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Kazim Esber ÖZBAS[*], Sedat BILGEN[*], Cahit HICYILMAZ[*], Mustafa Versan KÖK[**]

THERMOGRAVIMETRIC BEHAVIOUR OF SOME TURKISH LIGNITES OF DIFFERENT SIZES

In this study, thermogravimetric behaviour of Soma and Tuncbilek lignites of Turkey, and the effect of different particle sizes on thermal properties of these lignites were investigated. Samples were firstly crushed by jaw crusher under close control and four different size fractions were obtained. By using approximately 10 mg samples, non-isothermal thermogravimetry (TG/DTG) experiments were carried out in a temperature range of ambient to 900 °C in air atmosphere. Linear heating rate of 10 °C/min and air flow rate of 5 ml/min were chosen as operating parameters. Peak and burn-out temperatures were slightly decreased as the particle size decreased. Kinetic parameters of the samples were obtained from differential thermogravimetric data by using an Arrhenius type reaction model. TG/DTG thermograms of both samples showed two reaction regions at two different temperature ranges; first region was found to be due to the combustion of carbon part of the samples, and the second region was due to the decomposition of the mineral matter in the samples. Lower activation energies were found for Soma samples than Tuncbilek samples. Particle size had almost no effect on the activation energies in the major combustion region of the both samples. Thermogravimetry was found to be very suitable for combustion characterization of coal samples.

INTRODUCTION

Turkey has approximately 0.2% of the world total lignite reserves and the uses of lignites are mainly for power generation by thermo-power plants, household heating, and other industrial branches. In our country, electricity is produced by thermo and hydro-power plants, and 52% of the total production is obtained by thermo-power plants. Around 52% of the thermo-power plants of Turkey is lignite dependent for power generation (Köktürk and Narin, 1994; Esin, 1994). Therefore, it is very important to have a knowledge of combustion characteristics of such fossil fuels.

Thermogravimetric analysis (TG), differential thermogravimetric analysis (DTG) and the differential scanning calorimetry (DSC) are the methods widely used in characterizing fossil fuels undergoing combustion or pyrolysis (Kök and Okandan, 1992; Vasandani and

[*] Middle East Technical University, Mining Engineering Department, Ankara, Turkey.
[**] Middle East Technical University, Petroleum and Natural Gas Engineering Department, Ankara, Turkey.

Shah, 1994; Cumming and Mclaughlin, 1982; Warne, 1990; Shah et al., 1994; Cumming, 1989). Thermogravimetry, by definition, can be used to measure any reaction involving mass change.

Coal is the most important of all the fossil fuels for steam generation. In the design of industrial coal-fired boiler furnaces, it is of importance to have an assessment of the reactivity of the intended fuel, because coal is a physically heterogeneous and chemically complex mixture of organic and inorganic species which undergoes appreciable physico-chemical changes when heat-treated. If it is proposed to change the fuel supply for an existing installation, it is advantageous to have a test which allows the burning characteristics of alternative fuels to be compared with the original in terms of reaction burning rate. Ignition and combustion of coal by mechanical stokers, fluidized beds, or gasifiers is accompanied by weight loss, thermal decomposition, diffusion, and heat transfer. These, in turn, are influenced by the nature of the coal, particle size, density, and porosity, all of which affect the thermal processes occurring in the coal (Podder et al., 1995; Shah et al., 1994).

Cumming (1994) 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 weighted mean apparent activation energy, derived from simultaneous TG/DTG readings on 20 mg sample 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.

Gold (1980) 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. Morgan and Robertson (1986) pointed out that coal burning profiles obtained from thermogravimetric analysis depend on coal properties and particle size. Jayaweera et al. (1989) studied the effect of particle size on the percentage weight 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. Shah et al. (1994) studied combustion of different size 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.

The objective of this study is to determine the thermogravimetric behaviour of Soma and Tuncbilek lignites, and to determine the effect of different particle sizes on the thermal properties of these lignites.

MATERIALS AND METHODS

Samples

In this study, Soma and Tuncbilek lignites which are fed to the power plants were used. Both of the samples were crushed by using jaw crusher under close control, and four different size fractions of the samples were obtained. The size fractions were chosen depending on the feed sizes of the thermo-power plants of Soma and Tuncbilek region. The results of dry screen analyses of the samples were given in Table 1. Proximate analyses of the samples determined by TG/DTG experiments were given in Table 2.

Equipment

In order to determine the combustion and kinetic properties of the samples, non-isothermal thermogravimetry experiments were carried out by Polymer Lab. PL-TGA 1500 thermal analyser unit.

Operating procedure

Table 1. Dry screen analyses of Soma and Tuncbilek samples

Sample	Size fraction, mm	Weight, %	Cumulative weight, % screen oversize	Cumulative weight, % screen undersize
Soma	–30+18	22.05	22.05	77.95
	–18+10	23.51	45.56	54.44
	–10+0.5	45.07	90.63	9.37
	–0.5	9.37	100.00	–
Tuncbilek	total	100.00		
	–30+18	30.55	30.55	69.45
	–18+10	32.79	63.34	36.66
	–10+0.5	31.55	94.89	5.11
	–0.5	5.11	100.00	–
	total	100.00		

Table 2. Proximate analyses of Soma and Tuncbilek samples by thermogravimetry

Sample	Moisture, %	Volatile matter + fixed carbon, %	Ash %
Soma feed	4.54	56.11	39.35
Soma –30+18 mm	5.72	50.82	43.46
Soma –18+10 mm	6.40	51.99	41.61
Soma –10+0.5 mm	6.64	52.78	40.58

Soma –0.5 mm	6.99	51.58	41.43
Tuncbilek feed	2.60	46.31	51.09
Tuncbilek –30+18 mm	2.48	44.73	52.79
Tuncbilek –18+10 mm	2.30	43.80	53.90
Tuncbilek –10+0.5 mm	2.69	47.26	50.05
Tuncbilek –0.5 mm	2.40	41.28	56.32

The TG/DTG experiments were performed by using approximately 10 mg samples at a linear heating rate of 10 °C/min over a temperature range of ambient to 900 °C with an air flow rate of 5 ml/min. Prior to the experiments TG/DTG unit was calibrated for temperature readings using indium as melting standard.

RESULTS AND DISCUSSION

Thermogravimetric properties

Theoretically, combustion of fuel can be initiated whenever oxygen comes in contact with fuel. However, the temperature and composition of the fuel and oxygen supply dictate the nature of the reaction. In the temperature region of 200 and 350 °C all coals start to loose small amounts of pyrolysis water from decomposing phenolic structures, and oxides of carbon from carboxylic and carbonyl groups. At around 350 °C primary carbonization starts initially with the release of carbon dioxide and hydrogen. With increasing temperature, methane and other lower aliphatics are evolved together with hydrogen, carbon monoxide and alkyl aromatics.

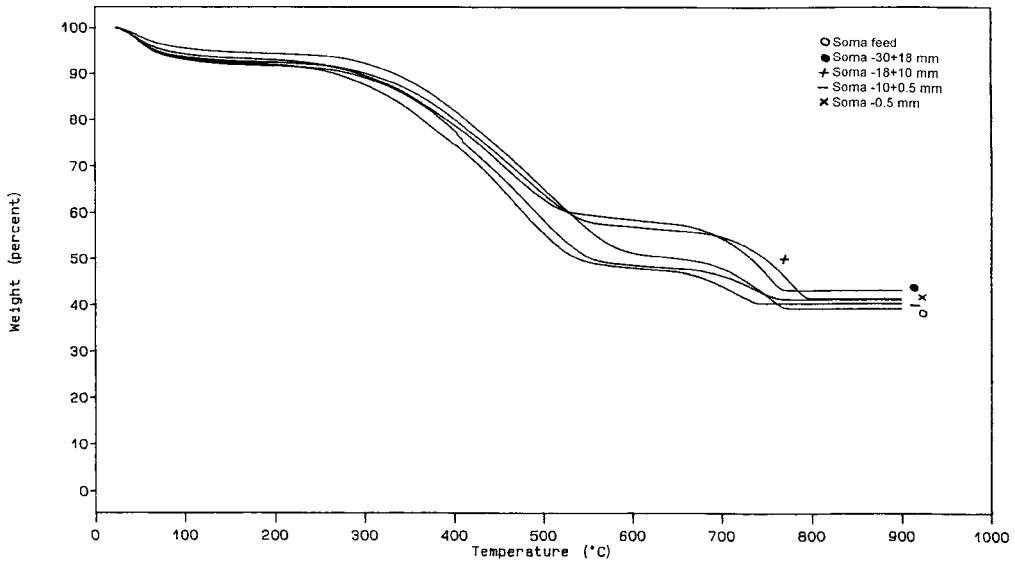

Fig. 1. TG curves of different size fractions of Soma lignite sample

Effect of particle size on the burning profiles of the samples used is given in Figs. 1, 2. The thermograms of all the size ranges show slight differences in peak and burn-out temperatures and residue amount depending on the mineral matter and

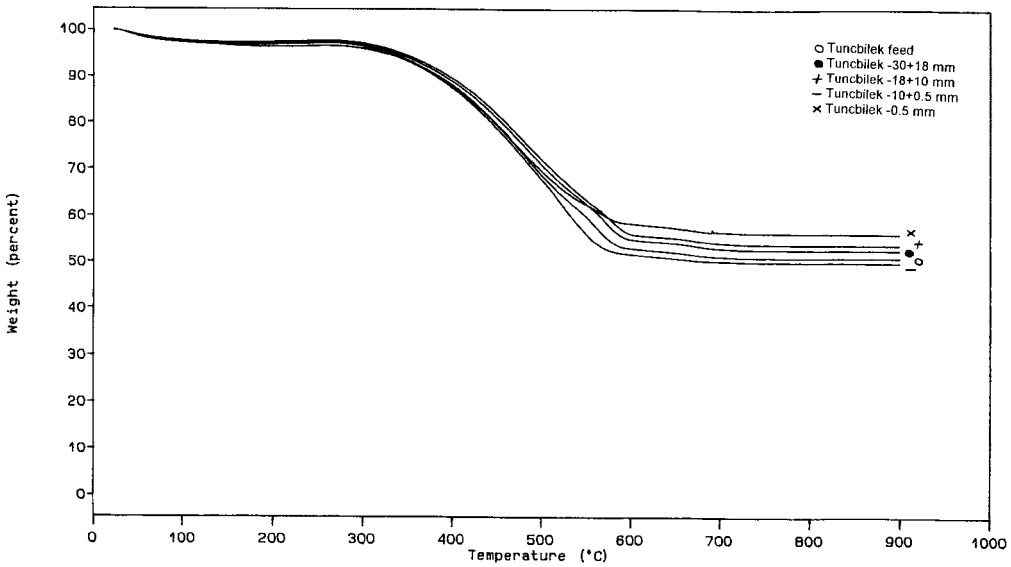

Fig. 2. TG curves of different size fractions of Tuncbilek lignite sample

fixed carbon content. Peak temperature is the temperature at which the rate of weight loss is at maximum. Peak temperatures of all size fractions of the two samples decreased slightly as the particle size decreased. The temperature at which the maximum combustion rate occurs is taken as a measure of combustibility. Lower temperature indicates more easily burned samples. The increased surface area of the samples due to decrease in size, allowed more rapid start of ignition. Burn-out temperatures indicating the end of the sample oxidation were also affected by the change in particle size. With the decrease in particle size, burn-out temperatures of the samples decreased slightly (Table 3).

Table 3. Thermogravimetric properties of Soma and Tuncbilek samples

Sample	Peak temperature, °C	Burn-out temperature, °C	Residue %
Soma feed	495.09	776.47	39.35
Soma –30+18 mm	458.27	769.51	43.46
Soma –18+10 mm	489.07	796.96	41.61
Soma –10+0.5 mm	468.21	738.58	40.58

Soma –0.5 mm	407.84	762.11	41.43
Tuncbilek feed	477.03	605.86	51.09
Tuncbilek –30+18 mm	570.78	607.69	52.79
Tuncbilek –18+10 mm	484.66	604.41	53.90
Tuncbilek –10+0.5 mm	520.63	591.27	50.05
Tuncbilek –0.5 mm	463.83	596.06	56.32

Kinetic analysis

Modeling of reaction kinetics for a combustion process is extremely complicated, because several components are simultaneously oxidized. In this study, thermogravimetric data were analyzed according to an Arrhenius-type kinetic model

$$dw/dt = A_r \exp(-E/RT) w^n$$

where dw/dt is the rate of weight change of the reacting material, A_r the Arrhenius constant, E the activation energy, T the temperature, and n the reaction order (Kök and Okandan, 1992; Kök, 1993).

For analyzing the TG/DTG data, the model assumes that the rate of weight loss of the total sample is dependent only on the rate constant, the weight of the sample remaining and the temperature with assumed unity reaction order (Kök, 1993). So, the equation of Arrhenius-type kinetic model takes the following form;

$$(1/w)(dw/dt) = A_r \exp(-E/RT)$$

When $\log(1/w)(dw/dt)$ is plotted against $1/T$, the straight line obtained will have a slope equal to E/2.303R and from the intercept the Arrhenius constant A_r can be estimated (Kök and Okandan, 1992). Table 4 lists the reaction parameters calculated by using this kinetic model.

Table 4. Kinetic parameters of Soma and Tuncbilek samples by thermogravimetry

Sample	Reaction region	Activation energy, kJ/mole	Arrhenius constant, 1/min
Soma feed	1	25.434	1.552
	2	152.376	$2.193 \cdot 10^6$
Soma –30+18 mm	1	26.047	1.828
	2	184.872	$1.406 \cdot 10^8$
Soma –18+10 mm	1	26.563	1.874
	2	203.149	$7.03 \cdot 10^8$
Soma –10+0.5 mm	1	26.146	2.296
	2	189.943	$3.148 \cdot 10^8$
Soma –0.5 mm	1	28.477	3.221
	2	193.618	$2.600 \cdot 10^8$
Tuncbilek feed	1	35.616	9.057
	2	85.661	$7.962 \cdot 10^3$

Tuncbilek –30+18 mm	1	35.807	8.570
	2	92.934	$1.854 \cdot 10^4$
Tuncbilek –18+10 mm	1	36.726	9.661
	2	143.266	$2.02 \cdot 10^7$
Tuncbilek –10+0.5 mm	1	31.979	4.988
	2	–	–
Tuncbilek –0.5 mm	1	41.778	26.242
	2	32.343	1.854

It was observed from the TG/DTG thermograms that both Soma and Tuncbilek samples have two reaction regions at two different temperature ranges. The first one of these regions starts approximately at 200 °C and ends at 500 °C, and the second region starts at 650 °C and ends at 750 °C. The first region represents the primary combustion region of the coal samples. Pyrolysis takes place in this region as well. The second region corresponds the decomposition of the mineral matter in the samples, because the decomposition temperatures of minerals in coals such as calcite, kaolinite are in the range of 650–850 °C (O'Gorman and Walker, 1973). It was also observed from the thermograms that the most of the weight losses occurred in the first regions, indicating combustion of carbonaceous parts of samples.

It was found that due to the decomposition mineral matter, both of the samples required higher activation energies in the secondary reaction regions. In general, Soma samples have lower activation energies than the Tuncbilek samples in the primary reaction region, but in the second region Soma samples have higher activation energies than Tuncbilek samples. The change in the particle sizes of the Soma and Tuncbilek samples had almost no effect in the activation energies of the primary reaction regions. Only –0.5 mm fraction of Tuncbilek sample gave higher activation energy than the feed sample. This is probably due to higher ash content of this fraction. On the other hand, depending on the mineral matter contents, different size fractions of the Soma sample showed slight changes in activation energies, whereas the size fractions of Tuncbilek sample required different activation energies in the secondary reaction regions.

CONCLUSIONS

Peak and burn-out temperatures of the samples studied were slightly affected by the change in particle size; as the particle size decreased peak temperatures and burn-out temperatures of the samples were decreased slightly.

TG/DTG thermograms of both samples showed two reaction regions at two different temperature ranges; first region which is in the range of 200–500 °C was found to be due to the combustion of carbon part of the samples, and the second region which was between 650–750 °C indicated that the decomposition of the mineral matter in the samples took place.

Lower activation energies were found for Soma samples than Tuncbilek samples by kinetic analyses of TG/DTG data. Particle size had almost no effect on the activation energies in the major combustion region of the both samples.

REFERENCES

CUMMING J. W., 1984, *Reactivity assessment of coals via a weighted mean activation energy*, Fuel, 63, 1436–1440.

CUMMING J. W., MCLAUGHLIN J., 1982, *The thermogravimetric behaviour of coal*, Thermochimica Acta, 57, 253–272.

CUMMING J. W., 1989, *A DTG combustion study on anthracitic and other coal chars*, Thermochimica Acta, 155, 151–161.

ESIN J., 1994, *Power generation by lignite dependent power plants and environment*, Proceeding of Lignite Sector of Turkey Towards the Years of 2000 Symposium, Ankara, Turkey, 63–73 (in Turkish).

GOLD P. I., 1980, *Thermal analysis of exothermic processes in coal pyrolysis*, Thermochimica Acta, 42, 135–142.

JAYAWEERA S. A. A., MOSS J. M., THWAITES, M. W., 1989, *The effect of particle size on the combustion of Weardale coal*, Thermochimica Acta, 152, 215–225.

KÖK M. V., OKANDAN E., 1992, *Effect of crude oil type and heating rate on combustion of crude oil-lignite mixtures*, Fuel, 71, 1499–1503.

KÖK, M. V., 1993, *Use of thermal equipment to evaluate crude oils*, Thermochimica Acta, 214, 315–324.

KÖKTÜRK, A., NARIN, R., 1994, *Lignite reserves, possible fields of usage and prospecting policy*, Proceeding of Lignite Sector of Turkey Towards the Years of 2000 Symposium, Ankara, Turkey, 43–60 (in Turkish).

MORGAN P. A., ROBERTSON, S. D., UNSWORTH J. F., 1986, *Combustion studies by thermogravimetric analysis 1. Coal oxidation*, Fuel, 65, 1546–1551.

O'GORMAN J. V., WALKER P. L. Jr., 1973, *Thermal behaviour of mineral fractions separated from selected American coals*, Fuel, 52, 71–79.

PODDER J., HOSSAIN T., MANNAN Kh. M., 1995*, An investigation into the thermal behaviour of Bangladeshi coals*, Thermochimica Acta, 255, 221–226.

SHAH M. R., RAZA M. Z., AHMED N., 1994, *Characterization of Lakhra coal by TG/DTG*, Fuel Science and Technology Int'l, 12 (1, 85–95.

VASANDANI A. G. M., SHAH M. R., 1994, *Differential thermal analysis of low-rank coals,* Journal of Thermal Analysis, 41, 1053–1061.

WARNE S. St. J., 1990, *Fossil fuels: an overview of trends, methods and applications of thermal analysis,* Thermochimica Acta, 166, 343–349.

Özbas K.E., Bilgen S., Hicyilmaz C., Termograwimetryczne w³aœciwoœci wybranych tureckich wêgli brunatnych w zale¿noœci od ich sk³adu ziarnowego. *Fizykochemiczne Problemy Mineralurgii* 32, 149–156 (w jêz. angielskim)

W pracy badano węgle brunatne pochodzące z miejscowości Soma i Tuncbilek w Turcji. Próbki węgli poddano kruszeniu w celu przygotowania czterech różnych klas ziarnowych. Przeprowadzono nieizotermiczne pomiary termograwimetryczne (TG/DTG) w zakresie temperatur od 20 do 900 °C w obecności powietrza stosując liniową szybkość ogrzewania wynoszącą 10 °/min przy przepływie powietrza wynoszącego 5 ml/min. Stwierdzono, że piki przemian i temperatura spalania nieznacznie malały z wielkością ziaren. Obliczono kinetyczne parametry procesu w oparciu o uzyskane dane

termograwimetryczne używając do tego celu zależności Arrheniusa. Termograwimetrogramy (TG/DTG) pokazały, że oba węgle posiadają dwa różne zakresy reakcji zachodzące przy różnych temperaturach. Pierwszy zakres jest wynikiem spalania substancji węglowej próbki podczas gdy drugi zakres jest powodowany rozkładem substancji mineralnej węgla. Niższe energie aktywacji uzyskano dla węgla pochodzącego z Soma niż dla węgla z Tuncbilek. Stwierdzono także, że wielkość ziarn nie miała prawie wpływu na energie aktywacji spalania obu próbek. Wyniki badań potwierdziły, że termograwimetria jest bardzo użyteczna do termicznej charakterystyki próbek węglowych.