Journal of Thermal Analysis and Calorimetry, Vol. 64 (2001) 1265–1270

CALORIFIC VALUE DETERMINATION OF COALS BY DTA AND ASTM METHODS
Comparative study

M. V. Kök and C. Keskin

Department of Petroleum and Natural Gas Engineering, Middle East Technical University,
06531 Ankara, Turkey

Abstract

This research comprises the applicability of complex thermal analysis technique (TG/DTG, DTA) in the determination of calorific values of coals of different origin. The calorific values, those obtained by thermal analysis are compared with an adiabatic bomb calorimeter by the standard ASTM method, and the results are discussed.

Keywords: ASTM method, calorific value, coal, proximate analysis, thermal analysis

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 the characterisation of high-pressure applications to coal hydrogenation, catalytic effects due to inorganic substances, combustion, pyrolysis and kinetic analysis. It is well recognised that differential thermal analysis (DTA) and differential scanning calorimetry (DSC) are rapid tools which have been used in a wide variety of areas related to proximate analysis, coal reactivity, heat effect associated with coal pyrolysis, combustion and heat of hydrogenation. Elder [1] used thermogravimetry for the automatic proximate analysis of solid fossil fuels (coals of varying rank, biomass samples and oil shales). The simplicity of the technique suggests that it may complement the classical ASTM method and could be used. Karatepe and Kucukbayrak [2] determined the moisture, ash, volatile matter and fixed carbon contents of lignite samples from different coal reserves by using thermogravimetry and ASTM standards. The mean difference in moisture, ash, volatile matter and fixed carbon contents between the thermogravimetry and ASTM methods are: 0.38, 0.68, 1.53 and 1.47% respectively. Richardson [3] measured the specific heats of a range of coals, cokes and ashes using differential scanning calorimetry. He developed a general equation expressing the heat capacity of coal in terms of proximate composition and temperature. Munoz-Guillena *et al.* [4] used thermal analysis techniques to determine the calorific

1418–2874/2001/ $ 5.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

values of coal samples of different origin and rank, and their corresponding chars and compared the results to those obtained by ASTM methods. Earnest [5] compared the calorific values of several coals obtained by DSC with the ASTM values, finding an agreement within the error limit of 3%. Hassel [6] using a high pressure DSC apparatus, determined the heat of combustion of selected coal samples and compares them with those obtained with an adiabatic bomb calorimeter, the agreement found was good. Unal *et al.* [7] investigated the effects of oxidation on the calorific values of lignites. The lignite samples have been vacuum dried and oxidised in pure oxygen at 35, 45 and 55°C at 100 kPa for 10 days. A relation has been observed between the extent of oxidation and in decrease in calorific values. Ream [8] studied the calorific values of various bituminous coal samples and discussed the effect of different parameters the calorific values of the bituminous coal samples. Shirazi *et al.* [9] studied the impact of mineral matter in coal and on its combustion. They proposed a new approach to the determination of the calorific values of the coals. Mazumdar [10] studied the theoretical oxygen requirements for coal combustion and explained the relationship with its calorific value. The success of the newly found correlation is also described.

Experimental

Measurement were carried out by means of complex thermal analysis with DuPont 2960 thermal analysis system. The coal samples studied in this research was prepared according to ASTM Standards (ASTM D 2013-72) and had a particle size <60 mesh. It is believed that for such a small particle size the effect of temperature distribution within the sample particle is eliminated. The DTA system was calibrated for temperature reading with calcium oxalate monohydrate prior to experiments. It was also essential to calibrate and balance for buoyancy effects to allow quantitative estimation of mass changes. The material chosen for investigating such effect was silver, which has a melting point of 960.8°C. TG/DTG and DTA curves were obtained using the following experimental conditions: atmosphere: nitrogen, air; flow rate: 50 ml min^{-1}; sample size: 10 mg; heating rate: 10°C min^{-1}; temperature range: 20–800°C.

Results and discussion

In this research, ten coal samples of different origin have been studied. Proximate and elemental analysis of the samples are given in Tables 1 and 2, respectively. Experiments (Figs 1a and 1b) were also performed to determine the proximate analysis of the samples (Table 3). Moisture and volatile matter contents could not be distinguished from each other due to the heating rate. Therefore proximate analysis results were compared considering the amount of moisture and volatile matter. A good agreement is found which confirms that thermal analysis is a convenient tool to determine the proximate analysis of the samples giving comparable results to those of ASTM standard methods.

Table 1 Proximate analysis of the samples

Samples	Moisture/%	Volatile matter/%	Ash/%	Fixed carb./%
Sample-1	1.40	5.17	5.13	88.30
Sample-2	1.80	11.56	12.44	74.20
Sample-3	3.20	11.24	31.44	54.12
Sample-4	0.80	3.65	58.14	37.41
Sample-5	2.10	9.98	48.78	39.14
Sample-6	0.74	6.05	51.07	42.14
Sample-7	1.60	8.50	18.14	71.76
Sample-8	1.87	4.58	47.14	46.41
Sample-9	2.10	11.20	19.58	67.12
Sample-10	0.72	1.50	17.66	80.12

Table 2 Elemental analysis of the samples

Samples	C/%	H/%	S_{total}/%	O+N/%
Sample-1	45.19	2.95	1.25	10.43
Sample-2	32.08	2.68	3.09	12.14
Sample-3	16.64	1.58	1.30	12.08
Sample-4	61.42	3.79	4.10	13.63
Sample-5	19.70	1.55	3.57	9.39
Sample-6	28.38	2.29	4.23	9.31
Sample-7	19.96	1.50	1.66	7.77
Sample-8	51.60	3.89	0.92	16.99
Sample-9	20.60	1.82	1.46	9.88
Sample-10	38.51	3.27	6.05	6.05

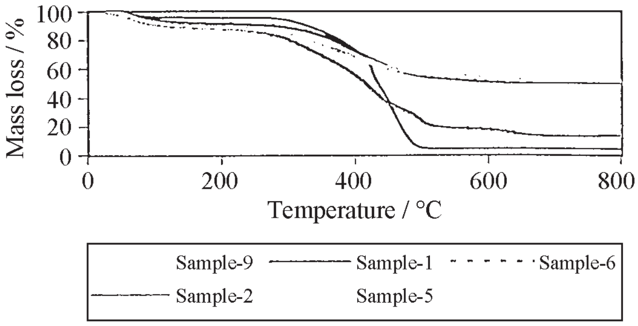

Fig. 1a TG curves of the samples (proximate analysis)

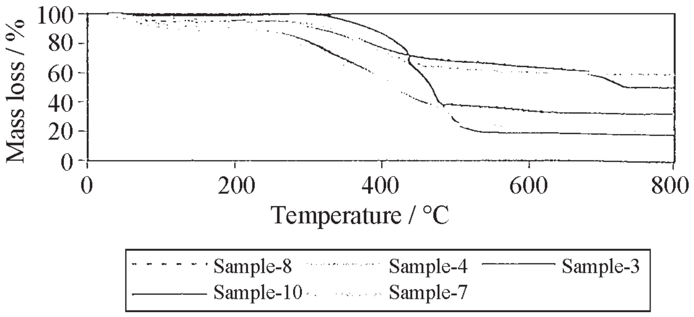

Fig. 1b TG curves of the samples (proximate analysis)

Table 3 Proximate analysis of the samples by thermogravimetry

Samples	Moisture+volatile matter/%	Ash/%	Fixed carbon/%
Sample-1	4.161	4.09	91.749
Sample-2	10.960	13.09	75.950
Sample-3	11.000	32.42	56.580
Sample-4	5.268	59.97	34.762
Sample-5	11.170	51.61	37.220
Sample-6	8.377	50.20	41.423
Sample-7	10.560	19.82	69.620
Sample-8	5.260	50.61	44.130
Sample-9	13.670	20.47	65.860
Sample-10	1.553	18.75	79.697

Table 4 Calorific values of the samples/kJ kg^{-1}

Samples	Calorific value (ASTM)	Calorific value (TG)
Sample-1	14644	17509
Sample-2	9724	12710
Sample-3	6209	5887
Sample-4	20606	24097
Sample-5	6251	7593
Sample-6	10799	11428
Sample-7	6531	7556
Sample-8	17167	20248
Sample-9	7393	8039
Sample-10	20920	16828

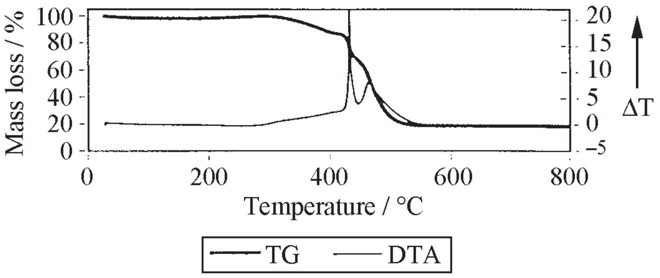

Fig. 2 TG/DTG curves of the sample-1

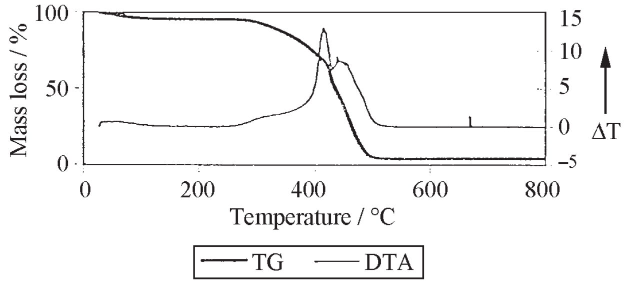

Fig. 3 TG/DTG curves of the sample-10

TG/DTG and DTA curves obtained in two different samples, heated in air, are given in Figs 2 and 3 respectively. Initially the burning profiles of the coal samples exhibit a small endothermic peak, due to the water loss, and one or two exothermic peaks, due to the combustion of volatile matter released on heating, followed by burning of the residual solid. The second burn appears as a shoulder and becomes more pronounced in some samples. The double burn behaviour observed for the coals suggests the presence of at least two types of combustibles. The calorific values of the samples obtained from the ASTM methods are compared with values calculated from the semi-empirical equations (Table 4). Several empirical expressions giving the relationship between the heat of combustion of the coal and elemental analysis can be used. The following expression has been found to give fairly accurate results.

$$\mathrm{CV(kJ\ kg^{-1})}=340.39\%\ \mathrm{C}+1320.83\%\ \mathrm{H}+ \\ 68.30\%\ \mathrm{S_{total}}-15.28\%\ \mathrm{ash}-118.5\%\ \mathrm{(O+N)]} \qquad (1)$$

References

1 J. P. Elder, Fuel, 62 (1983) 580.
2 N. Karatepe and S. Kucukbayrak, Thermochim. Acta, 213 (1993) 147.
3 M. J. Richardson, Fuel, 72 (1993) 1047.
4 M. J. Munoz-Guillena, A. L. Solano and C. S. Martinez de Lecea, Fuel, 71 (1992) 579.

5 C. M. Earnest, 'Thermal Analysis of Clays, Minerals and Coal', Perkin Elmer Corp. Norwalk 1984.
6 R. L. Hassel, 'Thermal Analysis Application, Brief No. TA-55' DuPont Co., Wilmington.
7 S. Unal, Z. G. Yalcin and S. Piskin, Energy Sources, 21 (1999) 269.
8 P. J. Ream, American Chemical Society, 216 (1998) 311.
9 A. R. Shirazi, O. Bortin, L. Eklund and O. Lindqvist, Fuel, 74 (1994) 247.
10 B. K. Mazumdar, Fuel, 79 (2000) 1413.