaned	31.5
	–0.5 cleaned	28.7
	cleaned product	25.6
	raw coal	38.6
	–30+18 uncleaned	38.8
	–30+18 cleaned	27.2
	–18+10 uncleaned	39.7
Tuncbilek	–18+10 cleaned	25.9
	–10+0.5 uncleaned	35.1
	–10+0.5 cleaned	27.2
	–0.5 uncleaned	44.7
	–0.5 cleaned	28.5
	cleaned product	24.3

The activation energy values obtained by Roger and Morris and Arrhenius models in the main combustion reaction region are given in Tables 4a and 4b, respectively. It was observed that the activation energies of cleaned samples were lower than that of uncleaned samples. Lower activation energies were the indication of easy combustibility of cleaned coal samples. It was concluded that the change of mineral matter composition after coal cleaning affected the activation energy of the coal samples studied.

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