Comparison of coal chars prepared in different devices at similar temperature.

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Abstract

The characteristics of chars prepared in both a drop tube furnace (DTF) and a flat flame burner (FFB) at 1300 ºC from seven coals of different rank and maceral composition are the subject of this study. Coal samples sized and sieved to 36-75 µm were fed. The flame temperature of the FFB was achieved with a mixture of methane, air and oxygen whereas two different gas compositions were used in the DTF to account for sub-stoichiometric (2.5% O_2) and close to stoichiometric (10% O_2) oxygen levels. Determination of micropore surface area was carried out by CO_2 adsorption isotherms at 0°C and char reactivity to air was measured at 550 °C in a thermogravimetric analyser (TGA). Overall similar combustion trends were obtained in both devices with burnout decreasing as coal rank increases and CO_2 surface areas decreasing up to the medium volatile bituminous coal rank and increasing again for the anthracites. The results reveal a reasonable agreement between burnouts of FFB chars and low oxygen DTF chars whereas higher burnouts were obtained for higher oxygen DTF chars. The CO_2 surface areas of the chars reasonably scattered without any systematic trend. The intrinsic reactivities of both series of chars from the DTF were similar to the corresponding FFB chars. Increasing coal rank, intrinsic reactivity of chars from the different combustion conditions decreased.

Keywords
Combustion, Reactivity, petrology

INTRODUCTION

The combustion of pulverised coal in a steam generating boiler is the most widely used process for power generation, supplying a significant proportion of the electricity worldwide. The optimization of coal combustion process in large utility boilers is relevant for the improvement of thermal efficiency and the subsequent reduction of carbon in ash, which increases the possibilities for fly-ash utilization. The conditions prevailing in pulverised fuel boilers are difficult to reproduce due to the high heating rates, high temperatures and short residence time. Many attempts have been done to reproduce the time-temperature history of the particles at laboratory scale in order to be able to work under well-controlled conditions. Among the devices used we will mention the hot wire mesh (Gibbins et al. 1989, Lim et al., 1997), the flat flame burner (FFB) (Alonso et al., 2001; Fuertes et al., 1993) and the entrained or drop tube reactors (Cloke et al., 2002) can be considered as the ones approaching better to at least some of the full scale conditions. The characteristics of the char generated during the early steps of the combustion process will depend on the characteristics of the parent coals as well as on the operating conditions (Yu et al., 2007). The influence of the operating conditions may be significant because the laboratory scale studies are often used to provide data for the combustion models. In this study the data from chars produced in a FFB from coals of different rank and maceral composition (Alonso et al., 2001) are compared with the results of chars from the same coals produced at two different oxygen concentration in a DTF. Burnout, Reactivity, Surface area and optical texture are characteristics compared.

EXPERIMENTAL

Materials

Seven coals from different rank (high volatile bituminous to anthracite) and maceral composition (vitrinite- to inertinite-rich) were used for this study. Ultimate, proximate and petrographic analyses were performed using standard procedures.

Char preparation

The same temperature (1300 ºC) and range of particle size (36-75 µm) were used for both experimental devices. The FFB was operated with a mixture of methane, air and oxygen in the proportions shown in Table 1. Coal particles were axially injected by a gas flow at the base of the flame. More details on the experimental device are provided by Alonso et al. (1999).

TABLE 1. Operating conditions of the methane/air burner

Gas flow rate (cm^3 min^{-1} STP)				Gas Composition (vol %)			Flame T (ºC)	
CH_4	Air (injector)	Air (flame)	O_2	CH_4	O_2	N_2	Measured	Adiabatic
2.0	1.5	3.2	0.5	28	20	52	1300	1550

In the DTF coal particles are injected by a fluidiser at the top of the reactor in a gas stream of pre-heated gas. The estimated residence time in the reactor was 200 ms, the feeding rate was $1gm^{-1}$ and the flow rate 15 cm^3min^{-1}. Two different gas compositions were used in the reactor to account for sub-stoichiometric (2.5% O_2) and close to stoichiometric (10% O_2) oxygen levels. Further details of the DTF can be found in Milenkova et al. (2003). Conversion was calculated using the ash tracer as follows:

$$conversion = \left[1 - \left(\frac{Ash_{coal}}{100 - Ash_{coal}}\right) x \left(\frac{Ash_{char}}{100 - Ash_{char}}\right)\right] x100$$

Char surface area

The surface area of micropores (< 2 nm in diameter) was calculated using the Dubinin-Radushkevich (D-R) equation from CO_2 adsorption data at 273 K, which were obtained using a Micromeritics ASAP 2020.

Thermogravimetric analysis

Char combustion was isothermally recorded at 550 ºC using a Perkin Elmemr TGA7 thermal analysis system. 12 mg of char were heated up to 550 °C under N_2 flow (50 cm^3 min^{-1}) at a heating rate of 20 °C min^{-1}; after weight stabilisation, N_2 was replaced by air at the same flow rate and the temperature was maintained until combustion was completed. Char reactivity is defined as

$$R_x = -\frac{1}{m_o}\left(\frac{dm}{dt}\right)_x$$

where m_o is the initial weight of ash-free sample and x is the conversion value chosen.

RESULTS AND DISCUSSION

Table 2 shows the results of the chemical and petrographic analyses of the selected coals. Coals are listed by increasing rank as determined by random collotelinite reflectance (R_r), which range from 0.64 to 5.63 %. Ash contents ranged from moderate to low with three coals having very low ash content. Data from chemical analysis (volatile matter, hydrogen, oxygen and carbon content) correlate well with the reflectance of the samples. There are some deviations which are due to differences in maceral composition as the low volatile matter content of BB2 compared to BMC which had similar vitrinite reflectance. The goal of having a vitrinite and an inertinite-rich counterpart for each coal rank interval was only partially accomplished. Both were available for the high volatile bituminous coal rank and the anthracite rank whereas the coals from medium and low volatile matter rank had moderate inertinite content.

TABLE 2. Proximate, ultimate and petrographic analyses of the individual fuels.

Fuel	**Ash**	**VM**	**C**	**H**	**N**	**O**	**S**	**R_r**	**V**	**L**	**I**
	Db (%)	daf (%)						(%)	vol (%)		
BMC	0.6	46.2	80.6	5.9	1.4	11.8	0.3	0.64	85.8	11.8	2.4
BB 2	18.7	24.8	80.1	3.5	1.8	14.2	0.4	0.66	1.2	1.6	97.2
PHA	15.3	36.7	81.3	5.2	1.3	9.6	2.6	0.84	80.4	10.2	9.4
CRA	7.3	22.3	89.5	4.6	1.8	3.9	0.2	1.23	53.0	-	47.0
SMK	12.8	18.1	90.6	4.4	1.1	3.5	0.4	1.53	57.8	-	42.2
DAN	2.3	6.2	92.1	3.2	1.7	2.5	0.5	3.20	61.8	-	38.2
VCB	1.9	1.6	94.9	1.2	0.9	2.8	0.2	5.63	98.0	-	2.0

VM= Volatile matter; R_r=random vitrinite reflectance; V=vitrinite; L=liptinite; I=inertinite. db= dry basis; daf=dry-ash-free basis, vol= volume

The conditions selected for the FFB experiments were aimed at producing a devolatilized char with limited burning. Nevertheless the extension of combustion in the external part of the flame could not be so easily controlled as in the DTF. Two set of experiments were conducted in the DTF to account for a devolatilized char with limited burning (2.5%O_2 in N_2) and a moderately to highly combusted coal (10% O_2 in N_2). Figure 1 shows the variation of burnout with rank. Overall similar combustion trends were obtained in both devices with burnout decreasing as coal rank increases up to the anthracite rank. The differences between both devices did not follow a systematic trend and were negligible for the vitrinite-rich lowest rank coal, positive (FFB>DTF) for the inertinite-rich low rank coal, PHA, the inertinite moderate low volatile coal and anthracite and negative for the others.

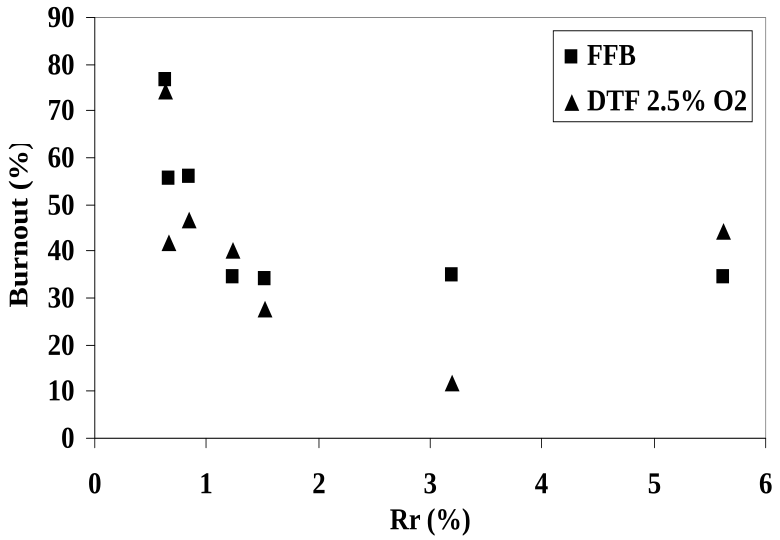

FIGURE 1: Variation of the char burnout from the FFB and the DTF, with 2.5 % oxygen, with the rank of the parent coal (Rr).

The conversions of the 10%O_2 runs were as expected higher compared with those from 2.5% O_2 runs except for anthracite DAN (Figure 2) and reached values as high as 94% for the most reactive coal (BMC).

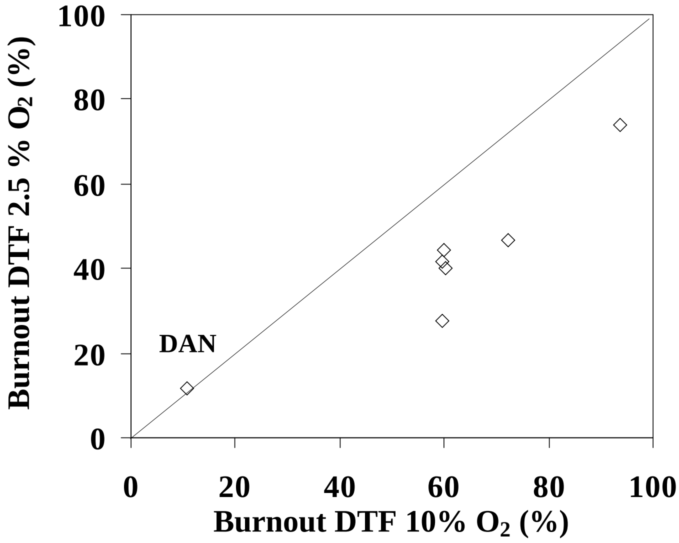

Figure 2. Relationship between the burnout of the chars from the DTF with the 2.5 and 10 % Oxygen.

Chars from this work were characterized by CO_2 adsorption at 273 K, because of its major facility to fill the small micropores compared to N_2. The values of CO_2 surface area (SCO_2) were referred to ash-free basis for comparative purposes. Most of the isotherms could be classified as type I, typical for microporous material.

The surface area of chars followed the trend with rank shown in figure 3 with a decrease up to the rank of the coking coals (1.6% Rr) and high surface area for the anthracite chars. This trend parallels that observed for coal microporosity (Gurdal et al 2001). The coking coals having the highest plastic properties pass through a metaplast stage in which rearrangement of the carbonaceous structure occurs annihiling the porosity and resulting in a strongly anisotropic optical texture with well-developed domains (SMK). The low rank coals having a highly crosslinked structure are not able to reorganize during the short heating step and yield a carbon-rich isotropic disordered char which maintain significant amount of porosity (BMC). The anthracites also had relatively high surface area but in this case is due to the slit-shape pores lead by the imperfect graphitic-like structure. This structure is rather stable and is only able of limited re-organization in such a short heating time, therefore maintaining high surface area similar to that of the raw anthracite (Díez and Marsh 2000). This situation was not observed in the highly reflecting vitrinite-rich VCB anthracite. The FFB anthracite char had a high surface area (193 m^2g^{-1}) but both DTF chars yielded a isotherm typical of non-porous material largely departing from the expected Dubinin-Raduskevich plot. The N_2 adsorption isotherm indicated a very low surface area of mesopores (~2 m^2g^{-1}). The most plausible explanation is the VCB suffered in the DTF a more drastic transformation of the structure than in the FFB resulting in a narrowing or sealing of pore mouths. In favour of this explanation is the maximum vitrinite reflectance of the chars which was 6.26% in the FFB (Alonso et al., 2001b), 6.90 % in the low oxygen DTF char and 7.13% in the 10% O_2 DTF char.

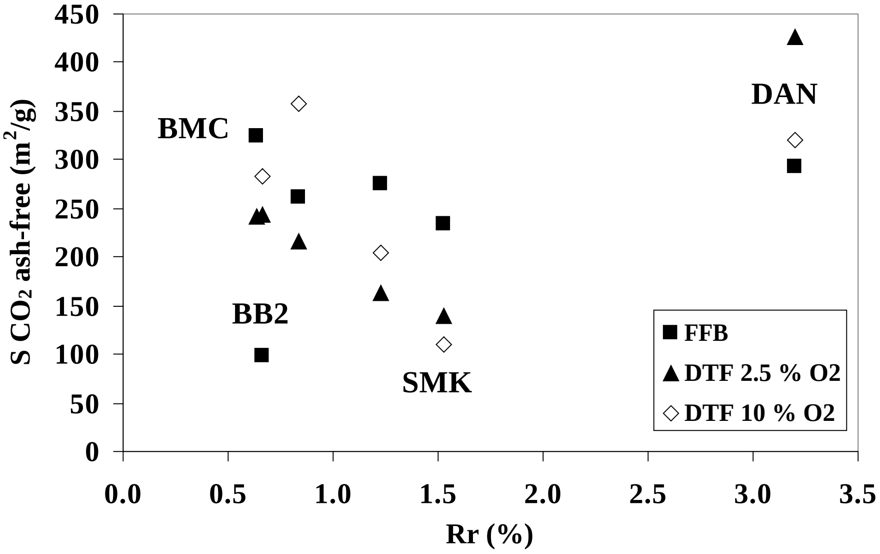

Figure 3. Diagram showing the surface area ash free from the chars of the FFB and the DTF, versus the rank of the parent coal (Rr)

The relationship between the CO_2 surface areas of the chars from FFB and the DTF using the two different atmospheres is shown in Figure 4 indicating a reasonable scatter at both sides of the mediatrix. Also the surface areas of the chars obtained under different oxygen concentrations were similar as observed for other coal chars (Alvarez and Borrego 2007). The differences observed affected the mesopore development but microporosity was rather similar up to very high burnout levels.

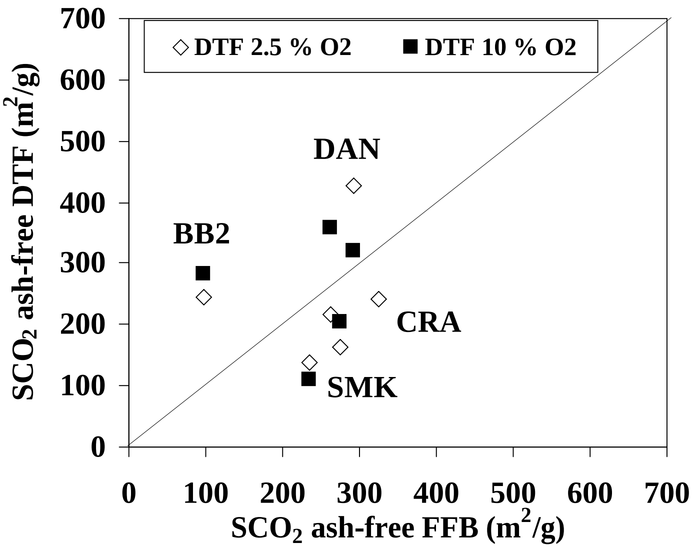

Figure 4. Correlation between the surface area ash-free of the chars obtained from the FFB and the DTF.

As char reactivity depends on the characteristics of the carbonaceous material and the surface available for the oxygen attack, a comparison of the intrinsic reactivity requires the correction of the values for surface area. As expected the intrinsic reactivity decreased with coal rank. The comparison between the reactivity of the chars from the DFT and the FFB is given in Figure 5. In general, reactivities of the chars from the DTF were similar or higher than those from the FFB. In particular those from chars obtained under 10% O_2 tended to be higher.

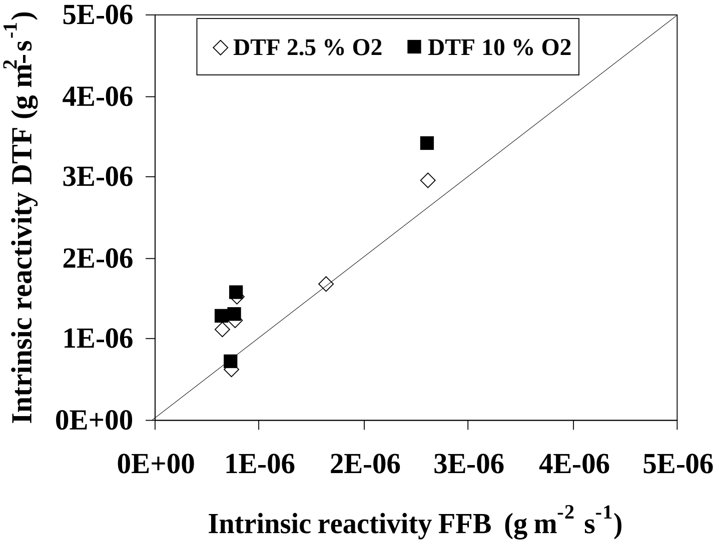

Figure 5. Relationship between the intrinsic reactivity of the chars from the FFB and the DTF.

CONCLUSIONS

Chars prepared in a flat flame burner with a flame of methane/air and in a drop tube furnace with 2.5% and 10%O_2 concentrations at 1300 ºC have been compared for burnout reactivity and CO_2 surface area. The results indicate that the transformations undergone by coal in both devices resulted in chars with rather similar characteristics. The most sensitive coal appears to have been a very high rank anthracite whose structure underwent a higher degree of ordering in the drop tube reactor.

Acknowledgements

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