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Fast pyrolysis of large coal particles in a novel hot plate reactor: Effects of the reaction atmosphere on the porous structure and char reactivity

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ABSTRACT

Fast pyrolysis of large particles of coal semi-anthracite (SA) in a novel Hot Plate Reactor (HPR) was carried out. Advantages of gas flow control of the HPR were used to compare the effect of the reaction atmosphere on the fast pyrolysis process, mainly in aspects such as chemical and porous structure, also in char reactivity. The effects of the heating rate and the reaction atmosphere were evaluated through characterization of the surface of the char by using Fourier Transform Infrared (FTIR). When CO_2 reaction atmosphere was used, evidence was found of thermoplastic effects, and such effects might have caused retention of aliphatic structures typical of volatile material. This shows that different processes apply to devolatilization of large coal particles compared to devolatilization under conventional combustion conditions. In addition, the possible presence of thermal annealing and graphitization of chars may explain their poor performance under combustion, due to carbonaceous structure chemical deactivation, which was stronger in those obtained under CO_2 atmosphere than those obtained under N_2 atmosphere. This allowed demonstrating that when it comes to large coal particles combustion, it is not advisable to assume as true the knowledge acquired during devolatilization under conventional combustion conditions.

1. Introduction

Several studies on devolatilization have been documented from different perspectives [1–5]; however, there are very few studies focused in the char structural changes (chemical and morphological) particularly under condition pulverized coal oxy-combustion [5–9], and non-existent for large coal particles. In general, very little, it has deepened in understanding the nature and extension of the coal structural changes [5]. In this regard, it is worth mentioning that during the development of this research, it has not been possible to find information about the relation between structure, swelling, thermal annealing, primary fragmentation and char reactivity of large coal particles, under oxy-combustion conditions. Nevertheless, based on the lessons extracted from the study of the conventional combustion process, it is possible to infer that as the particle size increases, the implications of the operating variables like the reaction atmosphere, the temperature, the pressure, the heating rate, and the coal physicochemical composition are much more relevant. The results reported in oxy-combustion show that they are not completely transferable from one technology to the other [8,10–13].

Regarding pyrolysis, most of the studies in an oxy-combustion atmosphere have been carried out in thermogravimetric analyzers (TGA) [14–16]; which are devices operating at low heating rates and adequately represent the values typically reached in fixed-bed reactors, but are far away from the operating conditions of the Entrained Flow Reactors – EFR or Drop Tube Reactor − DTR (both with pulverized coal) and fluidized beds (with large particles). In view of the foregoing, the high heating rate reactors such as those of wire mesh (WMR) or heated grid (HGR), hot plate (HPR) and Curie point (CP), have been used to research fast pyrolysis [17–20,5]. The WMR and other similar reactors, have in common with the TGA the fixed-bed condition that allows a direct contact of the particles with the heating element. Nonetheless, the high heating rates reached in the first mentioned reactors, allow that this type of reactors can properly represent the conditions of heat transfer of a fluidized-bed reactor (FBR) and EFR.

There are existing studies focused on the effects that the substitution of N_2 atmosphere with CO_2 has on the devolatilization times during fast pyrolysis of pulverized coal [5,8,10,13,21]. Recently, the same authors of this investiation developed experiments for evaluating the kinetic parameters governing the fast pyrolysis in a hot plate reactor (HPR) [5]; They identified substantial differences in the reaction rates, devolatilization times and in the micro-structure obtained due of the substitution the N_2 pyrolysis atmosphere by CO_2. Furthermore, a more organized char was obtained at the larger heating rates and the substitution of N_2

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by CO_2 enhanced the char aromaticity. This is related with the inhibition of secondary reactions (cross-linking, thermal deactivation and graphitization) caused by the CO_2 atmosphere and the short process times, which are smaller than those necessary for competitive processes to be relevant [8,9,22].

When it comes to large particles, few studies have been carried out. Among them stands out the study of Scala et al. [23], whom, based on measurement techniques, use the CO/CO_2 relation to establish the significant influence of gasification and partial oxidation on the oxy-combustion process of large coal particles in a fluidized bed [24]. Alternatively, Guedea et al. [25] measured the devolatilization times of large particles at 800 and 900 °C, under N_2 and CO_2 atmospheres. To this end (in order to achieve it), they used a similar definition to the one used by Stubigton [26] and Brix et al. [27], but instead of defining it as the time needed to mass loss of 95%, devolatilization duration was defined as the needed for the mass loss rate to be lower than 1% of the initial rate; however, significant differences for this parameter were not found when the substitution of N_2 atmosphere for CO_2 was performed.

In the works of Bu et al. [12,28], experiments addressed to the compression of the effects of the substitution of N_2 for CO_2 in fluidized beds of large particles were carried out. They found by means of different techniques, which the difference in the devolatilization duration due to changes in the reaction atmosphere, are hardly perceptible and do not have any clear tendency when it comes to high rank coals such as an anthracite. Nevertheless, as the volatile material content increases, the differences indicate a greater devolatilization duration in the oxy-combustion environments in comparison to those of conventional combustion. Furthermore, with the increment of the particle size, both the ignition and flame extinction time increase, this can be explained by the effects that the particle size has on the parameters that control the ignition of the volatile (concentration of volatile and O_2 around the particle).

In our work, fast pyrolysis of large coal particles was carried out in a HPR, in which by means of an optical temperature measurer (pyrometer) it was possible to record the thermal history of the particles up to 900 °C. The experiments were carried out in an independent and discrete form at 500, 700 and 900 °C, under CO_2 and N_2 atmospheres. It should be highlighted that pyrolysis under a CO_2 atmosphere at high temperatures, imposes the coexistence of processes (gasification and pyrolysis), and that is the reason to evaluate the influence of the reaction atmosphere on the devolatilization phenomenon (mass loss and devolatilization duration), the porous structure (morphology) and the reactivity of the resulting char.

2. Materials and methods

2.1. Experimental equipment

The tests at high heating rates are performed in an HPR. Further information about this device regarding its functioning can be found in the work published by Montoya [29] and Valdés and Chejne [5]. In Fig. 1, the separated isometric diagrams of the HPR used are shown. In Fig. 1, it can be observed the heating element (7), which is a cold-annealing steel sheet with the ASTM A1008 standard, with dimensions of 6.00 cm x 4.00 cm, and a thickness of 0.45 mm; this sheet is pressed by screws (5) to plates (6) of the two parallel electrodes (9), through which the current necessary to the heating is fed.

On its top lid, there is an Epsilon pyrometer model CT-SF25 (1), which operates in the spectral range of 8.00 μm to 14.00 μm, two circular viewers (2) for the monitoring of the process and two ¼ NPT connectors (3) for the gases way-out and temperature measurement with thermocouples. Finally, the reactor is connected laterally to the ¼ NPT connector (4), to which a DRUCK-DPI 104 manometric pressure sensor is connected to record changes in pressure (error of 0.07 mbar) generated by the reactions involved. Alterations of the system emissivity affect the reliability of the measurement of the temperature; therefore, the experimental calibration of the pyrometer was performed. Details of the experimental and calibration procedure and others considerations are presented in Fig. 1S and S1 section of supplementary information and information on the process control can be found in Román-Gutiérrez [30].

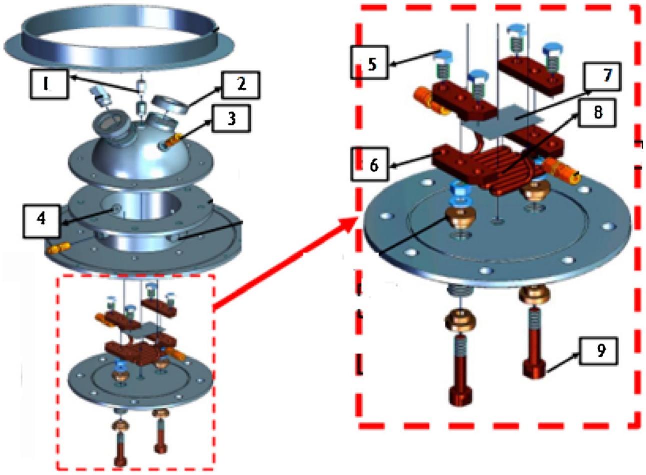

Fig. 1. Scheme of the experimental equipment.

A TGA (see scheme of TGA equipment, Linseis brand, STA PT1600 model with a L75/230 oven – Fig. 2S in S2 section of supplementary information) was used to carry out combustibility tests on chars obtained from pyrolysis process. The combustibility tests were carried out in a TGA equipment, since the char obtained come from large coal particles, these were reduced of size to less than 75 μm, that allowed to guarantee the conditions of kinetic control and the continuous monitoring of the mass loss. About 10 ± 0.01 mg of ground sample was weighed and placed in alumina crucibles of TGA.

Before heating, the TGA equipment was purged for 40 min with N_2 atmosphere, heated from room temperature to 110 °C with a heating rate of 10 °C/min, and held 30 min under N_2 (50 ml/min) to dry the samples. Then, samples were heated under N_2/O_2 mixture (50/13 ml/min) at 10 °C/min, from 110 °C to 900 °C and held for 300 min to validate the progress of the char combustibility. In order to reflect the repeatability and reproducibility, all the experiments were carried out at least three times.

2.2. Samples characterization

Semi-Anthracite coal (SA) from Colombia was the coal rank used in this research. Its physicochemical characterization was reported in a previous works of the authors [5,31]. The SA coal has low moisture and volatile matter content with 1.07 and 11.64 wt.%, respectively.

2.3. Samples preparation

For this research, SA coal samples were ground and then sieved in order to obtain a size distribution defined between 3.35 and 2.80 mm. It is important to note that given the fact that the particles are amorphous, for measuring of the average diameter it was performed a reading of three orthogonal dimensions to each other, as was proposed by Chirone and Massimilla [32]. The manual measurement tool, widely known as Vernier caliper (with ± 0.05 mm precision), was used with the aim of ensuring that width (d_1), height (d_2) and thickness (d_3) were orthogonally measured for each particle and fragments, in order to calculate the average particle diameter (d_m) of coal (Eq. (1)) or char.

$$d_{m,coal} = \sqrt[3]{d_1 d_2 d_3} \tag{1}$$

The sample mass is obtained by adding the masses of all the particles that make up the sample. For this purpose, a Mettler Toledo model