Turk J Chem
27 (2003) , 521 – 528.

Thermogravimetric Characterization of Turkish Bituminous Coals for Combustion

Sait KIZGUT[*], **Dilek ÇUHADAROĞLU**, **İhsan TOROĞLU**
Faculty of Engineering, Karaelmas University, 67100 Zonguldak-TURKEY
e-mail: kizguts@hotmail.com

Received 08.07.2002

This study focused on the thermal gravimetric characterization of Turkish bituminous coals for combustion. The combustion properties considered were based on the burning profile of coal samples and their chars produced in a PL 1500 TGA apparatus. The coal seam samples used in the study were obtained from TTK (Turkish Hardcoal Enterprise) mines as channel samples. The majority of the samples from 12 seams were medium-volatile bituminous and only three of them were high-volatile bituminous. Combustion profile parameters of coal samples and chars were correlated with petrographic, proximate and ultimate analysis data in order to establish the combustion differences of the samples. The results indicated that only the combustion profile parameters of ignition and burnoff temperatures of coal were correlated with H/C ratio, fuel ratio and petrofactor. The amount of total reactive macerals showed a strong relationship with char reactivity for the same rank coal samples. However, the same result was not obtained for the whole range of coal samples, since rank effect was not included. The petrofactor, combining both effects of petrographic composition and reflectance data, showed a strong relationship with char reactivity for the whole range of coal samples.

Key Words: Thermal analyses, Coal combustion, Char reactivity.

Introduction

Hardcoal mining in Turkey is carried out exclusively in the Northwest Anatolian Hardcoal Basin. The main marketing policy for these bituminous coals is to supply low-ash washed coals to the metallurgy industry and to use high-ash middling product in the local thermal power plant(s). The basin includes seams ranked as high- and medium-volatile bituminous coals with an extensively fracturated structure. This situation requires a detailed characterization of these coals according to consumption areas.

The characterization of coal is vital for the efficient operation of a power plant for electricity generation. Various methods are used for this purpose, e.g. proximate analysis, determining petrographic constituents and reflectance and thermal analysis. These analyses are also used for solving operational problems. Proximate and ultimate analyses are generally not adequate since they cannot be used explain high amounts of unburned particles and petrographic effects. Petrographically, the organic constituents of coal are classified as reactive and inert. Major coal characteristics such as calorific value, grindability, ash properties and char reactivity are related to rank and petrographic composition in combustion[1–5].

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[*] Corresponding author

The thermal properties of coal (e.g. ignition temperature) strongly depend on coal rank. The ignition temperature of coals increases with decreasing volatile matter content. It is about 200°C and 250°C for coals of 40% and 5% volatile matter contents, respectively[3]. The ignition temperatures of maceral groups increase in the order of liptinite-vitrinite-inertinite[6]. Petrographic analysis is also important in explaining the inefficient combustion of coals and the optimization of combustion. Microscopic examinations of unburned particles of some North American coals have shown that the majority of these unburned particles consisted of fusinite, semifusinite and oxidized vitrinite[7]. Nandi and co-workers reported that by optimizing the operation conditions (e.g. minimizing oversize material, air supply, combustion temperature and residence time), high inertine coals might burn better. Shibaoka linked unburnted particles in fly ash to coarse size group coal rather than petrographic composition[8,9]. He reported that if the combustion conditions were not optimized even vitrinite rich particles might stay in unburnted coarse material. Some recent studies have also shown that the combustion behavior of coal cannot be merely correlated to petrographic composition. Maceral interactions can occur and, depending on the rank of coal, liptinite has a more important role in the maceral interaction[10]. The rank or parameter comprising rank and petrographic composition has more effect on combustion behavior than merely maceral composition does[10−12].

Thermogravimetric analysis (TGA) and derivative thermogravimetry (DTG) studies are useful tools for the determination of combustion characteristics (e.g. peak temperature, burnout temperature and activation energy) of coals and chars and other combustible materials[10,13−16]. The procedure is strongly affected by particle size, ash content, sample amount, heating rate and gas flow rate[10,17,18]. The main objective in this study is to compare the thermal analysis data with proximate and ultimate analysis and petrographic data of various Turkish bituminous coals and chars to establish the differences in their combustion characteristics.

Experimental

Coal samples

Coal samples were taken as channel samples from 12 seams representing the majority of seams encountered within the basin. To reduce the effect of ash/mineral matter on characterization, float material with 1.50 g cm^{-3} density was used in all the analyses. Ground material at −200 mesh (75 μm) was used in the thermal analysis. This size group was chosen since it was the size generally used in pulverized coal power plants. Proximate and ultimate analyses of samples are given in Table 1. Proximate analysis was characterized as fuel ratio (theratio of fixed carbon to volatile matter), and ultimate analysis was characterized as H/C ratio in the evaluation of the test results. A Leco-S132 sulfur analyzer and a Leco-CHN 600 organic element analyzer were used in the determination of sulfur and organic element distribution respectively. The results of proximate and ultimate analyses were the mean value of triple analyses (deviation $\pm 0.1 - 0.3$).

Petrographic analyses

Petrographic analyses were carried out under incident light by using a Zeiss Axioplan microscope and MPM 400 operating system. The microscope was equipped with a fluorescent light source and a camera. Macerals were grouped as vitrinite, liptinite, inertinite or semi-fusinite on a mineral free basis. Maximum reflectance measurements were obtained from all the suitable vitrinite macerals. Polished block preparation, maceral group analysis and reflectance measurement were carried out as described in ISO 7404-2, ISO 7404-3 and ISO 7404-5, respectively. The results of the petrographic analyses are given in Table 2.

Table 1. Proximate and ultimate analyses of samples.

Parameter	Sample no.											
	1	2	3	4	5	6	7	8	9	10	11	12
Proximate (d.b.) wt. %												
Ash	11.1	6.2	9.6	5.2	7.6	5.3	9.5	7.9	5.1	3.8	10.4	8.0
Volatiles	25.3	27	27.3	24.8	28.5	31.1	27.7	28.7	36.5	34.9	29.2	38.1
Fixed carbon	63.6	66.8	63	70	63.9	63.7	62.7	63.4	58.4	61.4	60.4	53.8
Fuel ratio[a]	2.51	2.47	2.31	2.82	2.24	2.05	2.26	2.21	1.6	1.76	2.07	1.41
Ultimate (d.b.), wt. %												
C	77.2	81.9	78.9	83.8	80.7	82.4	79.4	80.3	78.8	83.7	77.6	72.4
H	4.6	4.5	4.3	4.5	4.4	4.8	4.3	4.6	4.8	4.8	4.4	4.5
N	0.8	0.8	0.9	0.6	0.7	0.7	1.1	0.9	0.9	0.9	0.8	0.6
O (difference)	6.3	6.6	6.2	5.9	6.6	6.8	5.7	6.2	10.4	7	6.8	14.5
S	0.7	0.5	0.6	0.4	0.4	1	0.6	0.7	0.4	0.8	1.1	0.6
H/C ratio	0.71	0.66	0.65	0.64	0.66	0.71	0.66	0.7	0.72	0.69	0.67	0.76

[a] The ratio of fixed carbon to volatile matter.

Table 2. Petrographic analyses of samples.

Parameter	Sample no.											
	1	2	3	4	5	6	7	8	9	10	11	12
Maceral Group[a]												
Vitrinite	64.0	80.7	66.3	83.4	74.2	85.5	83.1	84.7	56.6	91.7	88.3	75.5
Liptinite	5.2	4.1	4.8	2.2	5	5.2	3.6	2.8	8.5	3.3	0.8	3.2
Semi-fusinite	17.9	8	16	6	9.2	6.8	5.5	6.3	18.3	2.5	4.7	12.3
Inertinite	12.9	7.2	12.9	8.4	11.6	2.5	7.8	6.3	16.6	2.5	6.2	9.0
Total reactives	78.7	90	82.5	90.1	84.7	95.5	90.6	91	78.3	96.6	92.7	86.7
Mean reflectance[b]	1.01	1.02	0.98	1.11	0.99	0.92	0.99	0.98	0.81	0.96	0.99	0.65
Petrofactor	12.8	11.3	11.9	12.3	11.7	9.6	10.9	10.8	10.3	9.9	10.7	7.5

[a] Maceral data in volume % , mineral-matter free.

[b] Maximum reflectance measurements from all suitable vitrinites.

Reflectance measurements from inertinites were used to determine fusible inertinites as suggested by Thomas et al.[19]. To estimate fusible inertinites, their threshold reflectance was considered to be 1.5 for high-volatile bituminous coal samples and 1.6 for medium-volatile coal samples. The amount of fusible inertinites varied from 26 to 51.6% of total inertinites and from 53 to 75% of semi-fusinites.

A petrofactor (P_f) combining both maceral and rank data was used as suggested by Diessel and Guyot[10] for the comparison of thermal analysis and petrographic data. The petrofactor is calculated as

$$P_f = (R_m/\text{reactive macerals})*100$$

where R_m represents the mean reflectance, and reactive macerals include vitrinite, liptinite and fusible inertinites.

The effect of reflectance on the petrofactor was considerably higher than the effect of the amount of total reactive macerals on the petrofactor. The correlation coefficients (r) for reflectance vs. petrofactor and total reactive macerals vs. petrofactor are 0.85 and 0.33, respectively.

Thermogravimetric analyses

A PL TGA 1500 (Polymer Laboratories) thermogravimetric analyzer was used in the thermal analyses. A 10 ± 0.1 mg coal sample was heated to 850°C at 10 K min^{-1} in air with a flow rate of 15 cm^3min^{-1}. The thermal parameters (e.g. characteristic temperatures and maximum rate of mass loss) were derived from combustion profiles. The characteristic temperatures were designated as follows:

T_i = initial temperature where mass loss reaches a rate of 1% per minute,

T_p = peak temperature at the maximum weight loss rate,

$T_{1/2}$ = temperature at which 50% burnoff (weight, ash free basis) occurs and

T_b = burnout temperature where DTG profile reaches a 1% combustion rate at the tail-end of the profile.

Activation energy (E_a) was calculated by using the Arrhenius equation as detailed elsewhere[16,20,21]. Char reactivity was measured explained by Jenkins et al.[22] and Milligan et al.[10]. Coal chars were produced in a PL TGA 1500. A 10 mg coal sample was heated to 700°C at 10 K min^{-1} in nitrogen with a flow rate of 15 cm^3min^{-1}. The atmosphere was switched to air at the same flow rate following cooling of the furnace to 500°C for char reactivity calculation. A low temperature was chosen to allow oxygen to enter the interior of the chars and so allow burnout from inside the char as well as on the external surface. Char reactivity (R) was calculated as suggested by Milligan et al.[10] by the following expression:

$R = (-1/W_0)(dW/dt)$

where W_0 is the initial mass of char (dry ash free) and dW/dt is the maximum rate of mass loss, % min^{-1}.

Results

Coal combustion characterization

The results of petrographic, thermal, ultimate and proximate analyses were used to evaluate the combustion characteristics of samples. H/C ratio, fuel ratio and petrofactor were correlated with characteristic TGA temperatures (T_i, $T_{1/2}$, T_p, T_b), activation energy (E_a) and maximum rate of mass loss data of the samples (Table 3). The results given in Table 4 show that there is almost no relationship between activation energy and correlation parameters of the petrofactor, fuel ratio and H/C ratio. This was expected because there was almost no important difference even between the highest rank (R_m = 1.11) and lowest rank (R_m = 0.65) coal samples' activation energy data, which were 91.1 and 93.6 $kJmol^{-1}$ respectively (Table 3). The correlation coefficients were very good for ignition temperature (T_i) with the petrofactor (r = 0.88), fuel ratio (r = 0.88) and H/C ratio (r = 0.76). A very similar result was obtained for burnout temperature (T_b) with a slightly lower value with H/C ratio (r = 0.60). The 50% burnoff temperature ($T_{1/2}$) and peak temperature (T_p) showed a poor relationship with the petrofactor (r = 0.59), fuel ratio (r = 0.45) and H/C ratio (r = 0.24). The relationship between the fuel ratio and petrofactor was very significant (r = 0.91).

In summary, T_i and T_b revealed a stronger relationship with the petrofactor, fuel ratio and H/C ratio compared to T_p and maximum rate of mass loss. The correlation coefficients of T_i and T_b with the petrofactor were higher than those with fuel ratio and H/C ratio, which showed that petrofactor could well be used as a combustion prediction parameter for the samples.

Table 3. Combustion profile parameters of coal samples.

Parameter	Sample no.											
	1	2	3	4	5	6	7	8	9	10	11	12
T_i (°C)	329	324	325	329	329	323	332	328	310	314	317	283
$T_{1/2}$(°C)	535	522	524	507	530	527	537	525	526	507	508	495
T_p(°C)	528	517	515	493	521	523	527	518	524	499	500	481
T_b(°C)	636	629	631	626	631	631	634	627	626	623	627	602
Max. rate of mass loss (%)	7.1	7.3	7.1	8	6.9	6.7	6.7	7.1	6.5	7.1	7.6	6.7
E_a (kJ mol^{-1})	94	96	96	91	96	96	98	99	89	94	88	94

Table 4. Correlation coefficients for coal samples.

Correlation parameter	Correlation coefficient (r)		
	Petrofactor	Fuel ratio	H/C
E_a(kJ mol^{-1})	0.05	0.00	0.20
T_i (°C)	0.88	0.88	0.76
$T_{1/2}$ (°C)	0.59	0.45	0.24
T_p (°C)	0.61	0.34	0.14
T_b (°C)	0.84	0.73	0.60
Max rate of mass loss (%)	0.50	0.68	0.60
Fuel ratio	0.91	-	0.75

Char reactivity results

The char reactivity results and correlation data between char reactivity and activation energy, H/C ratio, fuel ratio and petrographic data are given in Tables 5 and 6. There was no relationship between char reactivity and activation energy. The relationship between char reactivity and mean vitrinite reflectance (r = 0.68, Figure 1) was better than the char reactivity-total reactive maceral amount relationship (r = 0.44, Figure 2). However, when relatively low rank coals (no. 6, 9 and 12 coal samples) were excluded, a sharply increased linearity in the total reactive maceral amount and char reactivity relationship was observed. The correlation coefficient varied from 0.44 to 0.93 when the data of these three coal samples were excluded.

Table 5. Char reactivity results.

Parameter	Sample no.											
	1	2	3	4	5	6	7	8	9	10	11	12
Initial mass, W_o (%)	75.2	75.4	71.5	78.7	76.1	74.4	75	74.6	70.8	71.5	75.2	75.3
Max. rate of mass loss (%)	1.46	1.68	1.44	1.73	1.62	1.72	1.63	1.77	1.64	1.82	1.76	2.07
Char reactivity (R)	1.94	2.23	2.01	2.2	2.13	2.29	2.17	2.37	2.32	2.54	2.34	2.75

Table 6. Correlation coefficients for char reactivity.

Dependent variable	Independent variable	Figure	Correlation coefficient (r)
Char reactivity	Mean vitrinite reflectance	2	0.68
	Total reactive macerals	3	0.44
	Petrofactor	4	0.90
	Fuel ratio	-	0.76
	H/C ratio	-	0.55
	Activation energy	-	0.00

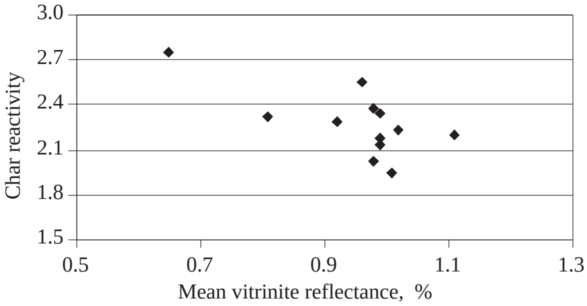

Figure 1. Mean max vitrinite reflectance vs. char reactivity.

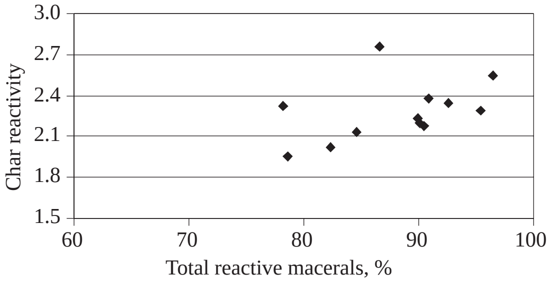

Figure 2. Amount of total reactive macerals vs. char reactivity.

The relationship between the petrofactor and char reactivity was almost linear (Figure 3). The correlation coefficient of char reactivity and petrofactor (r = 0.92) was considerably higher than the correlation coefficients between char reactivity and mean vitrinite reflectance (r = 0.68) and total reactive maceral amount (r = 0.41). The fuel ratio showed an important relationship with char reactivity (r = 0.76). The relationship between char reactivity and H/C ratio was very similar to that between char reactivity and mean vitrinite reflectance, with a slightly lower correlation coefficient (r = 0.55).

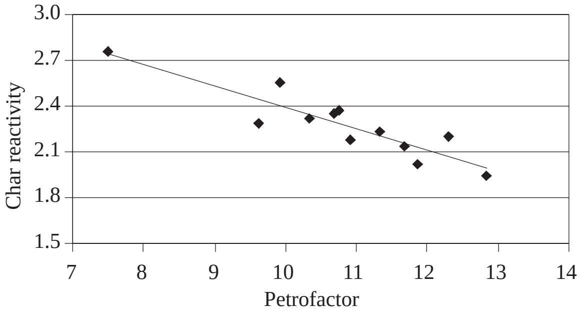

Figure 3. Petrofactor vs. char reactivity.

In brief, char reactivity showed a stronger relationship with the petrofactor compared to reflectance and total amount of maceral data for the whole range of coal samples. On the other hand,the total amount of reactive macerals could be related to char reactivity for the medium-volatile bituminous coal samples.

Conclusions

Ignition temperature (T_i) and burnout temperature (T_b) were better parameters to estimate combustion differences of the coal samples than other characteristic parameters derived from combustion profiles. T_i and T_b were correlated with the fuel ratio, C/H and petrofactor. The relationship between char reactivity and reactive macerals was almost linear for the medium-volatile coal samples. The total amount of reactive macerals could be used to assess combustion differences of same rank coals. However, the same result was not obtained for the whole range of coal samples, since rank effect was not included. Therefore, a petrofactor combining both effects of petrographic composition and rank as a function of vitrinite reflectance could be used to assess combustion differences of different rank bituminous coals.

Acknowledgement

The writers would like to thank the Turkish Hardcoal Enterprise for providing coal samples.

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