



Full Length Article

Separation and characterization of carbonaceous particulate (soot and char) produced from fast pyrolysis of coal in inert and CO₂ atmospheres

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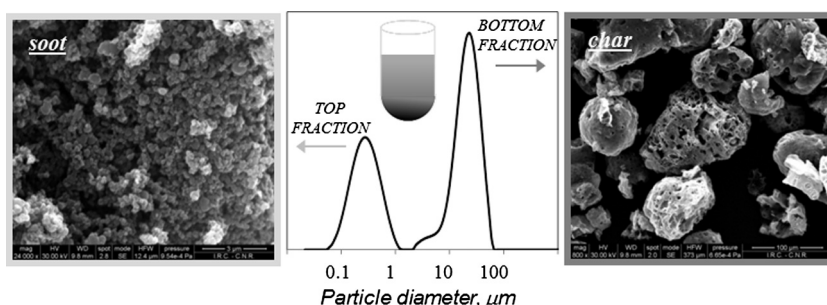
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HIGHLIGHTS

- Effect of inert and CO₂-rich atmospheres on the fast pyrolysis of coal.
- Separation method of soot and char from carbon particulate formed in coal pyrolysis.
- Structural characterization of coal-derived soot and char.
- Soot and char formation mechanisms.

GRAPHICAL ABSTRACT



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ABSTRACT

In a previous work [Heuer et al., 2016] a large production of a fluffy carbon-rich material was observed to accompany the char formed during the early stages of a medium rank (bituminous) coal pyrolysis in a drop tube furnace (1573 K, residence times < 130 ms). This peculiar material was found to be much more abundantly formed in CO₂ than in N₂ flow. SEM analysis showed that it contains a large portion of sub-micron soot-like particles mixed with particles of tenths of microns in size with the typical char morphology. The present work reports on the separation of the two differently sized fractions produced in CO₂ and N₂ flow and their subsequent analysis. The separation was performed dispersing the material in ethanol by ultrasonic mixing, followed by settling, and decanting to produce top and bottom products enriched in the fine and coarse particle fractions, respectively. The procedure was repeated several times and the size separation effectiveness was checked by SEM and laser granulometry sizing. Thermogravimetry, elemental and spectroscopic analysis were applied to the coarse and fine fractions to provide insights on their structural features. The fine soot particulate was almost ash-free, suggesting that its formation occurs in the gas phase, as typically soot does, while the coarse fraction presented significant residues of coal inorganic matter typical of char.

Both fine and coarse particulate resulted less reactive, and somewhat smaller in size, when produced in CO₂ in comparison to N₂/Ar pyrolysis conditions. Their lower reactivity is associated with higher aromaticity and structural order as well as with a lower presence of hydrogen and aliphatic functionalities.

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1. Introduction

The retrofit of traditional power plants into oxy-fuel combustion systems by means of recirculation of flue gases has recently re-inspired research on fundamental aspects of coal behavior under CO₂-rich atmospheres [1–5]. Coal pyrolysis studies have shown that a CO₂-based atmosphere does not modify the devolatilization times compared to a N₂-based atmosphere [6,7] while the nature of the pyrolysis products, both gaseous and solids, have been found to change [6,8–16].

Recent work from a collaboration of Bochum and Naples addressed the influence of gaseous N₂ and CO₂ atmosphere on the early products of fast pyrolysis at 1573 K of a high volatile bituminous coal (Colombia) [1]. The CO₂-char exhibited a lower reactivity compared to the N₂-char, which coupled well with differences in the distribution of C–O complexes on the char surface, as measured by XPS. These results could not be attributed to differences in time-temperature profiles upon substitution of N₂ with CO₂, as demonstrated by CFD calculations showing minor differences in the time-temperature profiles of the particles during the CO₂ and N₂ treatments [1].

Beside the different char reactivity, CO₂ environment appeared to cause the additional production of a fluffy carbon-rich particulate deposited at the sampling filter's wall. Specifically, this material was almost absent in both combustion and oxy-fuel combustion experiments, and only one-third in N₂ and Ar experiments [1]. In that work this material was named “soot” just to distinguish it from the char sample, because it contained aggregates of the submicron soot particles typically detected by microscopy [17,18]. But, an accurate inspection of SEM images showed that it was still contaminated by large size char particles [1].

Carbon-rich ash is obviously an undesirable product both because of the loss of carbon combustion efficiency and of the low quality of ash, which cannot be utilized for cement production as it has a high loss of ignition (LOI) value [19,20].

The presence of submicron soot-like particles was already observed at the exit of a pilot-scale furnace by Sadakata et al. [21], but without giving a separation and a structural characterization. Soot was identified by transmission electron microscopy in commercial coal-fired power plant fly ash [20] and on filter deposits from low NO_x pulverized coal combustion [22]. In another study, carbon-rich char particles > 50 μm were extracted from power plant fly ash using incipient fluidization, but the fine fraction of the carbon, perhaps including some soot, was not studied [23].

The present work reports a deep investigation of the composition and characteristics of the coarse and fine components separated from the fluffy carbon deposited at the filter walls during coal pyrolysis experiments carried out in CO₂ and N₂ environments at two different residence times [1]. In our previous work, the fine submicronic (soot) component of this carbon material, separated by suspension and settling in ethanol [24], has been deeply analyzed [25] whereas in the present work, the analysis has been extended to the coarse (char) component reporting a comparative analysis of the soot and char characteristics. The size distribution, composition, and combustion reactivity have been measured using diverse analytical diagnostics. Furthermore, a comparison between the char separated from particulate collected on the filter walls and the char collected out of the filter (in the chamber where the filter is placed) [1] is also reported.

2. Experimental apparatus and techniques

2.1. Experimental apparatus

A high volatile bituminous coal from Colombia (medium rank), whose main properties are reported in [1,25], was pyrolyzed in a

laminar drop tube reactor at 1573 K with CO₂, N₂, and Ar. More information on the experimental facility and operation are reported in detail in [1,25]. An oil-cooled probe was used to sample and quench reaction products. The probe was positioned at two locations along the reactor: L = 180 mm and L = 270 mm from the top, which, based to CFD calculations, corresponded roughly to residence times of 80 and 120 ms in Ar/N₂, 87 and 130 ms in CO₂. In the first 50 mm the particles reached the final temperature of 1504 K in Ar/N₂ and 1557 K in CO₂. Then an isothermal zone followed, which was 130 or 220 mm depending on the probe position. A heated ceramic filter at 300 °C intercepted the solid products at the end of the probe. Notably, the larger and heavier char particles fell to the ground of the chamber where the filter is placed, where they could be easily recovered and analyzed [1].

Beside the char deposited on the ground of the filter chamber, another form of carbonaceous material consisting of an apparently fluffy carbon particulate was observed and removed from the filter walls by scraping for further separation and characterization.

2.2. Procedure for soot and char separation

The procedure for separating soot and char consisted of suspending the carbonaceous particulate in a solvent, settling, and decanting to produce top and bottom products enriched in the coarse (char) and fine particle (soot) fractions, respectively as verified by SEM and granulometry.

The soot-char separation procedure set up in a previous work [24] has been modified increasing the number of extraction steps and reducing the settling time. About 100 mg of raw carbonaceous particulate was placed in a 50 ml Falcon tube with 40 ml of ethyl alcohol and agitated using an ultrasonic bath for 5 min. In order to reduce the operation time it was attempted to separate soot from char particles by using centrifugation instead of settling. However, the precipitation of a significant part of soot together with char was experimentally observed so that it was chosen to settle the suspension for 45 min. As indicated in [24] the top 20 ml of the suspension was decanted into a second tube, and the tube containing the bottom fraction was refilled. Both tubes were again ultrasonically agitated for 5 min and the settling was repeated. The top products, containing soot, have been in the decanted liquid at least three times whereas the bottom fraction, the char, had been settled at least four times, in dependence on the sample behavior. In particular, the solvent volume addition and the number of the extraction steps were repeated until the complete disappearance of suspended particles in the solution, as checked by the absence of any scattering signal to the UV-visible absorption spectroscopy. Soot and char, so separated, were dried by evaporation and weighed. The balance closure was used to check the quality of the quantitative separation results. Even though some material losses occurred during the separation procedure, the recovery was more than 90 wt.%.

The soot and char samples obtained by means of the procedure described above will be labeled according to the following denominations: (S or C)-(N₂ or CO₂ or Ar)-L, where S and C identify the soot and char fractions, respectively; L stands for the position of the sampling probe along the drop tube reactor (length in mm). The particulate samples, before separation, will be referred to as “soot + char”. The recovery percentage of the particulate sample was satisfactory. The percentage distribution of soot and char inside each particulate sample, reported in Table 1, are calculated on the mass of the sample collected on the wall filter, so expressing the quality of such peculiar samples, whereas the soot and char yields reported in previous work [25] were calculated on the basis of the carbon fed to the reactor. The soot percentage is up to four times higher in CO₂ with respect to experiments in inert environment (N₂) (Table 1) and Ar (data not reported). The error is about

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