Journal of Thermal Analysis and Calorimetry, Vol. 90 (2007) 3, 859–863

CHANGES IN COAL CHAR REACTIVITY AND TEXTURE DURING COMBUSTION IN AN ENTRAINED FLOW REACTOR

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Char particle combustion is the slowest step in the combustion of coal, therefore char reactivity and texture have an important influence on this process. In this work, two coals were devolatilised in an entrained flow reactor and the chars obtained were burned under different experimental conditions in order to achieve various degrees of burnoff. Char reactivity was determined by means of non-isothermal thermogravimetric analysis, and the conversion-time data were evaluated by the random pore model proposed by Bhatia and Perlmutter. Char texture was characterised by means of N_2 and CO_2 adsorption isotherms. The surface areas obtained were used to calculate intrinsic reaction rate parameters. It was found that under chemical controlled conditions, the available surface area during combustion is best represented by the N_2 surface area.

Keywords: *entrained flow reactor, intrinsic char reactivity, N_2 surface area*

Introduction

During combustion, coal particles go through four well-defined steps: drying and heating-up, devolatilisation, oxidation of the combustible volatiles, and char combustion. Char particle combustion is the slowest step in the overall process and it has a significant effect on combustion efficiency [1], and on the levels of unburned carbon in the fly ashes, which finally determine its suitability for use in a specific process [2].

In pulverised devices, coal combustion takes place under the diffusion regime (Zone III). However, some studies have shown that in the later stages of combustion, char reactivity may control the overall combustion process [3].

Thermogravimetric analysis is a useful, simple and fast tool for studying and ranking the reactivity and kinetic parameters of carbonaceous materials [4–6]. It is a technique which can be applied under isothermal or non-isothermal conditions. The non-isothermal approach has the advantage of requiring less experimental time, especially when low reactivity chars are studied [7]. Different models can be applied to calculate apparent reaction rate parameters using non-isothermal thermogravimetric analysis [8, 9].

The intrinsic reactivity of chars is obtained by dividing the reaction rate by the specific surface area. However, there is controversy about which is the more suitable surface area for this purpose [10]. The most frequently used methods to evaluate char microporosity rely on the physical adsorption of gases [11], N_2 and CO_2 are the adsorbates most widely used to characterise char texture. N_2 adsorption isotherms are usually performed at 77 K. At these conditions the results obtained with this method are associated with larger microporosity [12]. CO_2 is usually conducted at 273 K, in these conditions this adsorbate is able to fill the small micropores due to its greater diffusivity in comparison to N_2 [13].

The objective of the present work is to relate the reactivity and the texture of coal chars, obtained under conditions which resemble those encountered in pulverised coal combustion, and to determine the effect of surface area variation during burnoff on char reactivity. For this purpose two coals of different rank were devolatilised in an entrained flow reactor (EFR). The chars obtained were fired under various oxygen concentrations in order to obtain different char burnoffs, and the reactivity of the char samples was determined by using a thermogravimetric analyser. The aim was to compare the reactivity of both coal chars and to study their variation with burnoff. The texture evolution of the chars with burnoff was also studied by determining the N_2 and CO_2 surface areas.

Experimental

Two coals of different rank were used in this work, a semi-anthracite (HV) and a low volatile bituminous coal (DI). The coals were ground and sieved to obtain a 75–150 μm size fraction; the proximate (ash, volatile matter and fixed carbon) and ultimate (carbon, hydrogen, nitrogen, sulphur and oxygen content) analyses of this size fraction are shown in Table 1.

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1388–6150/$20.00

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Table 1 Proximate and ultimate analyses of the coals used

	HV	DI
Proximate analysis (% db)		
Ash	9.1	5.5
V.M.	9.0	15.0
F.C. (by difference)	81.9	79.5
Ultimate analysis (% daf)		
C	90.8	86.3
H	3.7	4.1
N	1.8	0.8
S	1.8	3.7
O (by difference)	1.9	5.1

% db: dry basis, % daf: dry and ash free basis

An entrained flow reactor described elsewhere [14], was used to obtain chars with different degrees of burnoff. This device is a vertical furnace with a gas flow along the axis. The gas velocity inside the tube is enough to entrain the particles and to ensure a laminar flow. Under these conditions, particle residence time in the EFR can be controlled by adjusting the gas flow along the tube. This reactor provides experimental conditions close to those of a real fired combustor in terms of particle heating rate, and residence time. The reactor has an internal diameter of 4 cm and a length of 200 cm. Coal and primary gas flow were introduced through a cooled injector to ensure that the temperature did not exceed 100°C before entering the reaction zone. The secondary gas flow was preheated at furnace temperature and injected through flow straighteners. The reactor is electrically heated and temperature was maintained at 1273 K during the experimental runs. The coals were devolatilised using a nitrogen flow of 6.4 L min^{-1}. The devolatilised chars were then fired under different mixtures of N_2 and air, in order to vary the oxygen concentration at the reactor inlet (5, 10, 15 and 21% O_2). A total gas flow rate of 6.4 L min^{-1} was fixed in all the combustion tests.

The reactivity of the chars was evaluated using non-isothermal thermogravimetric analysis. A Setaram TAG 24 thermogravimetric analyser has been used in this work. A mass sample of 5 mg was heated at a constant rate of 15 K min^{-1} at an air flow rate of 50 mL min^{-1}. Sample mass loss and temperature were recorded continuously and the data collected were examined by using the random pore model of Bhatia and Perlmutter [15].

The texture of the samples was evaluated by means of N_2 and CO_2 adsorption isotherms at 77 and 273 K, respectively. The textural parameters were derived by applying a linearised form of the BET equation to the N_2 adsorption isotherms [16], and by applying the Dubinin-Radushkevich (DR) method to the CO_2 adsorption isotherms [17].

Results and discussions

Char conversion in the EFR

Char burnoff is the mass loss in the EFR and it is represented in Fig. 1 at the different oxygen concentrations. The values at a concentration of 0% O_2 correspond to the high temperature volatile yield. As can be seen, coal DI is more reactive than HV. At low oxygen concentrations (5 and 10%), the char of coal DI shows an important increase in burnoff. At the highest oxygen concentration (21%), coal DI was burned up almost completely, whereas coal HV reached a burnoff of 74%.

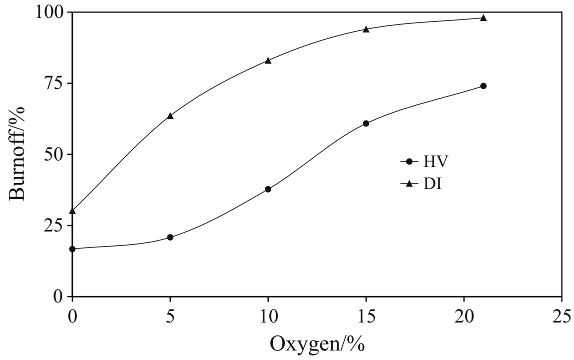

Fig. 1 Variation of chars burnoff with oxygen concentration in the entrained flow reactor

SEM micrographs of the chars are shown in Fig. 2. Considerable morphological differences can be appreciated between the devolatilised and partially burned chars. Char HV shows dense particles with a semi-angular shape. This non-plastic behaviour is typical of chars obtained from semianthracites. The devolatilised DI char exhibits highly fused particles with large pores, whereas the partially burned DI chars present open structures that are more accessible to oxygen during combustion under the diffusion regime. The higher reactivities of the DI chars in comparison to the HV chars are closely related to the chars morphology shown in the SEM images.

Reactivity of chars in TG

The Random Pore Model of Bathia and Perlmutter [15] was used in this work to study the oxygen-char reaction. The rate equation for this model can be written as follows:

$$\frac{dX}{dt}=k_0 e^{-E_a/RT}(1-X)[1-\psi\ln(1-X)]^{1/2}$$

where X is the char conversion on a dry ash-free basis, k_0 the overall frequency factor (s^{-1}), E_a the activation energy ($J\ mol^{-1}$) and ψ a structural parameter. Char conversion during TG test is defined in this work as:

$$X = \frac{M - M_f}{M_0 - M_f}$$

where M is the mass of sample remaining at any time and M_f and M_0 the final and initial mass respectively (excluding moisture). The initial specific surface area (S_0) is included in the overall frequency factor, k_0. The rate equation can be linearised and rate parameters can be determined from the data obtained in the non-isothermal thermogravimetric runs [9].

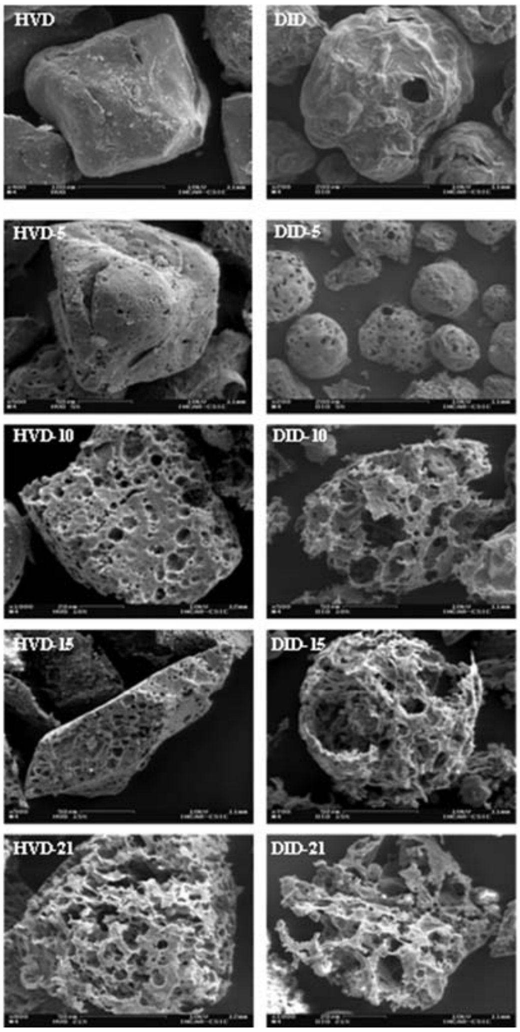

Fig. 2 SEM images of the chars obtained in the entrained flow reactor

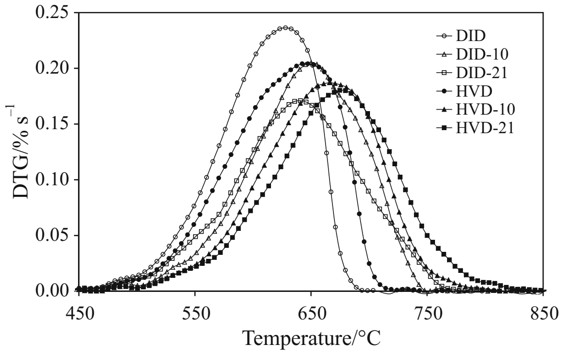

Fig. 3 Rate of mass loss of the chars during the non-isothermal thermogravimetric tests

The evolution of the mass loss rate of the chars with temperature is shown in Fig. 3. It can be seen that char reactivity decreases as particle burnoff increases; this is apparent from the shift of the curves to higher temperatures. The kinetic parameters calculated after applying the random pore model are presented in Table 2. The activation energy of the coal chars depicted in Fig. 4, remains almost constant with burnoff, and similar values for this parameter are attained for both samples. At very high burnoffs (94 and 98%) the activation energy of DI chars decreases appreciably. This could be attributed to the high ash content of these samples.

The variation of k_0 with burnoff is shown in Fig. 5. As combustion proceeds, a reduction in this parameter is observed for both coals. This tendency was expected as the activation energy did not show any appreciable variation with burnoff. However a decrease in reactivity with burnoff was observed. The

Table 2 Reaction rate parameters of the chars calculated using the random pore model

Sample	E_a/kJ mol^{-1}	k_0/s^{-1}
HVD	158	$5.59\cdot10^6$
HVD-5	162	$6.03\cdot10^6$
HVD-10	155	$2.01\cdot10^6$
HVD-15	157	$1.53\cdot10^6$
HVD-21	151	$8.54\cdot10^5$
DID	162	$1.31\cdot10^7$
DID-5	161	$6.97\cdot10^6$
DID-10	159	$2.14\cdot10^6$
DID-15	151	$1.49\cdot10^6$
DID-21	136	$2.16\cdot10^5$

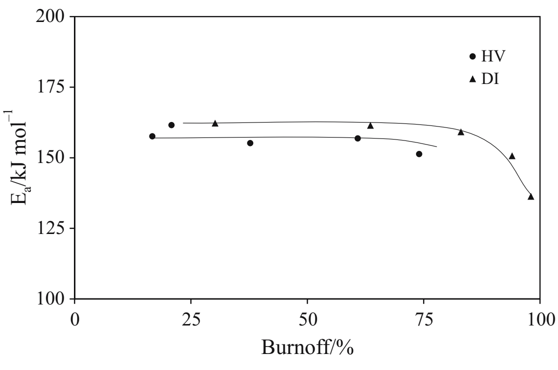

Fig. 4 Variation of the activation energy with burnoff

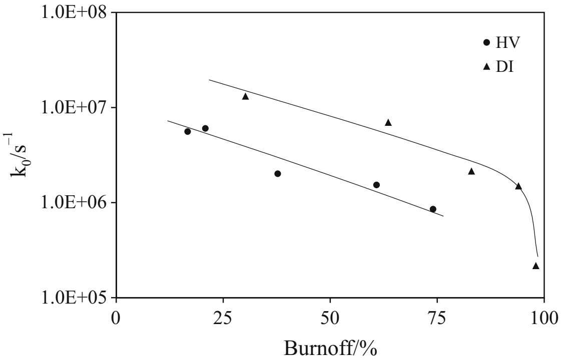

Fig. 5 Variation of the overall frequency factor with burnoff

higher reactivity of the DI chars is related to their higher k_0 values compared to those of the HV chars.

Texture of the coal chars

The specific surface area of the char samples was calculated from the N_2 adsorption isotherms using a linearised form of the BET equation [16]:

$$\frac{1}{n^{a}(1-p/p^{0})}=\frac{1}{n^{a}_{m}}+\frac{1}{n^{a}_{m}C}\left(\frac{1-p/p^{0}}{p/p^{0}}\right)$$

where n^a is the amount of gas adsorbed at a pressure p, n^a_m is the amount of gas required to form a monolayer, p^0 is the saturation vapour pressure of the adsorbate at the adsorption temperature and C is an equation parameter.

CO_2 specific surface areas were calculated using the Dubinin-Radushkevich equation [17]:

$$\ln W=\ln W_0-\left(\frac{RT}{\beta E_0}\right)^2\ln^2\left(\frac{p^0}{p}\right)$$

where W is the volume of the adsorbate within the micropores at a relative pressure p/p^0, W_0 is the micropore volume of the adsorbent, β is the affinity coefficient, E_0 is the characteristic adsorption energy, p is the partial pressure and p^0 is the saturation vapour pressure. Table 3 shows the parameters calculated with both methods. The CO_2 specific surface areas are one order of magnitude higher than the BET areas. This suggests that there are a significant number of micropores which are inaccessible to the nitrogen at 77 K.

Figure 6 shows the variation of the BET surface areas with burnoff. The BET surface areas of the parent coals present low values, reaching a maximum value for the devolatilised chars. As reaction proceeds, the BET area of the chars decreases due to the coalescence of the pore wall. The HV chars exhibit a significant decrease in BET surface area at low burnoff values, whereas this reduction occurs at higher burnoffs for DI chars.

Table 3 Textural parameters of the samples used

Sample	BET result		DR results	
	S_{BET}/ $m^2\ g^{-1}$	C	S_{DR}/ $m^2\ g^{-1}$	E_0/ kJ mol^{-1}
HV	0.6	39	158	31.3
HVD	49.8	273	288	36.1
HVD-5	34.9	135	272	35.3
HVD-10	19.2	337	225	33.7
HVD-15	12.7	387	132	30.9
HVD-21	20.4	542	112	32.9
DI	2.5	51	135	28.9
DID	55.3	133	222	35.9
DID-5	25.7	241	154	34.8
DID-10	7.7	180	119	32.7
DID-15	8.7	108	77	31.5
DID-21	10.4	48	61	28.9

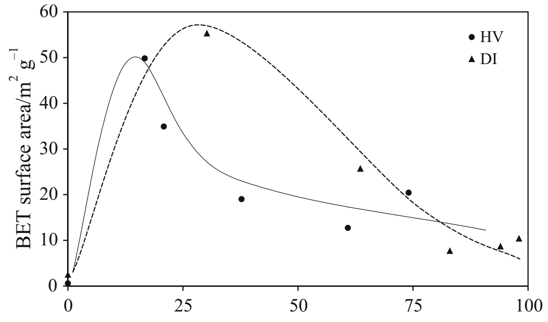

Fig. 6 Variation of the BET specific surface area with burnoff

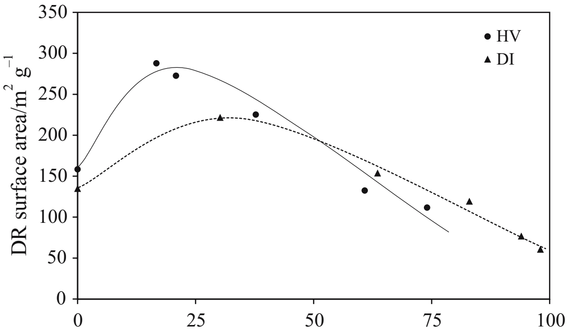

Fig. 7 Variation of the Dubinin-Radushkevich specific surface area with burnoff

The evolution of the DR surface areas of the samples are shown in Fig. 7. A similar trend with burnoff to that displayed by the BET areas was observed. The maximum value of the DR surface area is reached by the devolatilised chars, and a constant decrease occurs during combustion. At low burnoff values HV chars exhibit higher DR area values than the DI chars until a burnoff of approximately 50% is reached.

Intrinsic reactivity of the chars

The initial char surface area is included in the overall frequency factor, k_0. The intrinsic reactivity was computed by dividing k_0 by the specific surface areas. Figure 8 shows the overall frequency factor normalised with the BET and DR specific surface areas. As can be seen from this figure, the intrinsic values calculated from using the BET area remain almost constant with burnoff. The values corresponding to the highest burnoffs show a clear deviation, probably caused by the high ash content of the corresponding chars.

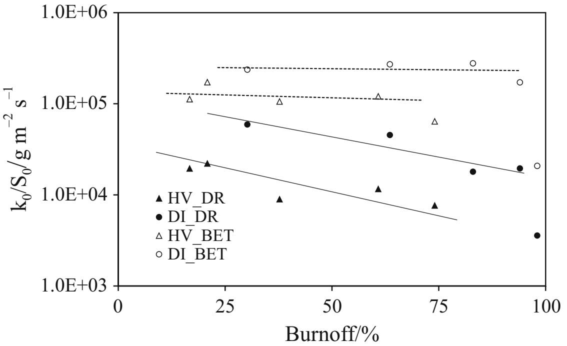

Fig. 8 Variation of the intrinsic frequency factor with burnoff

A different behaviour was observed when the overall frequency factor was related to the DR surface area. In this case a constant decrease with burnoff was observed for both char series. These results suggest that the specific surface area evaluated by using N_2 plays a significant role during the combustion tests. The different reactivity displayed by the coal chars under the kinetic regime is directly related to BET surface area.

In the EFR, combustion takes place under a different regime to that of TG. The combustion regime changes from diffusional/chemical control (zone II) to chemical control (zone I) in the final stages of char combustión [18]. Under the conditions of zone II, char reactivity is influenced by diffusional and chemical factors. Oxygen diffusion in the char particles of coal DI is higher than in coal HV due to the open structures of DI (see the SEM micrographs of Fig. 2). Moreover, the TGA experiments (zone I) revealed that DI chars present a higher chemical reactivity than the HV chars. These results explain the higher reactivity of coal DI observed in the EFR test compared to coal HV.

Conclusions

Chars from two coals of different rank, obtained after devolatilisation in an EFR, exhibited very different combustion behaviour when they were fired in the EFR at various oxygen concentrations. The results of the reactivity of the coal chars, determined by using non-isothermal thermogravimetric analysis, were analysed by means of the random pore model, and the activation energy and overall frequency factor were calculated. It was found that the activation energy remains almost constant during combustion, and similar activation energy values were obtained for the chars studied. The decrease in chemical reactivity of the chars with burnoff was related to the reduction in the overall frequency factor. The N_2 and CO_2 specific surface areas were used to calculate the intrinsic reactivity of the chars. Better results were obtained when the overall frequency factor was related to the N_2 surface area.

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Received: November 20, 2006
Accepted: January 23, 2007
OnlineFirst: April 29, 2007

DOI: 10.1007/s10973-006-8265-z