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Experimental study and kinetic modeling of pulverized coal devolatilization under air and oxycombustion conditions at a high heating rate

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ABSTRACT

This work aims to study the devolatilization of pulverized coal particles under air and oxycombustion conditions. To do so, a newly developed experimental test bench has been used to stabilize coal jet flames with fuel heating rates similar to those found in industrial combustors. The thermal history of coal particles has been experimentally monitored by coupling pyrometric and particle image velocimetry (PIV) measurements. Char samples have been collected at different residence times to obtain devolatilization profiles that have been compared with data issued from 4 empirical models. New sets of kinetic parameters have been proposed to simulate coal devolatilization under high heating rate ($>10^6$ K/s) with N_2- and CO_2-based atmospheres. The composition of the burnt gases has also been characterized at various heights above the burner (HAB). The analysis of the obtained results confirmed that an oxygen enrichment of the combustion atmosphere enhances the devolatilization process by favoring an increase of the coal particle temperature. From the comparison between measured and modeled data, it has been observed that apparent devolatilization rates and kinetics were influenced only by the thermal history of the fuel particles with no char-CO_2 gasification or CO_2-cross linking reaction at the surface of the char in the conditions investigated here. CO releases were found to depend on the devolatilization rates and on the temperatures of the flames. An increase of the SO_2 emissions has been strongly correlated to the oxygen concentration in the medium for a given devolatilization yield. NO emissions were not significantly reduced during experiments conducted under oxycombustion conditions compared to those performed under air which is due to the fact that NO emissions have been mainly related to the formation of fuel-NO in this work.

1. Introduction

Oxy-fuel combustion of coal with recycled flue gases mainly composed of CO_2 appears to be the most ready-made carbon capture and storage (CCS) technique to retrofit traditional power plants [1,2]. Combustion under such specific conditions has to be thoroughly understood, however, insofar as both the O_2 concentration and the nature of the diluent are different from those met during a conventional air combustion. Laboratory scale studies have thus been conducted during the last few years to analyze the fundamentals of oxy-coal combustion.

During an experimental work carried out using the Sandia's entrained flow reactor, Murphy et al. showed that oxygen enriched combustion (OEC) (with O_2 mole fractions ranging from 6% to 36% in N_2) of bituminous and subbituminous micrometric coal particles (106–125 μm) lead to an increase of the char combustion temperature and a decrease of the fuel burnout time [3]. Increases of the devolatilization rates have also been reported in this work and explained by a closer proximity of the volatiles flame to the coal particles and a higher temperature of such a flame due to the oxygen-enhanced combustion of devolatilization products. Molina et al. then concluded that OEC comprising O_2 mole fractions between 21% and 30% induces an acceleration of the particle ignition whatever the considered diluent (N_2 or CO_2) whereas ignition process was delayed when using CO_2 [4]. This behavior is consistent with trends issued from other works that studied OEC of various coals in N_2- and CO_2-based atmospheres using drop tube furnaces [5–7]. Bejarano et al. especially showed that for the same O_2 concentration, the char burnout time was longer and the particle temperature was weaker when using CO_2 [7]. They pointed out that the combustion of a bituminous coal in a O_2-30%/CO_2-70% mixture had equivalent properties to that under air as observed in [8,9]. In their 2007 study, Molina et al. found that the use of a CO_2-based atmosphere did not modify devolatilization times compared to a N_2-based one [4]. On the contrary, these authors, supported by the study of

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Shaddix et al. [5], pointed out that devolatilization durations were increased when using CO_2 as a diluent. This has been explained by the lower mass diffusion rate of volatile matters in CO_2 compared to N_2. On the other hand, it has been found that the increase of the oxygen concentration has an opposite effect on the devolatilization process as it improves the local mixture reactivity in the surroundings of volatile matters. As a consequence, it increases the heat flux released towards coal particles and thus improves devolatilization rates. Shaddix et al. explained that the above-mentioned delay in particle ignition could be due to the greater molar specific heat of CO_2 as well as its tendency to reduce the local radical pool [5]. Variations of the thermal conductivity of the gaseous environment surrounding the fuel particles, modifications of the structure of the char and reactions involving this latter (char-O_2 and char-CO_2) were also pointed out by Qiao et al. as being important factors affecting the fuel particle ignition behavior [10].

Even though some trends and physical considerations can be brought to explain the main differences between combustion under air and O_2/CO_2 atmospheres, opposite results reported in the literature highlight the fact that devolatilization characteristics in high CO_2 concentration environments still require additional researches to be conducted as pointed out by Chen et al. in a recent review [2]. For example, Rathnam et al. [11] measured increases up to 23% of the apparent devolatilization yields when using CO_2 instead of N_2 in the oxidizer stream which contrasts with trends observed by Shaddix et al. for instance. Rathnam et al. especially noted that coal devolatilization was similar under N_2- or CO_2-based atmospheres for temperatures below 1030 K while the measured weight loss in CO_2 was significantly higher above such a temperature due to a char-CO_2 gasification process. To the contrary, Borrego et al. reported a lower mass release in CO_2 during drop tube reactor experiments conducted at 1573 K [12]. The authors then suggested that CO_2 could be involved in a cross-linking process at the surface of the char inhibiting the release of volatiles. In contrast to the works referenced above, Brix et al. found no changes in volatile yields measured under N_2 and CO_2 environments during experiments conducted using an entrained flow reactor [13]. Data are thus still needed to better understand the mechanisms involved in coal devolatilization in oxycombustion conditions. Works coupling experimental measurements and kinetic modeling are of interest to this aim especially when considering the extensive need of devolatilization kinetic parameters thoroughly obtained in CO_2-rich medium with high heating rates as concluded by Chen et al. [2]. Such parameters are proposed in the present work while data published under similar specific conditions are quite inexistent in the literature to the authors' knowledge.

Oxycombustion of coal particles also influences NO_x, CO_x and SO_x releases. For instance, Hu et al. observed an increase of NO_x emission whatever the nature of the environment (N_2 or CO_2) when increasing the oxygen enrichment [14]. On the other hand, at a fixed O_2 concentration, it has been found that NO_x emissions decrease when using CO_2 instead of N_2 as a diluent. This trend can be explained by factors including a limitation of prompt-NO and thermal-NO formations due to the low level of N_2 into the reaction medium [15], a reduced fuel-N conversion to NO_x when O_2/CO_2 mixtures are used instead of air [6] and an important fuel-N conversion to N_2 [16]. On the other hand, no clear-cut conclusion has been drawn regarding the CO releases. For instance, CO concentrations were found to be higher under low heating rate thermogravimetric analyses from Li et al. [6] whereas lower CO emissions were observed in a 20 kW down fired-combustor [8]. Concerning the SO_2 releases, Toftegaard et al. reviewed experiments where SO_2 concentrations were the same in O_2/CO_2 mixtures and in air [15] which is consistent with the fact that SO_2 emissions mainly depend on the local O_2 concentration for a quantity of sulfur available into the medium [16].

A fine understanding of changes involved in coal oxidation, devolatilization and gaseous emissions under OEC and O_2/CO_2 atmospheres has still to be achieved. It is furthermore noteworthy that all the trends depicted above are closely dependent on the operating conditions used regarding factors such as residence times and heating rates as pointed out by Brix et al. [13]. Among laboratory scale test benches, flat flame reactors (FFR) are interesting devices allowing industrial combustion conditions to be reproduced in terms of particle heating rates and ignition mode [17]. A FFR has thus been designed in our laboratory [18] and previously used for OEC applications [19]. In the present study, characterization of devolatilization rates and gaseous emissions are studied for air combustion and various oxycombustion environments (O_2-21%/CO_2-79%, O_2-30%/CO_2-70% and pure O_2). The experimental methodology used to assess devolatilization rates is described and data are then confronted with those issued from empirical models, new kinetic datasets being proposed to this aim. Finally, the impact of the oxidation atmosphere on the measured gas releases is discussed.

2. Experimental facility and methodology

2.1. Experimental apparatus

The experimental facility allows studying coal jet flames within different environments. This newly developed test bench is represented in Fig. 1. The whole system previously described in [18–20] is composed of three distinct parts including a fuel feeding system, a hybrid flat flame burner and a sampling line connected to cyclones and gas analyzers. Briefly, coal particles are introduced in a tank connected to a motorized sprocket wheel. Particles then fall down into an acoustic sower by gravity effect. The coal mass flow rate (fixed to 12 g/h for all the experiments reported in this paper) is controlled by the motion of the sprocket wheel whose speed is monitored to ensure a constant delivery. Besides, a shaker avoids the formation of coal agglomerates in the sprocket. The acoustic sower consists of a glass-made enclosure set up on a thin vibrating membrane driven by a loudspeaker the frequency of which can be adjusted. Four lateral inlets allow the injection of a carrier gas into the sower to fluidize coal particles. Positions of the inlets were designed by a Computational Fluid Dynamic (CFD) approach in order to achieve the best quality mixing, to avoid coal accumulation in weak velocity zones inside the sower and to supply a constant fuel mass flow rate [20]. Coal is then pneumatically entrained by the carrier gas stream to the central injector of an atmospheric McKenna hybrid flat flame burner composed of a 60-mm diameter bronze porous plate with a central 1.75-mm inner diameter stainless steel injector. The composition of the gas mixtures used to stabilize the different flat flames on the porous plug has been adjusted depending on the investigated combustion atmospheres (see Section 2.2). Fuel coming from the acoustic sower then flows out through the central injector of the burner and is ignited with the hot gases produced by the flat flame. Pulverized coal jet flames of around 35 cm height and 3 cm width are obtained. A 400-mm height rectangular quartz chimney is set above the burner to isolate the flames from the surroundings while allowing optical diagnostics to be implemented. A motorized translation stage is used to move the burner and its chimney at various heights to collect char samples and combustion gases at different residence times. To do so, a sampling system is positioned above the burner. It is composed of a 51-cm height quartz collector (based on the probing system used in [21] for soot sampling) composed of two concentric tubes. Nitrogen is introduced into the annulus area and injected through the internal tube by means of four 7-mm diameter holes placed downstream of the collector inlet. The samples are thus immediately quenched and collected species can be either directed through a gas analyzer or a char collecting system. Gases are brought to the analyzer (Environnement-SA Topaze-32M and MIR-2M) through a probe whose temperature is regulated at 463 K to prevent water condensation. Concentrations are measured by infrared spectroscopy (CO_2, CO, SO_2) and chemiluminescence (NO). Particles are separated from the sampled flue gas into a heated cyclone (Dekati SAC-65) having a cut size of 14 μm. Its temperature is regulated at 453 K. The proximate analysis of the collected char is then carried out, ash being used as a tracer as explained in Section 2.4.