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REACTIVITY AND CHARACTERISATION OF VARIOUS RANK TURKISH BITUMINOUS COAL CHARS

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Abstract

A set of seven bituminous coal chars has been characterised by IR spectroscopy (FTIR), thermogravimetry (TG) and elemental analysis. FTIR study provided suitable information to establish differences between coal samples according to their chemical compositions. The reactivity of these samples was also studied and correlated with the coal parameters of mean vitrinite reflectance, fuel ratio and H/C ratio. The data suggest that reactivity as determined can be correlated with the mean vitrinite reflectance, fuel ratio and H/C ratio (0.90). The order of reactivity of samples were; Amasra (**S1**) (R_m=0.65)>Azdavay (**S4**) (R_m=0.99)≈Armutcuk (**S2**) (R_m=0.81)≈Acenta (**S3**) (R_m=0.92)>Ac2l2k (**S6**) (R_m=1.11) Cay (**S5**) (R_m=1.03)>Sogutozu (**S7**) (R_m=2.14).

Keywords: char reactivity, C/H ratio, DTG, FTIR, fuel ratio, reflectance, TG

Introduction

Various methods are used to predict the combustion behaviour of coal; experiment and indices, such as proximate analysis, determining petrographic constituents and reflectance. Experiment is a direct approach and very expensive. The latter is predicting the combustion behavior by using indices associated with the nature of coals so indices can also be used for solving operational problems of boilers. Infrared spectroscopy is widely used for many years for the study of structure of coal and its derivatives. Earlier studies were on determination of functional groups and extinction coefficients [1–3]. The development of FTIR spectrometers due to improved sensitivity and accuracy of the band position allowed the various functional groups such as OH, aliphatic and aromatic CH stretching, and carboxylic groups (COOH) and also used for the determination of hydrogen bonds [4–7]. The combustion performance of a particular coal is governed by pyrolysis and char combustion. The pyrolysis stage also affects the performance of the char combustion by influencing the type of char to be produced [8]. The combustion rate of coal particles mostly related to reactivity of char. The reactivity of a char and combustion efficiency of coal particles mostly linked to petrographic composition [9, 10], coal rank [11], particle size [12] and mineral content [13].

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Vitrinite macerals are known as the most reactive. The least reactive behavior of the inertinites is attributed to their aromatic nature [14]. The liptinites especially sporinites have lowest ignition temperature due to their higher volatile content than vitrinites and inertinites [14]. It has been reported that although vitrinite macerals begin combustion slightly higher temperatures than other macerals, they burn faster than semifuzinites and sporinites [9]. Unburned particles in fly ashes have been related to inertinites, semifuzinites and oxidized vitrinites [10]. However, some writers have linked unburnt particles in fly ash to coarse size group coal rather than petrographic composition [11, 15].

Thermogravimetric studies are strongly affected by particle size, ash content, sample amount, heating rate and gas flow rate [14, 16]. The present investigation is an experimental study using TG and FTIR to determine the char reactivity data for various rank coals to compare their combustion characteristics and characterization of these coals.

Experimental

Samples

Coal samples were taken as channel samples from seven mines of the Turkish Hardcoal Enterprise. To reduce the effect of mineral matter on characterization, float material with 1.50 g cm^{-3} density was used in all analyses. Ground material at 200-mesh (75 μm) was used in char reactivity program. Proximate and ultimate analyses were obtained by using a high temperature furnace, a Leco-CHN 600 organic element analyzer and a Leco-S132 sulfur analyzer (Table 1). FTIR spectra were taken on a JASCO FTIR 300E spectrometer by co-adding 100 scans at a resolution 1 cm^{-1}. IR spectra of the coal extracts in xylene and pyridine were taken as $CHCl_3$ solution in liquid cell. Seven coal samples were extracted in xylene and pyridine. 100 mL pyridine used to dissolve 3 g of coal samples at 70°C on magnetic stirrer for 5 h. Then solution filtered and solvent evaporated on rotary evaporator at vacuum. Solid coal extract was dissolved in 1 mL $CHCl_3$ and IR spectra were taken in liquid cell on FTIR spectrometer.

Petrographic analyses were carried out under incident light by using a Zeiss Axioplan microscope and MPM 400 operating system (Table 2). Maceral grouping was made as vitrinite, liptinite, inertinite and semi-fusinites on mineral free basis. Maximum reflectance measurements were made on all the suitable vitrinite macerals. Reflectance measurement on inertinites was made to determine fusible inertinites as suggested before [19].

As seen in Table 2, sample **S1** is high volatile C bituminous, **S2** is high volatile B bituminous **S3**, **S4** and **S5** high volatile A bituminous, **S6** is medium volatile bituminous and sample **S7** is low volatile bituminous coal. The similar classification can also be made by using volatile contents of samples (Table 1). Sample **S2** has the lowest reactive maceral content (78.3%) and sample **S3** has the highest reactive maceral content (95.5).

Table 1 Proximate and ultimate analyses of samples

Parameter	Sample No.						
	S1	**S2**	**S3**	**S4**	**S5**	**S6**	**S7**
Proximate, d.b/mass%							
Ash	8.03	5.14	5.28	10.42	9.33	5.15	8.78
Volatiles	38.13	36.47	31.04	29.20	31.02	24.83	10.11
Fixed carbon	53.84	58.39	63.68	60.38	59.65	70.02	81.11
Fuel ratio[a]	1.41	1.60	2.05	2.07	1.92	2.82	8.02
Ultimate, d.b./mass%							
C	72.38	78.82	82.40	77.63	80.22	83.83	82.47
H	4.54	4.75	4.83	4.36	4.29	4.48	3.16
N	0.60	0.90	0.72	0.80	0.93	0.63	0.70
O (difference)	14.45	10.39	6.77	6.79	5.23	5.91	4.89
S	0.60	0.36	0.55	1.13	0.62	0.44	0.65
H/C ratio	0.77	0.72	0.71	0.67	0.65	0.64	0.46

[a] The ratio of fixed carbon to volatile matter

Table 2 Petrographic analyses of samples

Parameter	Sample No.						
	S1	**S2**	**S3**	**S4**	**S5**	**S6**	**S7**
Maceral group[a]							
Vitrinite	75.5	56.6	85.5	88.3	60.4	83.4	84.1
Liptinite	3.2	8.5	5.2	0.8	5.3	2.2	0.1
Semi-fusinite	12.3	18.3	6.8	4.7	19.3	6.0	10.5
Inertinite	9.0	16.6	2.5	6.2	15.0	8.4	5.3
Total reactives	86.7	78.3	95.5	92.5	78.6	90.1	87.2
Mean reflectance[b]	0.65	0.81	0.92	0.99	1.03	1.11	2.14

[a] Maceral data in volume%, mineral-matter free
[b] Maximum reflectance measurements made on all suitable vitrinites

Methods

Coal chars were produced in a PL TGA 1500. A 10 mg coal sample was heated to 700°C at 10°C min^{-1} heating rate in nitrogen with a flow rate of 15 $\text{cm}^3\ \text{min}^{-1}$. The atmosphere was switched to air at same flow rate following cooling the furnace to 500°C for isothermal char reactivity determination. The detail of the char reactivity program is given elsewhere [18]. Low temperature has been chosen to allow oxygen to enter interior of the chars and so burnout from inside and external surface of the chars as suggested elsewhere [19]. Char reactivity (R) was calculated as:

$$R=(-1/W_0)(\mathrm{d}W/\mathrm{d}t)$$

where W_0 is the initial mass of char (dry ash free, at the beginning of isothermal heating) and $\mathrm{d}W/\mathrm{d}t$ is the maximum rate of mass loss (at isothermal section of DTG curve).

Results

Qualitative interpretation of the IR spectra

Infrared spectroscopy is sensitive to the presence of specific functional groups in organic materials. In IR spectra four regions of the spectrum have been of particular use: OH stretching modes near 3400 cm^{-1}, the aromatic C–H stretching modes between 3000–3100 cm^{-1}, the aliphatic C–H stretching modes between 2800–3000 cm^{-1} and C=C and C=O stretching modes in between 1550–1800 cm^{-1} (Fig. 1).

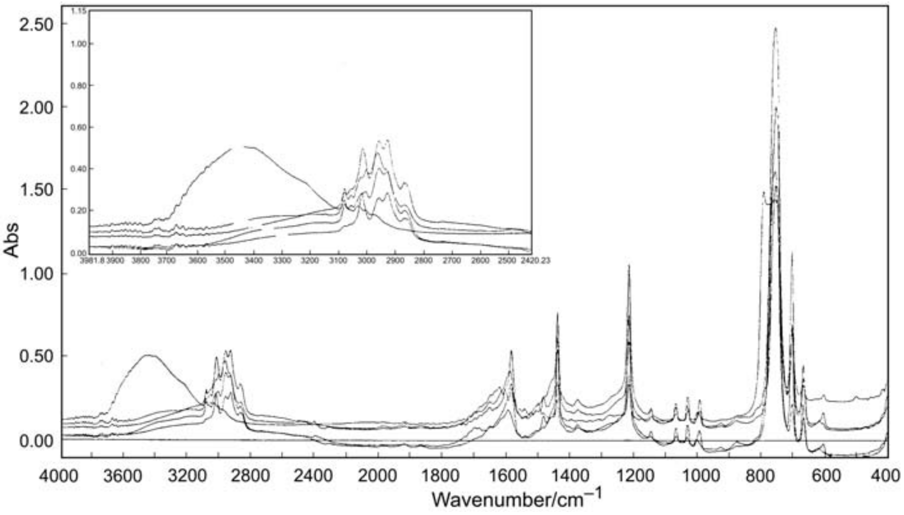

Fig. 1 FTIR spectra of some samples

A set of 7-coal extract has been characterized by FTIR. Both alkyl and OH groups can be identified. The band intensities were used for the evaluation of aromatic and aliphatic hydrogen concentration.

Assignment of O–H stretching modes: 3100–3600 cm^{-1}

The broad band in the range of 3100–3600 cm^{-1} could be attributed to O–H groups that form various types of hydrogen bands in between oxygen of ether and cyclic OH groups. Relatively strong OH band was observed at 3444 cm^{-1} in the spectrum of **S3**. The intensity of this band decreased in the sequence of **S3>S6**>**S7**>**S5**>**S2**>**S1**>**S4**.

Assignment of C-H aromatic stretching modes: 3000–3100 cm^{-1}

Stretching vibration of aromatic C–H groups appeared at 3080, 3018, 3015 and 3015 cm^{-1}. These peaks were weak in **S1** and overlapped by O–H in **S4** coal extract. The intensity of aromatic C–H vibration at about 3050 cm^{-1} was similar for **S3**, **S2**, and **S6** and high in **S5** and **S7**.

Assignment of C–H aliphatic stretching modes: 2800–3000 cm^{-1}

Aliphatic C–H groups absorb at this region. Peaks at 2962, 2957, 2927 and 2935 cm^{-1} are attributed to asymmetric CH_3 and CH_2 vibration. The intensity of absorption of aliphatic groups varies in dependence on coal extract of the regions.

Assignment of C=C and C=O stretching modes: 1550–1800 cm^{-1}

The band at 1600 cm^{-1} assigned to stretching C=C groups in aromatic ring showed variable intensity with maximum for **S7**, lower intensity in **S1** in IR spectrum was due to weaker absorption of C=C groups in condensed aromatic systems. The position of band maximum slightly shifted to lower wave numbers in **S1** coal extract. The band at 1730 cm^{-1} was attributed to carbonyl group [20]. This band was not observed in **S1** and **S5** coal extracts and other coal extracts contain small concentration of carbonyl absorption.

Interpretation of the DTG curves

The DTG curves of the coal samples are given in Fig. 2. The DTG curve shows both non-isothermal (char production section) and isothermal heating (char reactivity section) conditions approximately before and after 70th min, respectively.

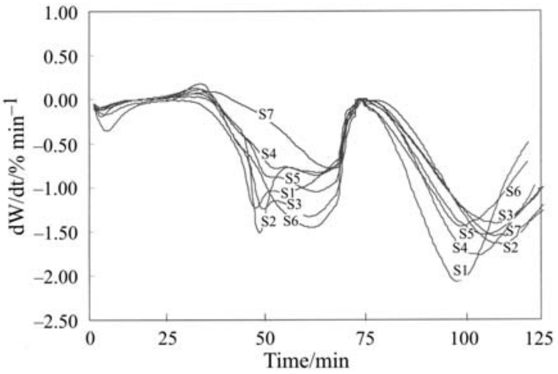

Fig. 2 DTG profiles of the samples at isothermal conditions to 70th min and non-isothermal conditions after 75th min

In non-isothermal section of DTG curves all the samples show two peaks except sample **S6** and **S7**. The volatile content of the samples affected the pattern of DTG curves. High volatile content samples **S1**–**S5** show very similar DTG patterns. The doublet in curve could be attributed to emission order of various volatiles and devolatilization rate of various petrographic components. A narrow and a single peak for sample **S5** could be ascribed to its low volatile content of about 10.11%.

Table 3 Char reactivity results

Parameter	Sample No.						
	S1	**S2**	**S3**	**S4**	**S5**	**S6**	**S7**
Initial mass, W_0/%	75.25	70.78	74.35	75.17	71.62	78.76	85.80
Max. rate of mass loss/% $\min^{-1}$	2.07	1.64	1.70	1.76	1.53	1.73	1.55
Char reactivity/R	2.75	2.32	2.29	2.34	2.14	2.20	1.81

In the isothermal section of DTG curves, samples **S2**–**S6** showed similar pattern. The sample **S1**, is the lowest rank coal, had the sharpest DTG peak and therefore the highest rate of mass loss (2.07% $\min^{-1}$) than the rest of the samples (Table 3).

Correlation of char reactivity data with basic coal parameters

The calculated char reactivity data were related with basic coal parameters of petrographic factors (as total reactive macerals, vitrinite reflectance), fuel ratio and H/C ratio. Except total reactive macerals the rest of the coal related factors can be linked to coal rank (coalification degree). However, variations in maceral distribution are known to be an important factor causing deviations in relation between the combustion parameters and coal rank [18].

The results of the char reactivity determination procedure are given in Table 3. These results include both calculated char reactivity data and the data derivated from isothermal section of TG and DTG curves.

The data indicate good correlations between char reactivity data and some basic coal data. The char reactivity decreased with increasing coal rank. The lowest rank sample (**S1**) had the highest reactivity (2.75) and the highest rank coal (**S7**) had the lowest reactivity (1.81). Mean vitrinite reflectance showed good relation with char reactivity. A general trend of decreasing char reactivity with the increase of the rank of parent coal was observed as reported [21–23]. The relation between char reactivity and mean vitrinite reflectance (Fig. 3) was far better than char reactivity-total reactive maceral amount relation (Fig. 4). This was expected since it has been known that chemical composition of maceral groups varies significantly with coal rank [14]. The deviations in the reactivity data by rank could be attributed to their maceral distribution in some cases. It was reported that reactivity values constitute a band of data rather than falling on a single line when related to the reflectance data [18]. Having higher vitrinite reflectance value, **S4** (R_m=0.99, R=2.34) had almost the same reactivity with **S2** (R_m=0.81, R=2.32). The amount of total reactive macerals of **S2** and **S4** were 78.3 and 92.5% respectively.

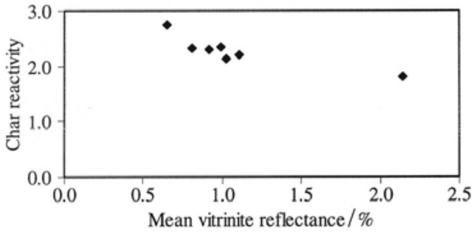

Fig. 3 Mean max vitrinite reflectance *vs*. char reactivity

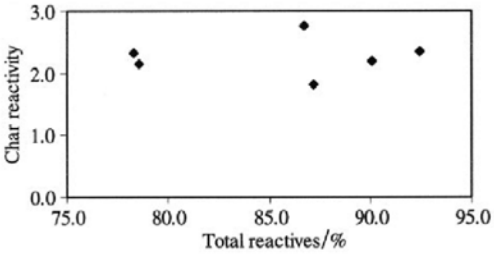

Fig. 4 Amount of total reactive macerals *vs*. char reactivity

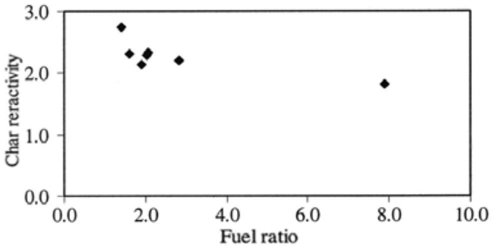

Fig. 5 Fuel ratio *vs*. char reactivity

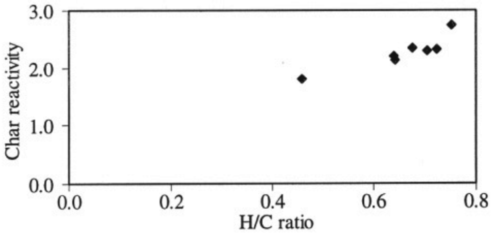

Fig. 6 H/C ratio *vs*. char reactivity

As basic coal data parameters, fuel ratio and H/C ratio were correlated with char reactivity. The relation between char reactivity and fuel ratio was fairly good, Fig. 5.

The char reactivity increased with reduced fuel ratio as reported by Young and his co-workers [24].

Ultimate carbon and H/C ratio have been widely used to correlate combustion parameters. There was almost linear relation between char reactivity and H/C ratio, Fig. 6. Young *et al*. [24] reported similar trend between the char reactivity and ultimate carbon.

Briefly, char reactivity could be correlated with mean vitrinite reflectance, and basic coal data parameters; fuel and H/C ratio.

Conclusions

The appropriate combination of conventional techniques used for coal char characterization, like elemental analysis, FTIR and thermal analysis. FTIR spectroscopy allows us to distinguish between coal chars from different origin.

The highest aromatic hydrogen concentration was observed for **S5**, **S6**, **S7**, **S6** and **S3** coal extracts and lowest for **S1** and **S4** in apolar aromatic solvent (xylene) but in polar aromatic solvent (pyridine) aromatic and aliphatic hydrogen were very close and similar for **S3** and **S2** coal extracts. The highest aromatic hydrogen concentration was observed for **S7**, **S5** and **S6** coal samples and lowest for **S4** and **S1**. On the other hand **S3** and **S6** coal extract contained high amount of polar OH group as aliphatic and aromatic compounds. This group was absorbed at 3444 cm^{-1} and there was relatively strong absorption at this wavenumber.

The data indicated that char reactivity could be correlated with reflectance data and basic coal data parameters; fuel ratio and H/C ratio. The correlation coefficients between char reactivity and coal parameters of mean vitrinite reflectance, fuel ratio and H/C ratio varied in between 0.8 and 0.9. There was almost no relation between char reactivity and total reactive macerals since chemical composition of coals vary with coal rank.

The reactivity of coal chars could be used to assess combustion differences of the various rank coal samples. A general trend of increasing char reactivity was observed with decreasing coal rank. As the reactivity increases rank will decreases and this could be observed from the FTIR spectra of these samples. The order of char reactivity of the samples were: **S1** (R_m=0.65)>**S4** (R_m=0.99)≈**S2** (R_m=0.81)≈**S3** (R_m=0.92)>**S6** (R_m=1.11)>**S5** (R_m=1.03)>**S7** (R_m=2.14). The deviations occurred in the order of char reactivity with coal reflectance could be attributed to reactive maceral contents of samples.

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