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Effect of reaction atmosphere on the products of slow pyrolysis of coals

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ABSTRACT

Slow pyrolysis of semianthracite (SA) and high volatile bituminous C (HVBC) coals was performed under two reaction atmospheres (CO_2 and N_2) and three different particle size distributions. It was found that the physicochemical properties of a char and its respective combustibility depend significantly on the reaction atmosphere under which it was produced. For SA char particles larger than 0.7 mm, the BET surface area increases when the atmosphere is enriched in CO_2 due to intraparticle side reactions, differences in the thermal-diffusive properties of N_2 and CO_2, and the reactive effects of the latter. When particle size decreases below 45 μm, no mesoporous surface area developed with either atmosphere. The combustibility of char formed in CO_2 was higher than in N_2; furthermore, the pore size distribution (PSD) is different in both environments. ATR-FTIR spectrometry indicates that char formed under N_2 is more aromatic. Additionally, FE-SEM visualization showed the occurrence of softening more evident in N_2 than in CO_2; however the char obtained in CO_2 looked as if it had lost more material, which agrees with other experiments showing lower elemental and fixed carbon contents for this condition.

1. Introduction

Devolatilization of coal is the first step in combustion and impacts all subsequent oxidation steps. Many studies and reviews in the last three decades have explored the release of volatiles [1–8]. Likewise, the devolatilization products have received considerable attention in the last decade [9–16]. Among these studies, only a few focus specifically in the understanding of the effects of the volatiles release on oxy-combustion [7,10,15–20]. It is important to note that despite the apparent abundance of reports on the effects of devolatilization in oxy-combustion, the fact is that only recently the groups of Senneca and Schiemann [15,16,20,21] have published studies on the quality of pyrolysis solid products under oxy-fuel conditions, and exclusively for pulverized coal.

Understanding the transformation of the carbonaceous structure during the conversion of coal into char is critical for the development of thermal decomposition models used to size and design reactors [22,23]. To understand coal devolatilization in a real system, one needs to consider that there is a wide heterogeneity even in high-ranked coal. Coals have a wide range of properties which make them sensitive to intraparticle crosslinking, swelling, fragmentation, and other phenomena [24,25]. These phenomena have been explored in the literature for conventional combustion conditions. Results recently published by the Senneca and Schiemann groups [15,16,20,21] show that in order to understand the substitution of N_2 by CO_2 in combustion, it is not possible to extrapolate data collected for traditional combustion to the oxy-combustion conditions.

In practical applications, devolatilization of coal is strongly influenced by operational parameters (equipment and coal properties), making it difficult to isolate individual phenomena in the process. In oxy-combustion, pyrolysis studies have been mainly focused on experimental determination of devolatilization time, ignition of volatiles, flame temperature, reaction mechanisms, and rate equation development [26–30]. The substitution of N_2 by CO_2 into the system modifies the combustion characteristics which, at least for pulverized coal, is a subject widely studied but with contradictory results [15]. For example, Kim et al. [31] and Tolvanen and Raiko [32] found that the temperature at the particle decreases when replacing N_2 with CO_2; these differences were also observed by the Levendis group [29,33,34] for combustion of coal and char with variations between 150–200 °C. These temperature variations are attribute to the differences in heat capacity and diffusivity between N_2 and CO_2. However, Heuer et al. [15] determined using CFD simulations that these huge temperature differences cannot be completely attributed to heat capacity and diffusion. Since these investigations were carried out in Drop Tube Reactors (DTR), the discrepancy on the effect of CO_2 in the particle temperature could be partly reconciled when differences in the residence times are considered and the methodology used for the measurement and estimation of the variable.

In the case of large particles coal, there are few comparative studies between conventional combustion and oxy-combustion [35–38]. Only

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Table 1
Physico-chemical characterization of coal samples.

Samples	Proximate analysis, wt.%				Ultimate analysis, wt.%					BET Area	CO_2 Area
	m	vm	fc	Ash	C	H	N	O	S	m^2/g	m^2/g
SA	1.07	11.64	79.86	7.50	75.40	3.23	0.16	12.98	0.73	0.46	90.62
sd	± 0.54	± 1.44	± 0.61	± 0.17	± 0.09	± 0.02	± 0.00	± 0.01	± 0.00	± 0.08	± 2.45
HVBC	5.29	39.72	50.71	4.28	64.59	5.24	1.79	24.06	0.62	0.03	61.71
sd	± 0.83	± 1.05	± 1.11	± 0.54	± 0.12	± 0.12	± 0.06	± 0.05	± 0.00	± 0.06	± 1.73
Method	D3173	D3173	D3173	D3173	D5373			By difference	D4238	Adsorption in N_2 to −196 °C	Adsorption in CO_2 to 0 °C

Note: vm: volatile matter, m: moisture, fc: fixed carbon, sd: standard deviation. BET Area corresponds to pores between 2 and 100 nm; CO_2 Area corresponds to pores < 0.7 nm.

recent studies by Bu et al. [39–42] and Guedea et al. [37] at high and low heating rates, respectively, have shown that the behavior of the oxy-combustion in a fluidized bed (large particles) is different than traditional combustion. These studies highlighted the characteristics related to volatile release (ignition, flame temperature, flame lifetime, devolatilization time). It has also been observed that during fast pyrolysis the fast release of volatiles and formation of bubbles expands pores, modifying the structure of char [7,43,44]. During slow pyrolysis, however, volatile compounds are released slowly from the inside of particles without dramatically changing the original pore structure. Based on these studies it can be concluded that the particle size, heating rate of coal particles, and the reaction environment impact devolatilization dynamics [45–47] and influence the oxy-fuel combustion process. However, the effects of CO_2 on the chemical-structural features of the chars formed from large particles in devolatilization remain unclear [19,48,49].

Similarly, there are valuable studies regarding the effects of CO_2 and steam on gasification pertaining to oxy-fuel combustion [31,50–52]. However, the chemical and structural evolution of char has received little attention [17–19]. One good study regarding the effect of environment on devolatilization of coal char was performed by Zeng et al. [17]. In this work, the authors used an entrained-flow reactor to study the changes in physical properties and reactivity of the chars of pulverized coal (106–125 μm) with three different ranks (lignite, sub − bituminous and high volatile bituminous) and high temperatures (900–1400 °C) under both CO_2 and N_2. The results showed that bituminous coal lost more mass in CO_2 than N_2 when the temperature was lower than 1400 °C [18,19,53]. However, above 1400 °C the mass loss was practically the same; this was not explained by researchers, but may be due to the presence of annealing phenomena as reported in other studies [14,54–56]. In addition, the char showed different pore size distributions in both environments. The BET and CO_2 surface areas were larger for the CO_2 environment, which is consistent with other investigations [10,57].

In another relevant study by Wang et al. [18], pulverized coal was pyrolyzed (105–150 μm) in a laboratory scale fluidized bed under atmospheres of N_2 and CO_2 using three types of Chinese coal (lignite, bituminous "high ash" and anthracite). Environmental effects on the char microstructure were analyzed by FTIR and Raman spectroscopy. These studies showed that the char formed under a CO_2 environment retained more functional groups from the original coal; this implies that CO_2 is more reactive and has a lower level of graphitization than N_2 [19,57].

Based on the literature review, we conclude that there are two important properties that need to be studied in coal chars. The first is the level of graphitization in the carbonaceous structure, which has only been studied for small particle sizes by Senneca Group [7]. Graphitization comes from structural rearrangements activated by temperature that include abstraction of volatiles, change of carbon hybridization and increase of crystallographic order due to stacking of graphene layers, lateral growth of polyaromatic domains, and loss of in-plane defects. The second is the development of pore structure and surface morphology. These two features depend on the heating rate, residence time, pressure, coal rank, and particle size. However, the effects on the structure due to reaction environment are less well-known. These are critical for the oxy-fuel technology where small changes in the devolatilization can have a large impact on the combustion stage.

In this research, two ranks of coal (high volatile bituminous C and semianthracite) and two reaction environments (N_2 and CO_2) were studied to compare products of slow pyrolysis. These studies are of particular relevance to fixed bed systems. For the first time, we determined the impact of particle size on the process and products. To study these effects, char product samples were physicochemically characterized using traditional techniques. Char samples were also analyzed using infrared spectroscopy (ATR-FTIR) to track the variation of the functional groups and with this, the change in aromaticity achieved by the heat treatment in each environment. In addition, the reactivity of the smallest particle size was analyzed. Finally, FE-SEM was used to find evidence of molten phases, formation/disappearance of voids, and chemical attack on the morphological structures of the chars.

2. Material and methods

2.1. Characterization of samples

Coal samples used in this study are of two different ranks: (1) Highly Volatile Bituminous C (HVBC) extracted from the prolific mining region called "*Cuenca del Sinifana*", located in the department of Antioquia and (2) Semi-Anthracite coal (SA) extracted from a mining region in the department of Santander, both in Colombia. Their physico-chemical characterizations can be seen in Table 1; which, it was carried out following the standard methods listed in the bottom row. The error shown here represents the population standard deviation (sd) of analyses carried. The more extensive characterization of raw coal samples can be seen in section S1 of the supplementary material.

A 6500 rpm tilt hammer mill was used to reduce the size of the samples coal; afterwards, it was size separated into three homogeneous particle size distributions for tests in the horizontal reactor as: 2.36–2.00 mm (named HVBCR10 and SAR10), 0.71–0.60 mm (named HVBCR35 and SAR35), and 45–38 μm (named HVBCR400 and SAR400).

2.2. Equipment and experimental procedure

Tests for studying slow coal pyrolysis (less than 10 °C/min) were conducted in a horizontal reactor (see Fig. 1a) which consists of a quartz tube with an external diameter of 3.5 cm (ID: 3.0 cm), long 50 cm; this tube is inserted into a 40 cm long horizontal annulus oven, heated by electric resistance and controlled by a PID loop. The sample is pushed into the reactor in a quartz sample holder 2.0 cm wide and 13.5 cm long.

Approximately 3 g of the sample was placed inside the reactor. A thermocouple was inserted into the sample bed, which was not compacted. The experiments were done between room temperature and

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