Journal of Thermal Analysis and Calorimetry, Vol. 69 (2002) 541–549

COMPARATIVE KINETIC ANALYSIS OF RAW AND CLEANED COALS

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(Received November 28, 2001; in revised form February 15, 2002)

Abstract

In this research, thermogravimetry (TG/DTG) was used to determine the kinetic analysis of different coals and effect of cleaning process on kinetic parameters of raw and cleaned coal samples from Soma, Tuncbilek and Afsin Elbistan regions. Kinetic parameters of the samples were determined using Arrhenius and Coats and Redfern kinetic models and the results are discussed.

Keywords: activation energy, coal, kinetic models, thermogravimetry

Introduction

Coal is a physically heterogeneous and chemically complex mixture of organic and inorganic species, which undergoes appreciable physico-chemical changes when heat-treated. 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.

Rai and Tran [1] conducted a kinetic study on non-catalyzed and catalyzed coal. In their kinetic model the apparent activation energy is measured to be a rectilinear function of the extent of reaction to describe the pyrolysis of Hanna coal. For hydrogasification of char the apparent activation energy was found to vary as a second-degree polynomial with respect to conversion. The order of reaction was found to be about 0.3 for the pyrolysis step and 0.67 for the hydrogasification step. Gold [2] demonstrated the occurrence of exothermic reactions associated with the production of volatile matter in or near the plastic region of coals studied. He concluded that the temperature and the magnitude of the exothermic peak was strongly affected by the heating rate, sample mass and particle size. Shah *et al.* [3] 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

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1418–2874/2002/ $ 5.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

in the ignition temperature. Rosenvold *et al.* [4] analyzed twenty-one bituminous coal samples by differential scanning calorimetry and non-isothermal thermogravimetry. Three regions of endothermic activity were distinguished where the first peak corresponds to devolatilization of the organic matter and a partially resolved probably corresponds to cracking and coking processes subsequent to the pyrolysis step. Cumming [5] has developed a method for describing the reactivity or combustibility of solid fuels, such as lignite, bituminous coals and petroleum coke, in terms of a weighed mean apparent activation energy, derived from simultaneous TG/DTG heated at a constant rate in a flowing air atmosphere. He proposed that, mean activation energy, is the established method, which involves recording overall temperatures on the burning profile curve. Morgan *et al.* [6] determined coal-burning profiles by thermogravimetric analysis. They have claimed that kinetic parameters from Arrhenius plots of profiles cannot readily be related to any specific stage of combustion. It was suggested that burning profiles could provide a valuable, rapid laboratory method of ranking coals in terms of their burnout performance. They also pointed out that coal-burning profiles obtained from thermogravimetric analysis depends on coal properties and particle size. Jayaweera *et al.* [7] studied the effect of particle size on the percentage mass loss of a low quality bituminous coal during combustion in air by thermal 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. Kök *et al.* [8, 9] determined the effect of particle size on combustion characteristics of coal. For this purpose, non-isothermal thermogravimetry (TG/DTG) experiments were carried out on twelve different size fractions, and the thermogravimetric data were analyzed by Arrhenius type kinetic model. The results indicated that activation energies were increased as the particle size decreased. It was also pointed out that as the particle size decreased, peak temperatures and burn-out temperatures of the samples decreased slightly and decrease in particle size caused more residue left at the end of the combustion process. Kök and Pamir [10] also determined the effect of particle size on coal pyrolysis by thermogravimetry. They performed experiments at non-isothermal heating conditions with a linear heating rate of 10°C min^{-1} in the temperature range of ambient to 900°C, under nitrogen atmosphere. Results indicated an increase of activation energies up to 48 mesh particle size, and then a decrease of activation energies from 48 to 400 mesh particle size. Durusoy *et al.* [11] reported pyrolytic behaviour 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 behaviour of the microbiologically treated lignite compared with raw lignite. They observed an increase in the activation energy after microbial removal of sulphur from coal.

The purpose of this study is to determine the combustion characteristics and kinetics of three different raw and cleaned Turkish coals, especially the ones used in thermo-power plants of Turkey, by thermal analysis methods.

Experimental

Sample preparation

In this research, thermogravimetry (TG/DTG) was used to determine the kinetic parameters of raw and cleaned coal samples from Soma, Tuncbilek and Afsin Elbistan regions. In order to prepare clean coal feed for TG/DTG experiments, it was necessary to wash (washing fluid was $ZnCl_2$) the lignite of each fraction at a definite density. 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 [12]:

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

Table 1a Proximate analysis of the raw coal samples

Coal	Basis of analysis	Moisture/%	Ash/%	Volatile matter/%	Fixed carbon/%
Tunçbilek	air dried	2.33	53.30	25.14	19.23
	dry	–	54.57	25.74	19.69
	dry, ash free	–	–	56.66	43.34
Afsin–Elbistan	air dried	9.17	26.58	42.10	22.15
	dry	–	29.26	46.35	24.39
	dry, ash free	–	–	65.53	34.47
Soma	air dried	4.47	39.34	36.26	19.93
	dry	–	41.18	37.96	20.86
	dry, ash free	–	–	64.53	35.47

Table 1b Proximate analysis of the cleaned coal samples

Coal	Basis of analysis	Moisture/%	Ash/%	Volatile matter/%	Fixed carbon/%
Tunçbilek	air dried	3.58	21.29	32.89	42.24
	dry	–	22.08	34.11	43.81
	dry, ash free	–	–	43.78	56.22
Afsin–Elbistan	air dried	11.39	19.70	42.70	26.21
	dry	–	22.23	48.19	29.58
	dry, ash free	–	–	61.96	38.04
Soma	air dried	7.00	14.74	39.52	38.74
	dry	–	15.85	42.50	41.65
	dry, ash free	–	–	50.50	49.50

Table 2a Elemental analysis of the raw coal samples

Coal	Basis of analysis	Carbon/ %	Hydrogen/ %	Nitrogen/ %	Sulphur combustib./%	Oxygen/%
Tunçbilek	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
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

Table 2a Elemental analysis of the cleaned coal samples

Coal	Basis of analysis	Carbon/ %	Hydrogen/ %	Nitrogen/ %	Sulphur combustib./%	Oxygen/%
Tunçbilek	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
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

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 mass percentages. The cleaned product and raw sample were ground (<60 mesh) and prepared for TG/DTG experiments.

Experimental procedure

PL 1500 thermogravimetry was used for the experiments. The experimental procedure of the TG/DTG 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 20–900°C at an airflow rate of 50 ml min^{-1}. Prior to the experiments, thermogravimetry instrument was calibrated for temperature readings, using indium as reference material. The balance was calibrated for buoyancy effect allowing the quantitative estimation of mass changes. The results of proximate and elemental analysis of the raw and cleaned samples are given in Tables 1 and 2. In proximate analysis, an increase is observed in moisture and fixed carbon content of the coal samples after cleaning process is applied. On the other hand, in elemental analysis, carbon content of the coal samples were increased after the cleaning process was applied.

Results and discussions

Modelling of a reaction for a combustion process of coal is extremely complicated because several components are simultaneously oxidized. In this research, thermogravimetric data were analyzed according to an Arrhenius and Coats and Redfern kinetic models [13, 14]. The calculation of the 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 the reaction, n is the order of reaction and k is the specific rate constant. The temperature dependence of k is expressed by the Arrhenius equation:

$$k=A_r\exp(-E/RT) \tag{2}$$

In Arrhenius model [13], rate of mass change with respect to time is equal to:

$$dW/dt=kW^{n} \tag{3}$$

$$k=A_r\exp(-E/RT) \tag{4}$$

Assuming first-order kinetics,

$$\log[(dW/dt)1/W]=\log A_r-E/2.303RT \tag{5}$$

where dW/dt is the rate of mass change, E is the activation energy, T is the temperature and A_r is Arrhenius constant.

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 [14] 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. The final form of the equation, which is used for the analysis;

$$\ln[1-(1-\alpha)^{1-n}/(T^2(1-n))]=\ln[(AR/(\beta E)(1-2RT/E)]-[E/(RT)] \tag{6}$$

where β is the heating rate.

Thus a plot of $\ln[1-(1-\alpha)^{1-n}/(T^2(1-n))]$ *vs.* $1/T$ should result in a straight line of slope equals $-E/R$ for the correct value of reaction order, n.

Theoretically, the combustion of fuel starts whenever oxygen comes in contact with fuel. The combination of fuel, oxygen availability and temperature controls the nature of this reaction. In TG/DTG analysis three reaction regions were observed at

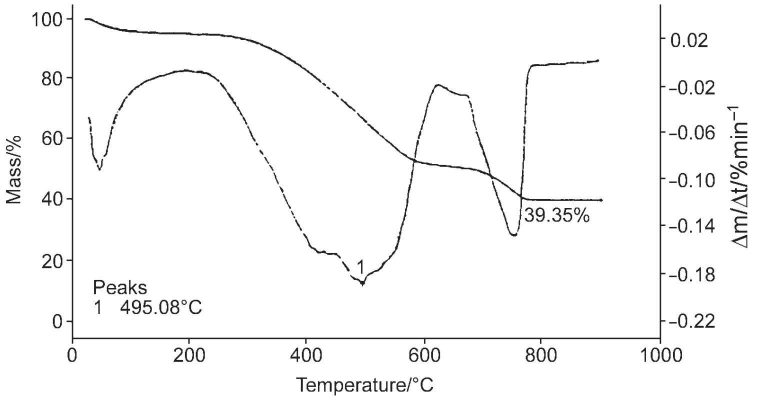

Fig. 1 TG/DTG curve of Soma feed

different temperature intervals of the coal samples studied. The first region was due to the evaporation of moisture in the sample. The second region was due to the release of volatile matter and burning of carbon and called as primary reaction region. The third region was due to the decomposition of mineral matter in coal. Main mass loss occurred in the second region, which proves the combustion of carbonaceous part of the sample (Figs 1 and 2).

Table 3 Activation energies (kJ mol^{-1}) of the coal samples (Arrhenius)

Sample	Basis of analysis	Reaction order	Activation energy/ kJ mol^{-1}
Tunçbilek	raw	1	35.6
	cleaned feed	1	21.2
Afsin–Elbistan	raw	1	125.2
	cleaned feed	1	122.5
Soma	raw	1	25.4
	cleaned feed	1	22.7

The results of kinetic analyses obtained by Arrhenius kinetic model of TG/DTG data for all coals studied in primary reaction region are given in Table 3. Linear least square correlation coefficients for the identified rectilinear portions varied from 0.95 to 0.99. The results show that, primary combustion region activation energies of cleaned feed were lower than that of feed. Lower activation energies were the indication of easy combustibility of cleaned coals. This is the effect of coal cleaning process, which improved the combustion characteristics of the sample. The change of mineral matter composition after coal cleaning affected the activation energy of the coal samples studied. Activation energies of Afsin-Elbistan coal are the highest values among all the samples. This may be due to the lowest coalification degree of Afsin–Elbistan coal.

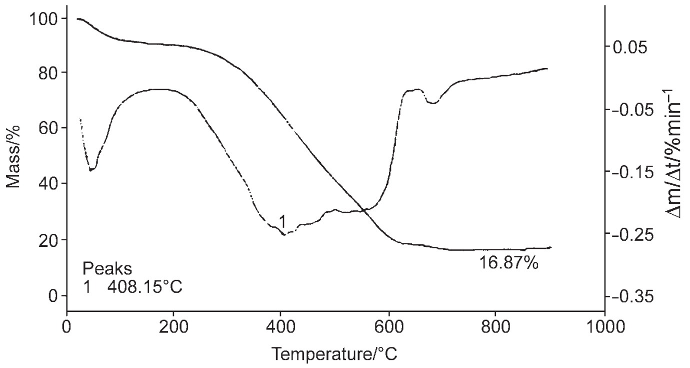

Fig. 2 TG/DTG curve of Soma clean feed

Table 4 Activation energies (kJ mol^{-1}) of the coal samples (Coats and Redfern)

Sample	Basis of analysis	Reaction order	Activation energy/kJ mol^{-1}
Tunçbilek	raw	0.5	36.1
		0.67	37.7
		1.0	40.8
		1.5	45.7
	cleaned feed	0.5	25.9
		0.67	28.5
		1.0	34.5
		1.5	42.8
Afsin–Elbistan	raw	0.5	2.8
		0.67	5.6
		1.0	12.2
		1.5	24.5
	cleaned feed	0.5	4.1
		0.67	8.8
		1.0	20.1
		1.5	44.9
Soma	raw	0.5	21.2
		0.67	22.4
		1.0	24.8
		1.5	28.6
	cleaned feed	0.5	17.1
		0.67	19.1
		1.0	23.7
		1.5	31.8

Activation energies of all coals for the primary combustion regions calculated by Coats and Redfern kinetic model for different reaction orders are given in Table 4. Highest linear least square correlation coefficients for identified rectilinear portions were obtained at 0.5 and 0.67 reaction orders for Soma and raw and cleaned feeds, respectively. The highest linear least square correlation coefficients for identified recti-

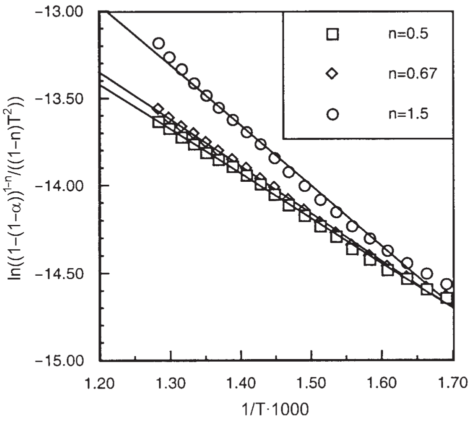

Fig. 3 Coats and Redfern plots of Soma feed for different reaction orders

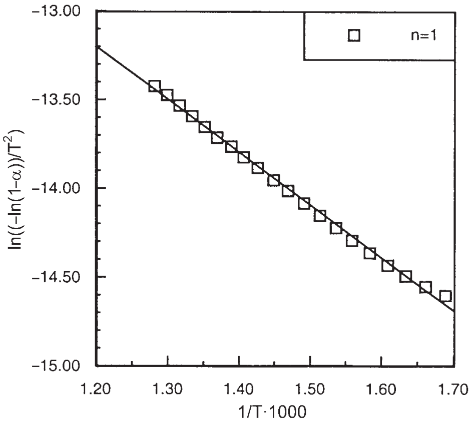

Fig. 4 Coats and Redfern plot of Soma feed for reaction order of 1

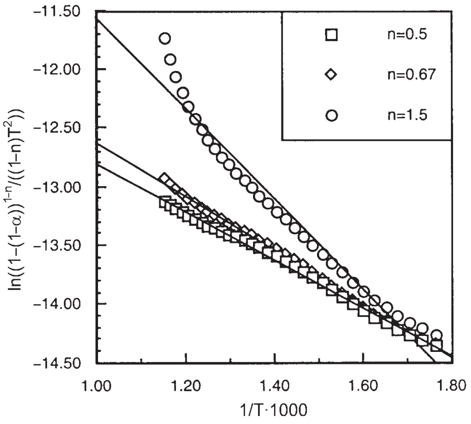

Fig. 5 Coats and Redfern plots of Soma clean feed for different reaction orders

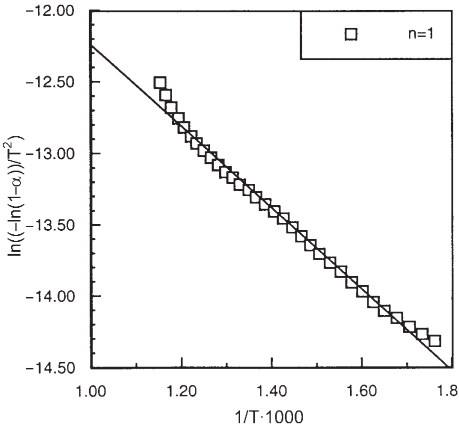

Fig. 6 Coats and Redfern plot of Soma clean feed for reaction order of 1

linear portions of Tunçbilek raw feed was found in the range of 0.5 and 0.67 reaction orders. On the other hand, the highest linear least square correlation coefficients for identified rectilinear portions of Soma and Tunçbilek coals were observed for reaction order of 1. The highest linear least square correlation coefficients for identified rectilinear portions were obtained at 1 and 1.5 reaction orders for Afsin–Elbistan raw and cleaned feeds, respectively. Activation energies calculated by two different kinetic models were close to each other for Soma and Tuncbilek coal samples. In contrast to this, for Afsin–Elbistan coal sample, activation energies calculated by Coats and Redfern kinetic model were different from the results of Arheneus type kinetic model, which may be the effect of incomplete coalification of the coal (Figs 3–6).

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