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EFFECT OF CHEMICAL DEMINERALIZATION ON THERMAL BEHAVIOR OF BITUMINOUS COALS

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Growing environmental concerns and the need for alternatives for oil and natural gas resulted in intensive researches on ultra clean coal (UCC). Therefore, the researches related to practice and application of various methods to produce UCC become more important. Thermal characterization of chemically demineralized coals by thermogravimetric analysis method is presented in this study. The aim of the study is to provide thermal data for HF–HNO_3 leaching system used for the production of UCC. Coal samples were first physically enriched by density separation. Then the enriched portion was chemically demineralized by using HF and HNO_3, respectively. Ash content of coal samples were reduced to a range of 0.12–0.41% by chemical demineralization process. The petrographic, ultimate and proximate analyses were carried out to determine main features of samples. Physically and chemically enriched coal samples were then analyzed in a TG by two different techniques separately. The first technique covered thermal characterization of samples under non-isothermal conditions. Characteristic temperatures for each sample were obtained from the TG and DTG data. The second technique involved the determination of reactivity of in situ produced chars of each sample.

Keywords: *demineralization, DTG, reactivity, thermal behavior, UCC*

Introduction

The production of low-ash coal (UCC) has a significant importance in the future of coal usage areas. It is considered as an alternative for heavy fuel oil and gas. UCC is cost competitive with oil and gas especially following sharp increases in the prices of these fuels [1].

UCC could be directly fired into a gas turbine with a high thermal efficiency, to produce electricity. Additionally, it could be used to manufacture carbon electrodes in the process for producing aluminum, and as a raw material for the production of carbon based chemicals and materials.

The use of UCC in combustion is environmentally friendly because of its limited ash content and restriction of CO_2 as the only significant emission to atmosphere. Additionally, as another advantage, a UCC fired gas turbine combined cycle power plant is more amenable to locating close to the electricity users consequently considered more efficient than is the case for conventional coal fired generators.

The production of UCC in plant scale with regeneration of leaching chemicals has been experienced in Australia, USA and Europe [1–3]. By-products like alumina and silica and trace elements like vanadium, thorium and uranium can be obtained along with the production of UCC.

Ash/mineral matter reduction to produce UCC is mainly performed by using physical or chemical techniques and lesser extent by using flotation and agglomeration techniques that have a basis of surface characteristics [4–7]. Physical separation techniques used to produce UCC are composed of density separation of feed material ground below liberation size of organic matter-mineral particles. The most important factor governing physical enrichment processes is necessity of very fine grinding, typically 3–5 μm median size, to separate organics/inorganics or organic constituents (macerals) from each other [8]. Therefore, these applications are limited by use of density separation under very high centrifugal forces [7, 9, 10].

Chemical enrichment processes either alone or following a physical separation (density separation) are extensively used in UCC production [4–6, 11–14]. The method involves the selective leaching of inorganic constituents by various solvents. The solvents used in chemical demineralization processes are various inorganic acids such as HF [4, 13, 14], HCl [13, 14], HNO_3 [4, 14], H_2SO_4 [15]; some bases like NaOH [12]; and oxidizing agents like H_2O_2 [16], $FeCl_3$ [15]. HF or the systems where HF applied are the most commonly used leaching agents among those solvents.

TG/DTG is used to obtain burning profile and parameters like characteristic temperatures and reactivity derived from these profiles. Although these parameters do not totally reflect burning conditions, they can be used to assess relative burning properties of various coals/coal blends and activated carbon [17–22].

Cuesta *et al.* [23] studied combustion behaviour of perhydrous coal that is known with their high hy-

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drogen content by TG/DTG. The study based on the reactivity and combustion profile data produced from TG and DTG profiles. They found a strong relationship between rank and reactivity data.

Miyake *et al.* [24] studied the effect of atmospheric conditions on the spontaneous ignition of activated carbon. They claimed that increased oxygen concentration increases oxygen adsorption by activated carbon. They used TG profiles to estimate the spontaneous ignition characteristics of activated carbon.

Arenillas *et al.* [25] used TG/DTG profiles to characterize the ignition behaviour of coal blends. They investigated the use of TG/DTA in characterization of combustion behaviour of coal blends. Since it is almost impossible to use one kind of coal in boilers they claimed that the determination of possible behaviour of coal blends during combustion has a significant importance.

Strezov *et al.* [26] studied the effect of different flow rate on specific heat during coal pyrolisis. They used a computer aided thermal analysis technique for continuous measurement of specific heat. The gases evolved during heating of coals analyzed by TG-FTIR.

Mineral matter content of coal has an important role in characterization and overall efficiency of coal combustion. Burning characteristics of chars produced from demineralized coals are significantly improved when compared to those of produced from original parent lignite [27]. Moreover, Rubiera *et al.* [5] showed that demineralization improved burning parameters of (T_{50}, T_b and reactivity) bituminous coals. They concluded that isothermal reactivity in a TG showed that the demineralized sample presented better combustibility characteristics than those of the parent coal.

Ozbaş *et al.* [28] reported that removal of mineral matter enhanced the burning parameters of peak and burnout temperatures. They concluded that cleaning improves the combustion characteristics of the lignite.

In this study, proximate, ultimate and petrographic (only applied on density separated samples) analyses were used for general characterization of samples. The TG and DTG thermal analysis techniques were carried out to determine and to compare burning properties of both density-separated and chemically demineralized samples.

Experimental

Materials

Coal samples were taken as channel samples from three mines of the Turkish Hardcoal Enterprise and from imported Australian and Polish coals that were provided by Ereğli Iron and Steel Factories. All samples, following gravity separation, were characterized by petrographic, proximate and ultimate analyses. Density separation was performed in solution of calcium nitrate for Turkish coals (at a density of 1.50 g cm^{-3} for the samples denoted as TB1, TB2 and TB3). The imported coal samples denoted as AB for Australian and PB for Polish coals were not subjected to any physical cleaning since they had been provided as clean coal. Following density separation, one part of the samples was stored for petrographic analyses. The rest of the sample was first crushed to –2 mm by using a roll crusher then it was ground to –74 μm in a ring mill. Here, staged grinding controlled with a 200-mesh screen was carried out to prevent over-grinding.

Methods

Proximate and ultimate analyses were carried out on ground material for –74 μm sizes and the data were obtained by using a high-temperature furnace, an adiabatic calorimeter, Leco-CHN 600 organic element analyzer and a Leco-S132 sulfur analyzer (Table 1).

Petrographic analyses were carried out under incident light by using a Zeiss Axioplan Microscope equipped with a photometer, a point counter and a mercury fluorescent light source. Blue light excitation, when applicable, was used to differentiate liptinite macerals from mineral matter and moulding resin. Maceral group analysis was carried out on mineral free basis. Sample preparation for petrographic analyses is described elsewhere [29–31]. The vitrinite reflectance was measured on telocollinite macerals based on 100 points as defined by ISO 7404-5 [32]. Point counting to determine the maceral group composition was employed for all the feed samples. 500 points were counted under reflected white light. Details of the determination of the maceral group composition are given elsewhere by ISO, 7404-3 [33]. The results of petrographic analyses are given in Table 2.

Table 1 Proximate and ultimate analyses of density separated coal samples

Sample	Proximate analysis				Ultimate analysis/%				
	ash/%	volatile/%	fixed C/%	cal. value/kJ kg^{-1}	C	H	N	O	S
AB	5.97	29.52	64.51	32635	78.95	4.78	1.30	8.49	0.54
PB	6.64	27.00	66.36	32292	81.82	4.42	0.43	5.95	0.74
TB1	8.27	28.15	63.58	32146	78.48	4.65	0.69	5.86	1.59
TB2	7.71	39.41	52.88	28506	69.92	4.96	0.26	16.60	0.65
TB3	7.65	12.18	80.17	32355	82.70	3.40	1.22	3.58	0.97

Table 2 Petrographic analyses of samples

Sample	Petrographic composition[1]/%				Vitrinite reflectance[2]/%
	vitrinite	liptinite	inertinite	semi-inertinite	R_m
AB	67.40	1.20	11.00	20.40	0.89
PB	76.10	3.90	10.10	9.90	1.06
TB1	84.68	0.80	9.20	5.32	1.02
TB2	77.18	4.17	7.70	10.95	0.71
TB3	82.10	0.30	6.18	11.42	1.95

[1]by volume mineral matter free basis, [2]on telocollinite macerals

After density separation, the chemical demineralization process was carried out in two steps by using analytical grade HF and HNO_3, respectively. The first step was leaching the sample with HF solution of 2 M. A mixture of about 25 g coal sample and 100 mL solution was prepared. The mixture was stirred 3 h on a hotplate-magnetic stirrer. Evolved gases via condenser were trapped and fed into to the flask during the leaching procedure. The temperature was increased from ambient to 70°C. The leached material filtered and rinsed with distilled water and dried overnight in a drying oven at 80°C. The material taken from HF leaching subjected to second demineralization with 2 M HNO_3 solution at previously given conditions. Moisture, ash content and organic elemental distribution of the products leaching experiments were determined.

The thermogravimetric analyses were carried out by using a PL TGA 1500 thermogravimetric analyzer. The tests were carried out with a 10±0.1 mg coal sample in a platinum crucible. The sample was heated to 850°C at 10°C min^{-1} in air with a flow rate of 15 cm^3 min^{-1} to determine the characteristic temperatures. The loss of mass, time and temperature were recorded simultaneously. This data then transferred to a computer to establish TG and DTG curves. The characteristic temperatures were designated as follows:

- T_{ic}=temperature of initial chemisorption
- T_{mc}=temperature of maximum rate of chemisorption
- T_i=initial temperature where mass loss reaches to a rate of 1% per minute
- T_p=peak temperature at maximum mass loss rate
- $T_{1/2}$=temperature at which 50% burnoff (mass, ash free basis) occurs, and
- T_b=burnout temperature where DTG profile reaches a 1% combustion rate at tail end of the profile.

The percentage of total oxygen chemisorption was the mass gain following loss of moisture.

Reactivity was determined on in situ produced coal chars as used previously [34]. Approximately 10 mg coal sample was heated from ambient temperature to 700°C at 10°C min^{-1} heating rate with 15 mL min^{-1} flowing nitrogen. The atmosphere of the furnace then switched to dry air following cooling the furnace to 500°C to determine isothermal char reactivity. Char reactivity (R) was calculated as:

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

where W_0 is the initial mass of char (dry ash free, at the beginning of isothermal heating) and dm/dt is the maximum rate of mass loss (at isothermal section of DTG curve).

Results and discussion

Demineralization

HF was used as the first step of chemical demineralization because of its very well-known effect on silicate group minerals that accompanied to coal [4–7, 13]. However, the effect of HF on sulphur is limited and also HF causes formation of insoluble compounds like CaF and MgF [13]. Following HF, HNO_3 was used for desulphurization and removal of those insoluble fluorite compounds formed during the HF treatment [4].

Proximate and ultimate analyses of chemically demineralized samples are given in Table 3. Ash level of coal samples, except for the TB2 (0.4%), decreases down to 0.2% which can be accepted as very low value according to some sources [4, 11, 12]. This makes coal samples to meet almost whole UCC usage conditions in the aspect of ash content.

There is a significant increase in volatile constituents of samples following chemical demineralization. In the TB3 coded sample, which has the highest rank, the increase of volatiles is from 12.2 to 35.0%. However, the increase of volatile constituent in the PB coded sample is limited with respect to other coal samples.

The highest change in fixed carbon percentage is in the TB3 coded sample having the highest rank. In this sample, there is a sharp decrease in fixed carbon percentage (from 80.2 to 64.8%) after chemical demineralization.

The change in calorific values is inversely proportional to that of fixed carbon percentage after chemical demineralization. Calorific value decreases significantly in all the samples. This decrease is in the range of 3205–6962 kJ kg^{-1}.

Table 3 Proximate and ultimate analyses of chemically demineralized coal samples

Sample	Proximate analysis				Ultimate analysis				
	ash/%	volatiles/%	fixed C/%	cal. value/kJ kg^{-1}	C/%	H/%	N/%	O/%	S/%
ABd*	0.19	41.93	57.88	25673	66.47	3.39	3.45	23.05	0.36
PBd	0.22	37.40	62.38	29087	74.33	3.73	3.89	17.31	0.52
TB1d	0.15	42.24	57.61	25761	67.99	3.95	3.71	23.25	0.95
TB2d	0.41	54.01	45.58	23790	62.43	3.99	4.20	28.42	0.55
TB3d	0.18	35.00	64.82	26803	70.70	2.78	4.40	21.24	0.70

*d stands for demineralized

The change in organic elemental composition of chemically demineralized samples verifies the proximate analysis data. While the percentages of carbon and hydrogen decrease, the percentages of oxygen and nitrogen increase drastically. The change in oxygen percentage is in the range of 11.4–17.7%. These changes explain the decrease in both fixed carbon percentage and calorific value. It can be considered that the increase in volatiles in chemically demineralized coal samples has resulted from oxidation and nitration [11, 35]. This situation is well-matched by the studies of Rubiera *et al.* [5].

Thermal characterization

In order to determine the burning properties of coal samples two separate programs were applied in TG, namely non-isothermal and char reactivity. Since it is assumed that the DTG curves are sufficient to give the general behaviors of samples in thermal analysis TG curves are not presented in the study. However, TG data were used to produce burning parameters.

Non-isothermal characterization

This program was composed of interpretation of DTG curves obtained in non-isothermal conditions and the data obtained from both TG and DTG curves.

The DTG curves of density-separated coal samples in non-isothermal conditions are given in Fig. 1. Moisture loss is completed around 100°C and it gives a peak in the range of 60–100°C in all density-separated samples. The peak corresponding mass loss, starting around 150°C and completed around 300°C, represents the chemically adsorbed oxygen (oxygen chemisorption).

Decomposition of density-separated samples starts between 310–340°C and is completed around 550°C in all samples. Doublet peaks seen in the DTG curves of the PB coded sample point out two-stage decomposition. The peak around 440°C corresponds to the primary decomposition in which volatiles and light products are vanished. However, the peak around 480°C corresponds to the burning of heavier products and remaining char.

The DTG curves of chemically demineralized coal samples are given in Fig. 2. As seen in the figure, moisture loss is completed around 100°C for all of the coal samples. Unlike density-separated samples, there is no oxygen chemisorption. This may be resulted from the active sites in coal structure being saturated by the adsorption of oxygen and the formation of nitrate compounds during the HNO_3 leaching. The curves corresponding decomposition of organic constituents are similar to those of density-separated coal samples.

Combustion profile parameters were derived from the TG and DTG curves of non-isothermal study (Table 4). Since there was no oxygen adsorption in chemically demineralized coal samples, no values which represent this behavior (T_i, T_{mc} and chemisorption) were obtained. As seen in Table 4, T_{ic} and chemisorption

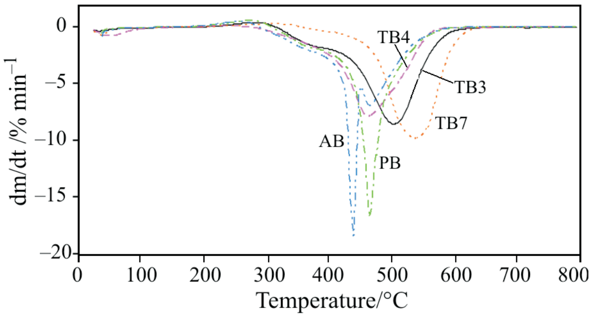

Fig. 1 DTG curves of density separated coal samples under non-isothermal conditions

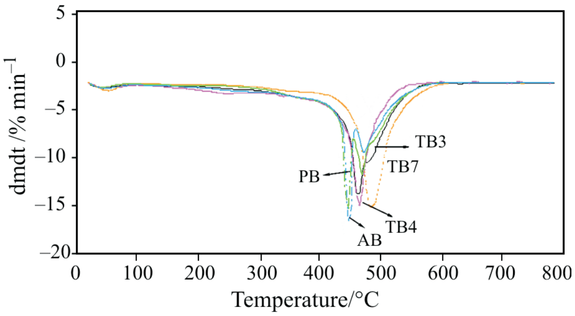

Fig. 2 DTG curves of chemically demineralized coal samples under non-isothermal conditions

Table 4 Combustion profile parameters of density separated and chemically demineralized coal samples

Sample	Parameter							
	T_{ic}/°C	T_{mc}/°C	T_i/°C	T_p/°C	$T_{1/2}$/°C	T_b/°C	chemisorption/%	R_{500}/min^{-1}
AB	138	259	293	439	444	588	3.49	0.1041
ABd[1]	nd[2]	nd	294	453	450	593	nd	0.2060
PB	140	277	311	465	466	590	4.37	0.1022
PBd	nd	nd	302	450	456	591	nd	0.2123
TB1	141	283	321	502	496	621	3.25	0.1063
TB1d	nd	nd	303	468	464	584	nd	0.2289
TB2	163	241	293	473	470	580	0.75	0.2210
TB2d	nd	nd	251	469	449	570	nd	0.2472
TB3	149	312	366	540	545	645	2.90	0.1521
TB3d	nd	nd	310	489	487	612	nd	0.2485

[1]d: stands for demineralized, [2]nd: not detected

values show a random distribution in density-separated coal samples. However, T_{mc} has the lowest value for the sample having the lowest rank and has the highest value for the sample having the highest rank.

Char reactivity characterization

The DTG curves of density-separated and chemically demineralized samples for reactivity determination are given in Figs 3 and 4. The two sets of DTG curves show both non-isothermal (char production section) and isothermal heating conditions. In both DTG curves, there is a deviation at about 70th minute and it results from the change of atmosphere from nitrogen to air. In isothermal section, the decomposition of density-separated coal samples begins at 200 and ends at about 700°C. Following the change of atmosphere to air there is a rapid burning. Chemically demineralized samples gained a hygroscopic behavior because of the probable activation during leaching. Thus, a moisture loss occurred, beginning at low temperatures. Decomposition of chemically demineralized samples starts at lower temperatures (180°C) when compared with that of density-separated coal samples, and it gives a peak at about 250–300°C. This peak was not observed in density-separated coal samples. It can be an indication of the release of nitrogen compounds which have been reported to be relatively unstable at high-temperatures [18, 36]. Following this behavior the devolatilization was completed.

In isothermal section where char burning occurred, the peaks seen in the DTG curves of density-separated samples shift to lower temperatures in chemically demineralized samples. The results of the reactivity parameter (R_{500}) calculated from data of both non-isothermal and isothermal sections are given in Table 4. The R_{500} data show that there is a clear increase in reactivity of chemically demineralized samples when compared to that of density-separated parent samples.

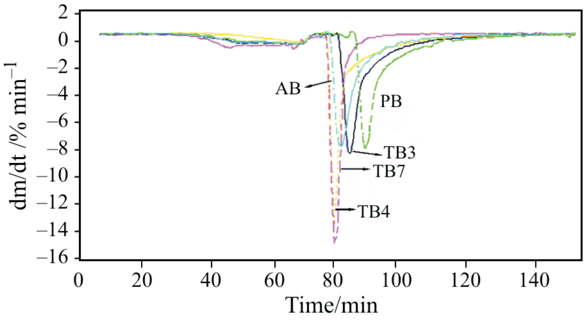

Fig. 3 DTG curves of density separated coal samples in char reactivity program

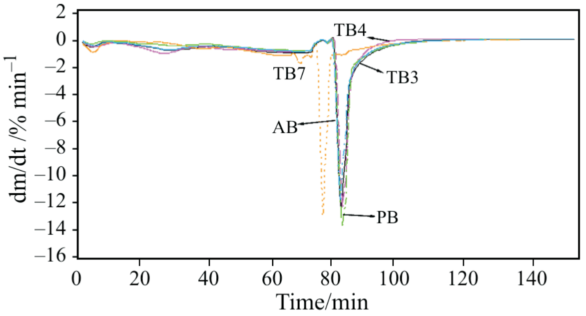

Fig. 4 DTG curves of chemically demineralized coal samples in char reactivity program

Conclusions

Applying chemical demineralization by HF and HNO_3 products having ash content ranging from 0.15 to 0.41% were obtained. There was an increase in N and O contents of chemically demineralized samples in the range of 2.15–3.94% for N and 11.82–17.66% for O. Unlike N and O contents, there was a decrease in C and H contents in the range of 7.49–12.48% for C and 0.62–1.39% for H. A decrease has occurred in calorific value of samples in the range of 3205–6962 kJ kg^{-1}. It can be deducted that these changes were resulted from the oxidation and nitrification effect of HNO_3.

The thermal analyses of chemically demineralized samples performed in non-isothermal conditions showed that; *i*) there was no oxygen adsorption in the resulting product of chemical demineralization, *ii*) T_i, T_p, $T_{1/2}$ and T_b values shifted to lower temperatures with respect to those of density-separated samples.

The result of reactivity program showed that *i*) a peak that was only observed for chemically demineralized samples formed around 250–300°C and it was an indication of release of nitrogen compounds bounded to coal during HNO_3 leaching, *ii*) The reactivity values of chemically demineralized samples calculated from TG and DTG data were lower than those of their density separated parent samples.

TG data can be used to compare the changes in burning properties and structure of chemically demineralized coals with their parent coals. The net effect of HNO_3 on samples as supported by both ultimate and TG analyses was to cause oxidation and nitrification that reduced calorific value. Moreover, significant amount of NO_x products will be evolved to atmosphere because of the formation of nitrogen compounds.

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