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Effect of particle size on the thermal and combustion properties of coal

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Abstract

In this research effect of particle size on the combustion properties of Çayırhan coal sample was studied. Non-isothermal thermogravimetry and derivative thermogravimetry (TG/DTG) experiment were carried out for twelve different size fractions of the Çayırhan coal sample. Thermogravimetry experiments were performed from ambient to 900°C in air atmosphere. Differential thermogravimetric data were analysed using an Arrhenius type reaction model assuming a first-order reaction. Kinetic parameters of the samples are determined and the results are discussed. © 1997 Elsevier Science B.V.

Keywords: Particle size; Çayirhan coal; Thermogravimetry

1. Introduction

Coal is 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 characterisation of high pressures application to coal hydrogenation, catalytic effects due to inorganic substances, combustion, pyrolysis and kinetic analysis. In the selection of coals for combustion it is useful to have knowledge of their combustion characteristics. 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 govern the thermal processes occurring in the coal. Thermal analysis methods play an important role in the investigation of useful mineral substances. Their application to the study of coals and its products has increased considerably in the last two decades. Thermogravimetry (TG), differential thermogravimetry (DTG) and the differential scanning calorimetry (DSC) are the methods widely used in characterisation of fossil fuels undergoing combustion or pyrolysis. Gold [1] demonstrated the occurrence of exothermic reactions associated with the production of volatile matter in or near the plastic region of coal studied. He concluded that the temperature and the magnitude of the exothermic peak were strongly affected by the heating rate, sample mass and the particle size. Morgan and Robertson [2] pointed out that coal burning profiles obtained from thermogravimetric analysis depends on coal properties and particle size. Kok

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and Okandan [3,4] determined the effect of crude oil type and heating rate on combustion of lignite using DSC and TG. Their results indicate that the characteristic shape of combustion of lignite was not changed by the addition of crude oil and the effect of high heating rate was to cause the reactions to occur at higher temperatures. Morris [5] carried out pyrolysis runs in the temperature range ambient to 900°C for different particle sizes, and the established empirical correlation's for the evolution rates of hydrogen, carbon monoxide, and methane as a function of particle size and instantaneous temperature. Jayaweera et al. [6] 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 has significant effect on the results. Shah et al. [7] studied combustion of different size coal samples. The results revealed that the effect of reduction in particle size of coal was advantageous in so far as a reduction in particle size caused a decrease in the ignition temperature. Russel et al. [8] incorporated temperature and particle size in mass transfer equations for gaseous species, but their model could not predict the product distribution. Recently Morris [9] correlated yields of hydrogen and methane as function of particle size and final temperature, and yields of carbon monoxide and carbon dioxide as a function of particle size at a final temperature before decomposition of the carbonates in the mineral matter.

The objective of this research is to study the effect of particle size on the combustion properties of Çayırhan coal.

2. Experimental

2.1. Sample

The sample used in this research was Çayırhan coal which was prepared according to ASTM standards. The coal sample was crushed to −10 mesh size, then different size fractions of this sample were obtained (Table 1). Proximate analysis of the samples were also determined by TG/DTG equipment (Table 2).

2.2. Equipment

During the research heat of combustion of the samples are determined by Parr 1261 bomb calorimeter. Carbon, hydrogen, nitrogen and sulphur contents are analysed by Eager 200 element analysis unit. Non-isothermal thermogravimetry experiments are carried out by Polymer Lab. 1500 thermal analyser unit in order to determine the combustion and kinetic properties of the samples studied.

2.3. Operating procedure

The TG/DTG experimental procedure involves placing ~10 mg of sample, setting the heating and

Table 1
Dry screen analysis of Çayirhan coal sample

Screen size (mesh)	Screen size (micron)	Weight (remaining (%))	Screen (oversize (wt%))	Screen (undersize (wt%))
−10 + 14	−1651 + 1168	20.19	20.19	79.81
−14 + 20	−1168 + 833	17.95	38.14	61.83
−20 + 28	−833 + 589	13.29	51.43	48.57
−28 + 35	−589 + 417	10.47	61.90	38.10
−35 + 48	−417 + 295	8.45	70.35	29.65
−48 + 65	−295 + 208	8.59	78.94	21.06
−65 + 100	−208 + 147	5.07	84.01	15.99
−100 + 150	−147 + 104	4.90	88.91	11.09
−150 + 200	−104 + 74	4.68	93.59	6.41
−200 + 270	−74 + 52	4.67	98.26	1.74
−270 + 400	−52 + 37	1.22	99.48	0.52
−400	−37	0.52	—	—

Table 2
Proximate analysis of Çayirhan coal sample by thermogravimetry

Mesh size	Moisture(%)	Vol. matter (%)	Fix. carbon(%)	Ash(%)	Heat val. (cal/g)
−10 + 14	11.70	14.38	52.99	20.93	3771
−14 + 20	6.16	9.89	52.17	26.78	4334
−20 + 28	6.41	9.75	54.86	28.98	4492
−28 + 35	6.08	12.89	54.04	26.99	4482
−35 + 48	6.13	10.95	57.08	25.84	4473
−48 + 65	6.44	11.89	56.50	25.17	4463
−65 + 100	6.69	13.25	55.35	24.71	4450
−100 + 150	6.55	12.76	53.42	27.27	4319
−150 + 200	5.73	14.55	43.01	36.71	3628
−200 + 270	6.38	16.59	48.95	28.08	4215
−270 + 400	5.98	17.50	43.84	32.68	3979
−400	5.43	16.37	40.67	37.53	3581

gas-flow rate, then commencing the experiment. All experiments were performed at a linear heating rate of 10°C/min over a temperature range of ambient to 900°C with an air flow rate of 50 ml/min. Prior to experiments TG/DTG was calibrated for temperature readings using calcium oxalate monohydrate as a reference material. It was essential to calibrate the balance for buoyancy effects to allow quantitative estimation of weight changes. Experiments were performed twice for repeatability.

3. Results and discussion

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 carbonisation starts initially with the release of carbon dioxide and hydrogen. With increase in temperature, methane and other lower aliphatics are evolved together with hydrogen, carbon monoxide and alkyl aromatics. Heat of combustion values of the samples were determined in an oxygen bomb calorimeter (ASTM D 2015-82) by a substitution procedure. Different fractions of Çayırhan coal showed slight differences among each other which may be due to the mineral matter composition of the fractions (Table 3). Carbon, hydrogen, nitrogen and sulphur contents of the fractions were also determined and slight differences were observed Table 3.

Effect of particle size on burning profiles of Çayırhan coal sample are given in Fig. 1(a and b). The thermograms of all the different size fractions shows slight differences in peak and burn-out temperatures and residue amounts depending on the mineral matter and carbon contents. The main characterisation point in TG/DTG thermogram is the peak temperature where the rate of weight loss is at maximum. As the particle size decreased, peak temperatures decreased slightly. The increase in surface area of the coal allowed more rapid start of ignition. Burn-out temperatures, that represents the temperature where sample oxidation is complete, are also affected by the change in particle size. With a decrease in particle size, the burn-out temperatures of the samples decreased slightly. It was also observed that decrease in particle size caused more residue at the end of the combustion process (Table 4).

3.1. Kinetic analysis

Non-isothermal kinetic study of weight loss under combustion process is extremely complex for coals and crude oils because of the presence of the numerous complex components and their parallel and consecutive reactions.

Table 3
Element analysis results of the samples

Mesh size	Carbon (%)	Hydrogen (%)	Nitrogen (%)	Sulphur (%)
−10 + 14	50.773	4.758	1.813	6.215
−14 + 20	40.109	3.602	1.342	6.572
−20 + 28	43.978	4.318	1.478	8.576
−28 + 35	43.908	4.043	1.446	7.639
−35 + 48	45.205	4.075	1.830	6.524
−48 + 65	53.138	4.217	2.150	6.528
−65 + 100	55.841	6.597	2.236	6.258
−100 + 150	46.514	4.004	1.829	6.472
−150 + 200	40.224	3.644	1.276	6.405
−200 + 270	43.937	3.952	1.462	6.877
−270 + 400	40.070	3.723	1.338	7.194
−400	26.235	3.384	3.191	7.529

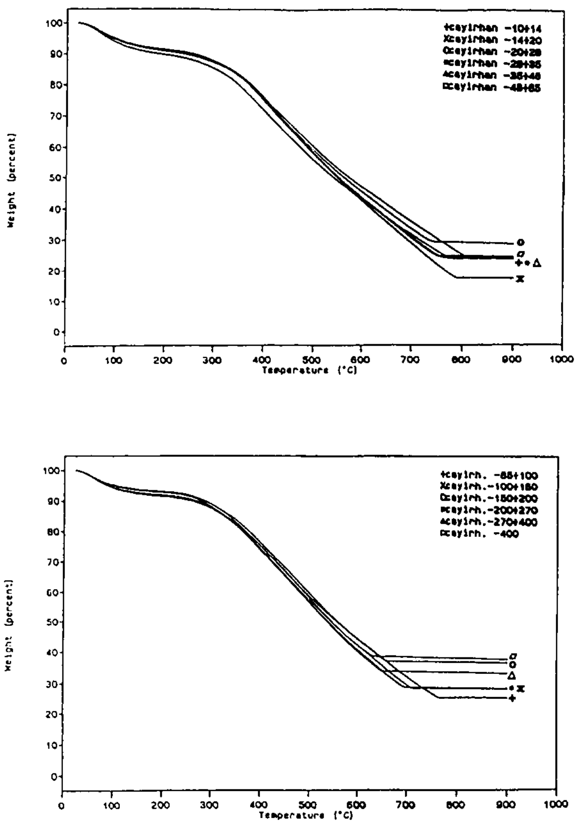

Fig. 1. Thermograms of different size fractions of Çayirhan coal.

For analysing the kinetics of 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 remaining sample and the temperature with reaction order of unity. Application of this method to the TG/DTG thermograms are easy and fast. So the equation of Arrhenius-type kinetic model takes the following form [10];

Table 4
Thermal properties of the samples

Size (mesh)	Peak temp. (°C)	Burn-out temp. (°C)	Residue left (%)
−10 + 14	398	770	23.9
−14 + 20	405	765	24.0
−20 + 28	406	760	24.2
−28 + 35	410	755	24.4
−35 + 48	410	750	24.5
−48 + 65	412	750	24.6
−65 + 100	421	740	25.9
−100 + 150	435	710	28.1
−150 + 200	440	690	30.2
−200 + 270	419	680	32.2
−270 + 400	419	650	33.1
−400	433	620	37.6

$$\mathrm{d}W/\mathrm{d}t = kW^n$$

$$k = A_r \exp(-E/RT)$$

Assuming first-order kinetics,

$$\mathrm{d}W/\mathrm{d}t = A_r \exp(-E/RT)W$$

$$(\mathrm{d}W/\mathrm{d}t)(1/W) = A_r \exp(-E/RT)$$

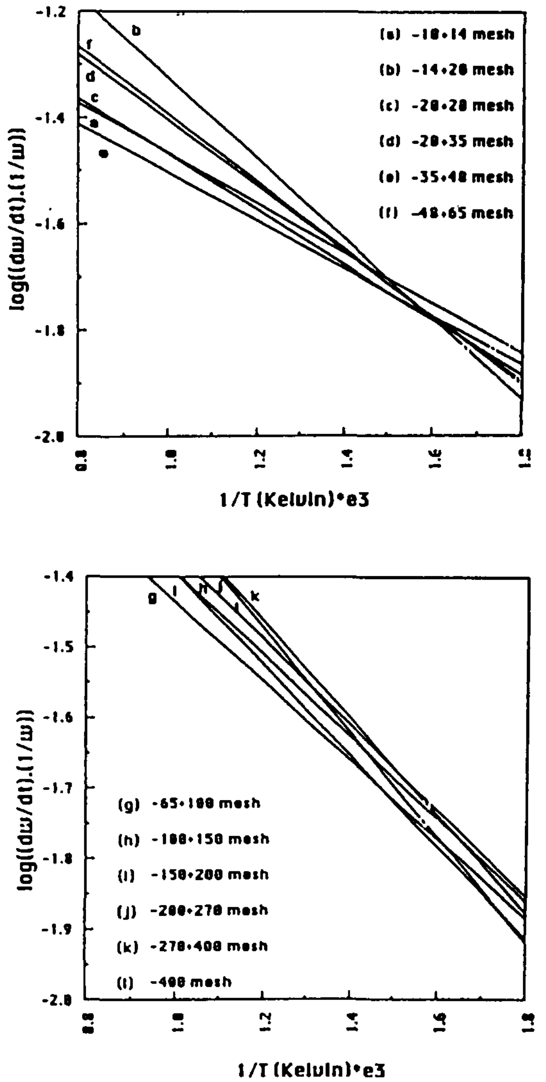

Fig. 2. Arrhenius plots of different size fractions of Çayırhan coal.

taking the logarithm of both sides and assuming $n = 1$,

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

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. When $\log[(dW/dt)1/W]$ is plotted against $1/T$, 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. Linear least square correlation coefficients for the identified rectilinear portions varied from 0.95 to 0.99 and $\log[(dW/dt)1/W]$ vs. $1/T$ diagrams (Fig. 2(a and b) where activation energy and Arrhenius constant were determined are given in Table 5. A slight increase is observed in the activation energy values as the particle size decreased.

Table 5
Kinetic properties of the samples

Size (mesh)	Activation energy (kJ/mol)	Arrhenius constant (1/min)
−10 + 14	9.03	0.101
−14 + 20	9.48	0.108
−20 + 28	9.98	0.113
−28 + 35	11.81	0.163
−35 + 48	10.65	0.089
−48 + 65	12.21	0.176
−65 + 100	10.69	0.132
−100 + 150	11.14	0.154
−150 + 200	12.36	0.177
−200 + 270	11.65	0.174
−270 + 400	13.16	0.229
−400	14.18	0.261

4. Conclusions

Effect of particle size on the thermal and combustion properties of Çayırhan coal was studied by thermogravimetry (TG/DTG) and the following conclusions are derived.

Different fractions of Çayırhan coal showed slight differences in heat of combustion values which might be due to the mineral matter composition of the fractions. 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.

References

[1] P.I. Gold, Thermochimica Acta, 42 (1980) 135.
[2] P.A. Morgan, S.D. Robertson and J.F. Unsworth, Fuel, 65 (1986) 1546.

[3] M.V. Kok and E. Okandan, Fuel, 71 (1992) 1499.
[4] M.V. Kok and E. Okandan, Fuel, 73 (1994) 500.
[5] R.M. Morris, Journal of Analytical and Applied Pyrolysis, 27 (1993) 97.
[6] S.A. Jayaweera, J.M. Moss and M.W. Thwaites, Thermochimica Acta, 152 (1989) 215.
[7] M.R. Shah and N. Ahmed, Fuel Science and Technology Int'., 12 (1994) 85.
[8] W.B. Russel and D.A. Saville, M.I. Greene., AIChE, 25 (1979) 65.
[9] R.M. Morris, Fuel, 69 (1990) 776.
[10] M.V. Kok, Thermochimica Acta., 214 (1993) 315.