Biomass devolatilization at high temperature under N₂ and CO₂: char morphology and reactivity

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Abstract

Oxy-fuel combustion is usually performed in pf reactors under an enriched O₂ atmosphere of CO₂ to obtain a high CO₂ content in the flue gases. The effect of the differences in thermal properties of N₂ (conventional air combustion) and CO₂ (oxy-fuel combustion) on the devolatilization process needs to be evaluated. The morphology and reactivity of biomass chars obtained by devolatilization in an entrained flow reactor (EFR) at 1300 °C under N₂ and CO₂, simulating air and oxy-fuel combustion atmospheres, were studied. Four biomasses were selected: pine sawdust (PIN), olive waste (OW), olive stones (OS) and coffee waste (CW). The apparent volatile yield under CO₂ was greater than under N₂. The morphology of the chars was assessed using scanning electron microscopy (SEM). The higher mass loss and the lower char particle size obtained during CO₂ devolatilization indicate that a char-CO₂ reaction occurred. The reactivity indices indicate a lower reactivity of the CO₂-chars than the N₂-chars. The devolatilization atmosphere had a significant effect on the biomass chars, suggesting that gasification had occurred during CO₂ devolatilization. The OW, OS and CW chars showed a very high reactivity up to intermediate conversion levels, probably due to the catalytic effect of inherent alkali metals.

Keywords: Biomass; Char; Oxy-fuel combustion; Reactivity; Entrained flow reactor

1. Introduction

Fossil fuels are currently the most important source of energy production in the world. The share of coal, oil and natural gas in world energy consumption in 2013 was 30.1%, 32.9% and 23.7%, respectively, while renewable energies only represented 2.7% [1]. However, the combustion of fossil fuels in power plants generates a large amount of

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CO₂, which is the main contributor to global climate change. Biomass is a renewable fuel with a limited greenhouse effect, since the equivalent quantity of carbon dioxide evolved during its combustion is recycled as an integral part of the carbon cycle when it is absorbed by the biomass during its growth via photosynthesis. It is therefore considered as carbon-neutral. Biomass can be classified into the following types: residues (e.g., sewage sludge, agricultural and algae-based residues), herbaceous (e.g., grass and straw), aquatic (e.g., kelp), woody (e.g., sugarcane and sawdust) and derivatives (e.g., paper sub-products) [2]. Biomass is being increasingly used as an energy source for residential and industrial heating, for electricity production in modern biomass power plants and for co-firing with other fuels such as coal. It also has an important advantage as a fuel due to its high reactivity and volatiles content. However, compared to solid fossil fuels, biomass contains much less carbon and more oxygen and it has a lower heating value.

Direct air-combustion is the traditional way of using biomass, but other technologies such as pyrolysis or gasification have also been employed [2]. The use of renewable energies, such as biomass, is included as part of a diverse power generation portfolio, which is needed to reduce atmospheric CO₂ to below 1990 levels. Other CO₂ abatement strategies such as Carbon Capture and Storage (CCS) are also included. The oxy-fuel combustion process is considered one of the most promising CCS technologies since it can be adapted to conventional steam power plants. Thus, oxy-fuel combustion can be used as retrofit technology in conventional pulverized coal boilers with only minor modifications required. The oxy-fuel coal combustion process has mainly been focused on pulverized coal (PC) combustion, although it is also applied in circulating fluidized beds (CFB), since both technologies are considered mature for conventional air combustion. CFB technology presents some advantages such as fuel flexibility and high ability to adjust and control the combustion temperature by means of the circulating solid mass flow, although further research is required on the use of low recycled flue gas (RFG) ratios and on the heat transfer in CFB boilers. The oxy-fuel combustion technology involves the combustion of the fuel in a mixture of high-purity oxygen and recycled flue gas, which consists mainly of CO₂ and H₂O. In this process, the net volume of flue gas (and hence the boiler size) is reduced and a rich stream of CO₂ (> 95%) is produced, which after purification and compression is ready for transport and

storage [3]. The oxy-fuel combustion of biomass could provide a CO₂ capture method that would avoid further CO₂ emissions, besides reducing costs and efficiency penalties [4]. Although some problems might arise from the use of biomass, such as milling or transportation costs, these could be overcome if adequate consideration were given to the fuels, design and operating conditions of burners and boilers.

During the fuel combustion process, fuel conversion occurs in two main stages: fuel devolatilization and the subsequent combustion of the remaining char formed from the pyrolysis process. Although the devolatilization step lasts in a short time in relation to the duration of the complete combustion process, it can have a great impact on the overall process since it determines the characteristics of the ensuing steps (e.g., char reactivity and NO formation). The structure of the char plays a determinant role in its reactivity during combustion. In the case of oxy-fuel combustion technology, the substitution of an inert (N₂) for a reactive (CO₂) gas in the devolatilization atmosphere could affect the morphology, porosity and surface area of the resultant char and in turn its reactivity [5]. H₂O is also present in the RFG at a considerably lower concentration (up to ~10%) than that of CO₂, so its effect on the devolatilization step is expected to be low. However, it has been found in the literature a slight worsening of the coal burnout when steam (5-20%) was added to the oxy-fuel combustion atmosphere [6]. A precise knowledge of the reactivity of chars is fundamental for designing oxy-fuel boilers.

Several authors have undertaken preliminary studies to compare the devolatilization process in N₂ and CO₂. They have studied the differences in the chars obtained by devolatilization in N₂ and CO₂ in drop tube furnaces or entrained flow reactors in order to elucidate the firing differences between a conventional combustion process and the oxy-fuel combustion process. Thus, Rathnam et al. [7] studied the differences of coal chars obtained after devolatilization in N₂ and CO₂ in a drop tube furnace (DTF) at 1400 °C. Li et al. [8] compared the coal chars obtained in N₂ and CO₂ atmospheres in a DTF at 800-1400 °C. Gil et al. [9] studied the oxy-fuel combustion reactivity of coal chars obtained in N₂ and CO₂ atmospheres in an entrained flow reactor (EFR) at 1000 °C. Borrego and Alvarez [10] also compared the coal chars obtained under N₂ and CO₂ combustion atmospheres in a DTF at 1300 °C. In general, these works suggested a possible reaction of the char with CO₂ during the devolatilization under this atmosphere when the devolatilization temperature was high enough. Also, the differences between

the chars obtained under both atmospheres were higher for lower rank coal chars. However, all these studies were carried out on coal samples.

To the best of our knowledge, very few studies have been published on the effect of the devolatilization atmosphere on the characteristics of biomass chars, and in these cases the biomass chars were obtained at temperatures between 950-1000 °C. Thus, Gil et al. [11] studied the oxy-fuel combustion kinetics of biomass chars obtained after devolatilization in N₂ and CO₂ in an EFR at 1000 °C, but not relevant differences were observed between both atmospheres. This was attributed to the high oxygen content (30%) in the oxy-fuel combustion atmosphere that could have concealed possible differences in the reactivity of both chars. However, Borrego et al. [12] focused on the characteristics of the biomass chars prepared under N₂ and CO₂ atmospheres in a DTF at 950 °C and they also found that similar morphology, optical texture and specific surface were shown by the biomass chars generated under both atmospheres. Therefore, more research is needed on the differences in the chars obtained by devolatilization in N₂ and CO₂ of biomass samples to achieve an effective introduction of biomass in the oxy-fuel combustion technology. Moreover, the studies in literature about the effect of the devolatilization atmosphere on the biomass char characteristics are carried out at relatively low temperatures, which are not representative of the industrial boilers conditions. Consequently, the study of the properties and reactivity of chars after biomass devolatilization at the high temperatures representative of oxy-fuel combustion conditions in boilers is lacking. The effect of the gasification reaction of CO₂ with biomass char on the char burning rate under oxy-fuel combustion at high temperature is also a topic that requires further clarification.

Accordingly, the aim of the present work was to study the morphology and the combustion reactivity of four biomass chars obtained by devolatilization under N₂ and CO₂ atmospheres in an entrained flow reactor at high temperature (1300 °C). For this purpose, isothermal combustion experiments of the biomass chars were performed in a thermogravimetric analyzer. The surface area of the chars was determined from CO₂ adsorption isotherms at 0 °C. The morphology of the biomass chars was evaluated by scanning electron microscopy (SEM).

2. Materials and methods

2.1. Biomass samples

Four biomass samples were used in this work: pine sawdust (PIN), olive waste (OW), olive stones (OS) and coffee waste (CW). The PIN sample was supplied by Pellets Asturias, S.L. (Spain). The OW and OS samples were supplied by ELCOGAS, S.A. (Spain). The OW biomass is the wet solid residue that remains behind after the process of pressing and extraction of the olive oil. The CW samples used in the present work were the husks of coffee grains and they were supplied by the Asturian Foundation of Energy (FAEN, Spain). The biomass samples were ground and sieved to obtain a particle size fraction of 75-212 μm , which was used for the devolatilization tests. The results of the proximate and ultimate analyses together with the higher heating values of the raw biomass samples are shown in Table 1. In addition, the ash elemental composition of the biomass samples was determined by X-ray fluorescence spectrometry (XRF) in a Siemens SRS3000 device.

2.2. Devolatilization experiments for char preparation

The devolatilization process of the raw biomass samples was carried out in an EFR in streams of 100% N_2 or 100% CO_2 (under a total gas flow of 3 NL min^{-1}) at a reactor temperature of 1300 $^{\circ}\text{C}$ and a particle residence time of 2.5 s. A schematic flow diagram of the experimental device used for preparing the biomass chars is shown in Fig. 1. The reactor consists of a ceramic tube (height, 1480 mm; internal diameter, 38 mm) which is electrically heated and is able to work at a maximum temperature of 1500 $^{\circ}\text{C}$. A R-type thermocouple is used for controlling the temperature. The heating element is controlled by a PID (proportional band integral derivative) temperature controller. The biomass samples were stored in a hopper and fed in through an air-cooled injector to ensure that their temperature did not exceed 100 $^{\circ}\text{C}$ before entering the reaction zone, so as to avoid chemical reactions in the course of transportation of the fuel particles. The particles and the carrier gas were introduced from the top of the reactor and conducted along the centerline of the ceramic tube. The mass flow was controlled using a mechanical feeding system. The gases were preheated to the oven temperature before being introduced into the reactor through flow straighteners. The flow rates of N_2 and CO_2 from the gas cylinders were controlled by mass flow controllers. A water-cooled

collecting probe was inserted into the reaction chamber from below to collect the char samples. A cooling nitrogen stream was fed in through the top of the probe to quench the reaction products.

The apparent volatile yield (V^*) of the biomass samples was calculated from the EFR experiments as the percentage of mass loss experienced by the fuel during the devolatilization process. Fuel mass loss during the experiments was determined by the ash tracer method. The Q -factor value was also calculated as the ratio of the apparent volatile yield (V^*) to the volatile matter (V.M.) content which was calculated by proximate analysis.

2.3. Char characterization

The external morphology of the raw biomass and char samples was examined by means of scanning electron microscopy (SEM). Secondary electron images of the char samples were obtained using a Quanta FEG-650-FEI field emission scanning electron microscope operating at 30 kV.

The micropore surface area of the chars was determined from the CO₂ adsorption isotherms at 0 °C, which allow the narrower microporosity (pore sizes <1 nm) to be evaluated. The isotherms were obtained on a Quantachrome Nova 4000 volumetric instrument. Prior to analysis, the samples were outgassed overnight at 120 °C under vacuum. The Dubinin-Radushkevich (DR) equation [13] was applied to the CO₂ adsorption isotherms to obtain the corresponding micropore volume, W_0 , which was then used to calculate the micropore surface area, S_{DR} , of the chars.

2.4. Char reactivity

The reactivity tests applied to the biomass chars resulting from devolatilization in the EFR were conducted under an air atmosphere in a thermobalance (Setaram TAG92) at atmospheric pressure. A char sample of approximately 6 mg was placed in a crucible with a circular base (diameter, 5 mm; height, 2 mm). A thermocouple was positioned close to the platinum basket to monitor the temperature and to close the oven control loop. Experiments were performed under isothermal conditions at different temperatures (375-475 °C), which were individually chosen for each char sample to ensure kinetic control of the reaction. The sample was swept with N₂ at a flow rate of 50 NmL min⁻¹

and heated up to 850 °C at a heating rate of 15 °C min⁻¹. This temperature was then maintained for 10 min. After that, the sample was allowed to cool down to the desired reaction temperature. After mass stabilization, the isothermal combustion of the char sample was initiated by switching on an air current that passed through the reactor at a total flow rate of 50 NmL min⁻¹. The sample was allowed to react until complete combustion, i.e., when mass loss no longer occurred. The starting time of the air inflow was taken as the initial time (t_0). The char conversion, X , which represents the loss of mass fraction or mass conversion ratio, was calculated according to the following equation:

$$X = (m_0 - m_t)/(m_0 - m_f) \quad (1)$$

where m_0 is the initial mass of the char sample at time t_0 , m_t the mass of the char sample at time t and m_f the final mass of the char sample.

In order to compare the air combustion reactivity of the biomass chars obtained under N₂ and CO₂ atmospheres, the reactivity index at two conversion times was calculated as follows:

$$R_{0.5} = 0.5/\tau_{0.5} \quad (2)$$

$$R_{0.9} = 0.9/\tau_{0.9} \quad (3)$$

where $\tau_{0.5}$ and $\tau_{0.9}$ represent the time required to reach 50% and 90%, respectively, of char conversion. Higher reactivity indices indicate higher reactivities.

3. Results and discussion

3.1. Apparent volatile yield

The apparent volatile yield of the four biomass samples studied after devolatilization in both N₂ and CO₂ at 1300 °C in an entrained flow reactor are shown in Table 2. For all the biomass samples studied and for both devolatilization atmospheres, the apparent volatile yield (V^*) calculated from the EFR devolatilization experiments was higher than their respective volatile matter (V.M.) contents obtained by proximate analysis, indicating an enhanced devolatilization at the higher temperature and heating rate used in the entrained flow reactor. Therefore, the Q -factor (i.e., the ratio of V^* and V.M.) was higher than unity in all cases.

The V^* of the biomass samples measured after devolatilization in the CO₂ atmosphere was higher than that obtained under N₂ by 12.8, 11.7 and 2.7% for CW, OW and PIN,

respectively (Table 2). However, the difference was lower in the case of the OS biomass sample and the V^* measured after devolatilization in CO_2 was only slightly higher (0.8%) than that obtained in N_2 . The greater mass loss observed after devolatilization in the CO_2 atmosphere could have been caused by the gasification reaction between the char and CO_2 . Previous works in literature [7-9] reported higher apparent volatile yield values after devolatilization of coal at temperatures of 1000-1400 °C under CO_2 than under N_2 and they attributed this effect to the char- CO_2 gasification reaction. However, other authors [8, 12] obtained slightly lower values after devolatilization in CO_2 at lower temperatures (800-1000 °C), since the gasification reaction rate was considered to be not significant at low temperature. Brix et al. [14] found similar results in the apparent volatile yield under both devolatilization atmospheres, attributing this to the low residence times (0.15-0.20 ms), which limited the access of CO_2 to the surface of the particles. In summary, the results reported in the literature show that, apart from the atmosphere under which the fuel devolatilization is carried out (N_2 or CO_2), the conditions used during the devolatilization process can also significantly affect the characteristics of the resulting chars and that factors such as temperature, heating rate and particle residence time must all be taken into account simultaneously when the data are compared. Moreover, the properties of the biomass samples are different to those of coal, especially in the composition of the ashes, and different oxides in the biomass ash could have influenced the char- CO_2 reaction during the devolatilization process in the present work. Therefore, gasification of the biomass samples seems to be a reasonable explanation for the higher apparent volatile yield during devolatilization in CO_2 obtained in the present study in view of the relatively long residence time and high temperature used for the devolatilization experiments in the EFR. The char- CO_2 gasification is an intense endothermic reaction which can only take place when high temperatures are present.

3.2. Char morphology

The raw biomass samples and the chars obtained from the devolatilization of the biomass in N_2 and CO_2 atmospheres in the EFR were examined using a scanning electron microscope (SEM), images from which are shown in Fig. 2. Comparison of the

biomass chars and their corresponding parent materials shows that significant morphological changes occurred during the devolatilization stage.

In Fig. 2a it can be seen that the raw PIN biomass particles have a fibrous nature. A typical raw PIN biomass particle is made of solid cells but with visible cavities or slits, that seem to continue inside the particle. However, the cell structure of the raw PIN particles is not apparent in the PIN chars, PIN-N₂ (Fig. 2b) and PIN-CO₂ (Fig. 2c). The lack of a cell structure in biomass chars produced at high heating rates has been attributed by Cetin et al. [15] to the melting of the cell structure followed by plastic transformations. These authors emphasized that even at short residence times in a drop tube furnace at 1000 °C, melting still occurs at very high heating rates, and spherical particles may be formed. In the present work, after devolatilization in N₂ the surface of the PIN char particles became smoother than in the raw PIN. Also, the char particles showed signs of swelling and their size was reduced to below 100 µm. During biomass devolatilization in N₂ at atmospheric pressure, the particle first swells and then melts, evolving into a droplet before it ruptures and loses its volatile matter [15]. In the present study, after devolatilization in a CO₂ atmosphere there is no clear evidence of swelling from the SEM image of the PIN-CO₂ char, which shows particles of a smaller size, as well as the formation of clusters of small particles as a result of melting and the subsequent fusion of particles. This suggests that melting might have a more pronounced effect on the structural characteristics of PIN-CO₂ biomass chars than swelling.

Figs. 2d-f show the morphology of the OW sample before and after devolatilization in the N₂ and CO₂ atmospheres. The raw OW biomass particles do not have the fibrous shape found in the raw PIN particles, but they are more spherical (Fig. 2d). The OW-N₂ char particles show signs of swelling after devolatilization and they grew during the plastic stage to form hollow surface char particles as a result of the generation of volatiles (Fig. 2e). The OW-CO₂ char image shows the formation of rounded-shape particles with smoother surfaces after devolatilization in CO₂ (Fig. 2f), their average size being much smaller than those of the raw OW and the OW-N₂ char particles. There are no evident signs of swelling in such small particles. It can be seen that many particles have a size below 50 µm after devolatilization in CO₂, which might indicate that the CO₂-gasification reaction consumed part of the resulting char.

SEM images of the OS particles before and after devolatilization in N_2 and CO_2 atmospheres are shown in Figs. 2g-i. The raw OS biomass particles have a non-porous fairly rigid structure (Fig. 2g). Both the OS- N_2 (Fig. 2h) and the OS- CO_2 (Fig. 2i) char particles have retained some of the morphology of the original raw OS particles, but they have a more porous structure and a smaller particle size. In general, the OS char particles obtained in both devolatilization atmospheres have a fairly similar external appearance. However, Fig. 2h suggests that during devolatilization in N_2 the raw OS particles passed through a phase where volatiles were released through the pores, leading to some swelling in the OS- N_2 char particles. In contrast, after devolatilization in CO_2 , the OS- CO_2 char image (Fig. 2i) shows the formation of more compact particles with no signs of swelling and of a slightly smaller size. In the case of the OS biomass, the char- CO_2 gasification reaction during devolatilization in CO_2 probably occurred to a lesser extent since the decrease in particle size compared to that of the OS- N_2 char particles was not as great, which would agree with the only slightly higher apparent volatile yield observed after the devolatilization of OS in CO_2 compared to that measured in N_2 (Table 2).

Finally, Figs. 2j-l show the morphology of the CW sample before and after devolatilization in N_2 and CO_2 in the EFR. The raw CW biomass particles clearly have a sheet-like structure, their size ranging between 100-200 μm (Fig. 2j). The CW- N_2 char particles show signs of intense bubbling and swelling after devolatilization compared to the raw CW particles and it seems that a very large growth must have occurred during the plastic stage (Fig. 2k). In contrast, the CW- CO_2 char image shows the formation of rounded-shaped particles with smooth surfaces after devolatilization in CO_2 (Fig. 2l), and an average size that is much smaller than that of the raw CW and the CW- N_2 char particles with no such clear signs of swelling. Moreover, the formation of small particle clusters after devolatilization in CO_2 as a result of melting and the subsequent fusion of particles can also be detected. These results again suggest that melting has a greater effect on the structural characteristics of the biomass chars obtained in CO_2 than swelling and that the reaction between char and CO_2 reduced the particle size under the conditions studied. In contrast, Gil et al. [9] studied coal devolatilization in N_2 and CO_2 atmospheres in an entrained flow reactor at 1000 $^{\circ}C$ and found that devolatilization under CO_2 caused a greater degree of swelling in char particles than under N_2 , although

both types of char particles showed greater signs of swelling after devolatilization than in the present work. It should be noted, however, that they used a much lower temperature in their coal devolatilization experiments. They also concluded that a gasification reaction had probably occurred between the char and CO₂ in the case of some of the bituminous coals under study since they found evidence of partially reacted surfaces on the particles.

3.3. Reactivity of biomass chars

Fig. 3 shows the values of carbon conversion during air combustion of the biomass chars obtained in an EFR under N₂ and CO₂ devolatilization atmospheres. The reactivity of each biomass char was evaluated at two temperatures. It can be seen that in the case of PIN (Fig. 3a), the reactivity of the chars obtained after devolatilization in CO₂ was much lower than that of the same chars obtained under N₂ atmosphere for all the conversion values. However, in the case of OW (Fig. 3b), OS (Fig. 3c) and CW (Fig. 3d), the reactivity of the chars obtained under both devolatilization atmospheres was fairly similar up to conversion values of around 0.5-0.6. After that, the reactivity of the chars obtained in CO₂ was lower than that of the same chars obtained in N₂, as in the case of PIN. It can also be observed that the time required by the CO₂-chars to reach total conversion was higher in all cases. The decrease in the reactivity of the CO₂-chars can be ascribed to the consumption of a larger amount of reactive material under this devolatilization atmosphere, which agrees with the conclusions deduced from the SEM images in relation to the gasification reaction between the char and CO₂.

In their study on coal devolatilization in N₂ and CO₂ atmospheres in an entrained flow reactor at 1000 °C, Gil et al. [9] found that the reactivity index values of the coal chars produced under both devolatilization atmospheres were quite similar, although there was a slight trend towards higher reactivity values in the case of the N₂-chars. Besides the lower devolatilization temperature used for obtaining the chars, char reactivity was measured in a highly reactive oxy-fuel combustion atmosphere (30% oxygen content), so possible differences in reactivity could have been concealed. The fact that in the present work reactivity was measured in an atmosphere with a lower percentage of oxygen (21%) could explain the differences in the reactivity results between the CO₂-

chars and N₂-chars. A higher oxygen concentration would weaken the effect of the physical and morphological properties of the char on the combustion reactivity.

Naredi and Pisupati [16] reported that the reactivity of coal chars generated in Ar and CO₂ atmospheres in a drop tube reactor differed only when the chars had been obtained at high temperatures (>1300 °C) due to the contribution from char-CO₂ gasification reaction. It is therefore possible that gasification occurred during the devolatilization in CO₂ in the present work and that this affected air char reactivity.

Due to the differences in the gas properties of N₂ and CO₂, oxy-fuel combustion differs from conventional air-firing combustion. CO₂ has a higher specific molar heat capacity than N₂, which may cause a decrease in gas and particle temperatures for the same oxygen concentration. The speed of flame propagation and stability may decrease while the unburned carbon content may increase. During the oxy-fuel combustion process, these problems can be overcome by increasing the oxygen concentration in the oxidizer (up to approximately 30%) in order to match the combustion performance achieved in air in relation to the flame temperature, ignition time, heat transfer, gas temperature profile and char burnout [17]. This implies that the differences in reactivity found in the present work between the chars obtained in N₂ and CO₂ reflect to some extent their different morphological and structural characteristics. However, the differences would probably not have a significant effect on the oxy-combustion reactivity of these samples under a 30%O₂-70%CO₂ atmosphere. At high oxygen concentrations, the effect of the char properties on combustion behavior decreases [18]. For such high O₂ concentrations in oxy-fuel atmospheres, the reaction process is mainly dominated by the diffusion of O₂ to the surface of the solid fuel, decreasing the effect of the carrier gas [19]. Nevertheless, it should be borne in mind that if gasification occurs when biomass is treated at high temperatures in a CO₂ environment, in the later stages of the oxy-fuel combustion process, when the oxygen partial pressure has significantly decreased, the gasification of unburned char could have a significant effect on char burnout [8]. Thus, high concentrations of CO₂ could increase the char-CO₂ gasification rate and in turn the total combustion rate.

Table 3 shows the values of the reactivity index at two conversion times, $R_{0.5}$ and $R_{0.9}$, calculated from Equations (2) and (3), respectively, for the studied biomass chars during their combustion at two temperatures. Their values agree with the results shown in Fig.

3. The PIN char samples were less reactive than the other biomass chars. The reactivity index at 50% of conversion corresponding to the biomass chars obtained in N_2 was higher than that of the CO_2 -chars only in the case of the PIN and OW chars, whereas $R_{0.9}$ was significantly higher in the case of the N_2 -chars than for the CO_2 -chars for all the biomass char samples, as explained above.

Table 4 shows the textural parameters of the biomass chars calculated from the CO_2 adsorption isotherms at 0 °C. For all the biomass chars, the micropore surface area, S_{DR} , was much higher in the chars produced under N_2 atmosphere than that in the chars obtained under CO_2 , probably due to the char- CO_2 gasification reaction. The high temperature used during the devolatilization process of the biomass samples (1300 °C) may have caused a severe gasification of the material, resulting in a widening and enlargement of pores, followed by the collapse of adjacent pore walls or pore coalescence and a reduction in the microporosity with the conversion of micropores into mesopores or even macropores. This would corroborate the enhancement of the gasification reaction between the char and CO_2 when devolatilization is carried out under CO_2 atmosphere at high temperature. Borrego and Alvarez [10] also obtained higher micropore surface areas from CO_2 adsorption isotherms at 0 °C using the DR equation in the case of coal chars obtained in N_2 compared to those obtained in CO_2 and they concluded that the size distribution of the porosity had shifted to a larger size for the CO_2 -chars. Surface area is one of the main parameters that affects the reaction rate of carbonaceous materials at low temperatures. In the present work, Fig. 4 shows the relationship between the char reactivity and the micropore surface area of the biomass chars. As can be seen there is a clear linear correlation between the reactivity index of the chars at conversion values of 0.5 ($R_{0.5}$) and 0.9 ($R_{0.9}$) and their micropore surface area for each temperature and devolatilization atmosphere (see Table 3). This correlation is in agreement with the conclusions of Pohlmann et al. [20]. These authors found that the reactivity to air measured at low temperature reflects a kinetically controlled regime in which the reacting gas has time to diffuse through the pores and reach the narrowest porosity.

Therefore, the results obtained in the present study show that the devolatilization of biomass samples at high temperature using a high heating rate under a CO_2 atmosphere had a significant influence on the morphology and reactivity of the resulting chars,

which seems to confirm that the gasification reaction between the char and CO₂ effectively occurred.

On the other hand, in Fig. 3 it can be seen that for all the biomass chars studied, the time required to reach 50% of conversion is extremely short in comparison with the time required for their total combustion. This is particularly true in the case of the OW, OS and CW chars. It is also reflected by the much higher reactivity indices at low conversion values ($R_{0.5}$) in comparison with those obtained at high conversion values ($R_{0.9}$), as shown in Table 3. It has been reported in the literature that, apart from the conditions of devolatilization, inorganic constituents can play a very important role in char reactivity due to their catalytic effect. Some authors [21, 22] reported an increased combustion reactivity in biomass chars due to the catalytic effect associated to the water- or acid-soluble minerals or to the high alkali content of the samples. Thus, Jones et al. [23] demonstrated the catalytic effect of the potassium remaining in the char in conditions of high heating rate and temperature, which influenced both the devolatilization and char burnout stages during the combustion of willow biomass in methane-air flames. Table 1 shows the ash elemental composition of the biomass samples studied in the present work, expressed as metallic oxides. It can be seen that, among the catalytically active elements that might be present in the mineral matter of biomass char samples, the potassium content of OW, OS and CW is much higher (~30%) than that of PIN (16%), which might explain the higher reactivity of the OW, OS and CW chars up to intermediate conversion levels.

5. Conclusions

The morphology and reactivity of biomass chars obtained by the devolatilization of four raw biomasses (PIN, OW, OS and CW) in N₂ and CO₂ atmospheres at 1300 °C and at a high heating rate in an entrained flow reactor were investigated by determining the apparent volatile yield, and performing SEM analyses and combustion reactivity tests in a thermobalance. The apparent volatile yield of the biomass samples was higher during devolatilization in a CO₂ than in a N₂ atmosphere. Melting seems to have had a greater effect than swelling on the morphological characteristics of the biomass chars obtained in CO₂; these chars also had significantly smaller particle sizes. The reactivity indices at 90% of conversion indicated that the chars obtained in CO₂ were less reactive than those

obtained in N₂. Furthermore, the micropore surface area of the CO₂-chars was much lower than that of chars obtained under N₂. These findings show that the devolatilization atmosphere influenced the morphology and reactivity of the resulting chars, mainly due to a gasification reaction between the char and CO₂ during devolatilization in CO₂.

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Fig. 1. Schematic diagram of the EFR used for the preparation of chars.

Fig. 2. SEM images of the raw biomass and biomass char particles obtained under N_2 and CO_2 in an EFR at 1300 °C: (a-c) PIN, (d-f) OW, (g-i) OS and (j-l) CW.

Fig. 3. Effect of the devolatilization atmosphere (N_2 or CO_2) in an EFR on the carbon conversion (X) of the biomass char samples during air combustion: (a) PIN, (b) OW, (c) OS and (d) CW.

Fig. 4. Reactivity index for air combustion as a function of the micropore surface area of the biomass chars at the lowest (a) and highest (b) temperatures studied for each biomass char (see Table 3).

Table 1. Proximate and ultimate analyses, higher heating value and ash elemental composition of the raw biomass samples

Biomass sample	PIN	OW	OS	CW
Proximate analysis (wt.%, db) ^a				
Ash	3.8	7.6	0.8	7.6
V.M.	79.8	71.9	83.8	73.7
F.C. ^b	16.4	20.5	15.4	18.7
Ultimate analysis (wt.%, daf) ^a				
C	45.9	54.3	52.0	51.9
H	6.1	6.6	6.2	6.5
N	0.7	1.9	0.1	3.8
S	0.0	0.2	0.0	0.4
O ^b	47.3	37.0	41.7	37.4
Higher heating value (MJ kg ⁻¹ , db)	18.9	19.9	20.3	19.8
Ash content (wt.%)				
SiO ₂	22.9	13.5	10.0	5.1
Al ₂ O ₃	2.8	2.2	3.0	3.9
Fe ₂ O ₃	3.1	1.9	4.2	2.9
CaO	34.7	9.3	26.5	28.6
MgO	10.5	3.9	4.1	11.8
Na ₂ O	1.3	14.8	0.5	0.5
K ₂ O	16.4	31.8	28.3	33.8

V.M.: volatile matter; F.C.: fixed carbon; db: dry basis; daf: dry and ash free basis.

^a The proximate analysis was conducted in a LECO TGA-601, and the ultimate analysis in a LECO CHNS-932.

^b Calculated by difference.

Table 2. Apparent volatile yield of the biomass chars obtained under N₂ and CO₂ in an entrained flow reactor (EFR) at 1300 °C

Char sample	PIN	OW	OS	CW
V.M.-proximate analysis (wt.%, daf)	82.9	77.8	84.5	79.8
V^* -N ₂ (wt.%)	96.1	79.6	91.9	84.0
Q -factor-N ₂	1.16	1.02	1.09	1.05
V^* -CO ₂ (wt.%)	98.4	88.7	92.6	94.2
Q -factor-CO ₂	1.19	1.14	1.10	1.18
V^* increase in CO ₂ compared to N ₂ (%)	2.7	11.7	0.8	12.8

daf: dry and ash free basis.

V^* : apparent volatile yield; Q -factor = $V^*/\text{V.M.-proximate analysis}$.

Table 3. Reactivity indices of the biomass chars obtained in N₂ and CO₂ calculated at different temperatures

	Temperature (°C)	PIN		OW		OS		CW	
		N ₂	CO ₂	N ₂	CO ₂	N ₂	CO ₂	N ₂	CO ₂
$R_{0.5}$ (h ⁻¹)	375							31.5	35.8
	400			28.6	11.6	14.5	14.6	31.4	43.4
	425			28.8	18.4	18.3	14.8		
	450	1.2	0.5						
	475	2.5	1.0						
$R_{0.9}$ (h ⁻¹)	375							7.3	3.4
	400			7.3	2.0	2.8	1.7	15.2	9.3
	425			12.7	5.1	8.0	5.1		
	450	0.8	0.4						
	475	1.4	0.7						

Table 4. Textural characteristics obtained from the CO₂ adsorption isotherms at 0 °C corresponding to the biomass chars obtained in N₂ and CO₂

Char	CO ₂ adsorption at 0 °C	
	W ₀ (cm g ⁻¹)	S _{DR} (m ² g ⁻¹)
PIN-N ₂	0.08	173
PIN-CO ₂	0.01	27
OW-N ₂	0.16	353
OW-CO ₂	0.04	98
OS-N ₂	0.12	275
OS-CO ₂	0.04	96
CW-N ₂	0.18	403
CW-CO ₂	0.09	197