Combustión de briquetas preparadas con co-carbonizados de lignitos y biomasa

Combustion of briquettes prepared with co-carbonized of lignites with biomasa

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Abstract

The production of smokeless briquettes requires previously the carbonization of the starting materials so that their final characteristics are adequate. They should have a lower content of volatile matter than the original materials. The calcium additives is used to improve combustion and retain sulfur in the ashes. The combustion of the briquettes showed an excellent duration, between 40 and 50 min, taking into account their shape and size. They burned uniformly, without smoke or evolution of tars, starting from the outermost layer and evolving depending on the diffusion of oxygen to the interior. These briquettes were burned, in general, without flame, reaching almost zero carbon values in the ashes, which makes them suitable for domestic use. SO_2 emissions were reduced by increasing the relative amount of biomass in the cocarbonized material and obtaining materials with low sulfur content. Retentions of 99% of sulfur were achieved for briquettes prepared with co-carbonized of both coal and olive pits and molasses as a binder.

Resumen

La producción de briquetas sin humo requiere carbonizar previamente los materiales de partida para que sus características finales sean adecuadas. Se obtienen materiales con menor contenido de materia volátil que los originales. El uso de los aditivos de calcio tiene por objeto mejorar la combustión y retener el azufre en las cenizas. La combustión de las briquetas mostró una duración excelente, entre 40 y 50 min, teniendo en cuenta su forma y tamaño. Se quemaron uniformemente, sin humo, ni alquitranes, comenzando por la capa más externa y evolucionando dependiendo de la difusión del oxígeno hacia el interior. Se quemaron practicamente sin llama y con valores de carbono en las cenizas casi nulos lo que las hace adecuadas para su uso doméstico. Las emisiones de SO_2 se redujeron disminuyendo la cantidad relativa de carbón en el co-carbonizado y obteniéndose materiales de bajos contenidos de volátiles y azufre. Se lograron retenciones del 99 % del azufre para briquetas preparadas con co-carbonizados de carbón y huesos de oliva con melazas como ligante.

1. Introduction

Coal combustion in domestic installations and in small industrial boilers has been commonly used for heating and steam production. Its use may produce environmental problems in densely populated areas, in which the use of coal was widespread. This problem was increased if the sulfur content of the burned coal was medium-high or in the case of using coal briquettes with asphalt binders or tar derivatives.

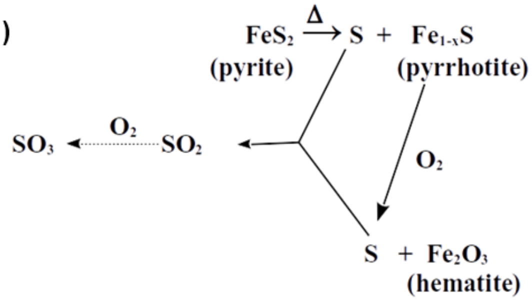
The markets and the regulations regarding the emission of pollutants during combustion have drastically restricted the important use of coal and its briquettes in the aforementioned sectors. The preparation of smokeless fuel briquettes currently constitutes, if technical and economic factors continue to be adjusted, an interesting alternative for certain energy sectors. These materials burn slowly and evenly, have adequate mechanical resistance, generate a low amount of smoke and few particles, and their combustion is effectively controlled [1]. However, and despite all these advantages over traditional briquettes, there is no question of recovering the extensive lost markets and returning to the large briquette production of the 1960-1970s.

Sulfur is one of the elements that constitute coal, it appears in inorganic and organic form and its total content ranges between 0.1 and 12%. Pyrite, an iron disulfide, is the main inorganic sulfur compound. Organic sulfur is chemically bound to the organic matrix of the coal and its presence is normally lower than that of pyritic sulfur. The composition of organic sulfur varies widely depending on the rank of the coal and its origin. It is generally estimated that in low rank coals organic sulfur is in the form of aliphatic structures, thiols, sulfides and disulfides, in approximately 70% and the rest in the form of aromatic structures, mainly as thiophene and its derivatives [2]. In high-rank coals these proportions are reversed.

Coal combustion produces, among other compounds, sulfur oxides, mainly SO_2, whose emission into the atmosphere contributes to acid rain and causes severe disorders in living beings.

During heating, the mineral matter rapidly decomposes within the char particles and both these and the decomposition products of the mineral matter are completely oxidized. Pyrite decomposes at a temperature of about 300 ºC to form pyrrhotite and then oxidizes at about 500 ºC to form hematite and magnetite [3,4]. The released sulfur is oxidized to SO_2 and SO_3, whose SO_2/SO_3 ratio is a function of excess air and combustion temperature (1).

(1)



The amounts of sulfur oxides emitted in the combustion of a briquette of coal or related materials depend, to a large extent, on the sulfur content and the content and nature of the mineral matter. If the formation of oxides of Ca, Mg, K and Na is quantitatively important, the ashes can retain up to 60% of the sulfur; the rest will be emitted as SO_x [5].

SO_2 removal is proportional to the coalcombustion rate and is controlled by the rate of oxygen diffusion in the ash layer [6]. According to the decreasing core model, the core of the briquette remains unreacted and a layer of ash is placed around it. The reactions that take place at the interface are:

$$C + O_2 \rightarrow CO_2 \quad (2)$$

$$S_{char} + O_2 \rightarrow SO_2 \quad (3)$$

$$CaS + 2O_2 \rightarrow CaSO_4 \quad (4)$$

According to this model, there is no oxygen left in the unreacted core, so the SO_2 produced diffuses to the surface of the briquette together with the combustion gases, N_2, O_2, CO_2, CO, NO_x, and passes through the ash layer where it reacts with the limestone added:

$$SO_2 + \tfrac{1}{2} O_2 + CaO \rightarrow CaSO_4 \quad (5)$$

The calcite present in the mineral matter of the carbonaceous materials and the added limestone act as adsorbents in the SO_2 retention process. From 800 ºC, the calcination of calcite occurs, which favors the formation of $CaSO_4$. However, at lower temperatures, such as 700 ºC, a certain amount of H_2S can be formed due to the characteristics of the atmosphere that is generated inside the briquette. The optimal desulfurization temperature is between 800 and 1000 ºC. When the temperature is higher, the desulfurization efficiency decreases due to sintering processes of the sorbent and the decomposition of $CaSO_4$.

Previous research indicates the desulfurization characteristics for coal briquettes. When limestone is used as a desulfurizer, it is not convenient to add a Ca_{added}/S molar ratio > 2.5 because the efficiency practically does not increase [7].

In this study, the sulfur retention in combustion of the prepared briquettes with co-carbonized of M2 and S/O and molasses as ligand will be followed, taking into account their characteristics, the added desulfurizers, the biomass content and heating rates between 10-30 ºC/min.

2. Experimental

For the preparation of these smokeless fuel briquettes, both carbonaceous materials with a reduced volatile matter, less than 18%, and environmentally acceptable binder are necessary, and, in some cases, additives specially designed to both capture sulfur and decrease the ignition point, and also to improve the combustion.

The CECA project [8], in which this work is framed, made necessary to use a low-rank coal. Among the coals from Aragón, the one from the María mine (M2), owned by SAMCA and belonging to the Ariño area (Teruel) was chosen as it was one of the most representative coals in this basin. To carry out this study, sawdust (S) and olive stones (O) were selected as biomass. Biomass is characterized by its high volatile matter and low sulfur content per unit of energy. The pine wood sawdust came from *Maderas Navarro in Villanueva de Gállego (Zaragoza)* and the olive stones from *Pina Oils in Puebla de Hijar (Teruel)*. Molasses, a byproduct of sugar refining, was chosen as ligand for its known use in briquetting processes. Cane molasses was supplied by the *Center Pyrolyse du Charbon de Marienau (CPM, France)*. The composition of molasses is affected by both the variety of cane from which it comes and the degree of maturity reached due to climate and soil conditions. Dry matter composition of cane molasses can be found in the literature [9].

Moisture is a characteristic of the materials which has a considerable influence on agglomeration and determines the choice of a particular briquetting process. The results of the immediate analysis and of the calorific power of the starting materials have been reported in the literature [10].

3. Results

Experiments were carried out in order to simulate the combustion of briquettes in a grate whose evolution would presumably be different from that already studied for a briquette in a quartz reactor [12, Chapter 7.3]. In this series of experiments, molasses-briquettes were prepared with co-carbonized coal (M2)-sawdust (S) and coal (M2)-olive pits (O) at 600º C (6) of temperature, varying the proportion of coal carbonized to 33 and 25%, (M2+S)6, 33, (M2+O)6, 33, (M2+O)6,25 [11]. They were mixed with molasses (14 wt%) and this blend was cold pressed as it was described in the literature [12]. The heating rates, before starting combustion without external heat input, were 10, 20 and 30 ºC/min. The influence of these rates, the addition of calcium, the type of biomass and the presence of sulfur were studied in the combustion of these briquettes.

All the tests were carried out in a large combustion chamber, described in Experimental Section [13]. which allows the visualization of the experiment with regulated air inlet and large gas outlet. The limitations of the weight of the briquettes to be burned in each experiment was about 20 g, and there was an inevitable dilution of the gases to be followed continously, so that it was decided to study the combustion in a discontinuous manner, taking solid samples over time.

Heating rate to start combustion

Figure 1 a) and b) show the results of the evolution of sulfur (%S) and carbon (%C) content in the combustion of briquettes with co-carbonized (M2+S)6, 33 using 10 ºC/min , 20 ºC/min and 30 ºC/min as heating rates.

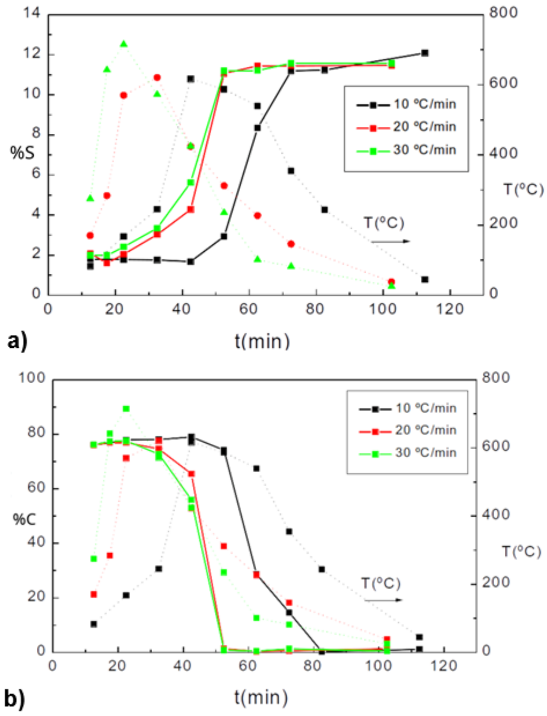


Figure 1. Influence of heating rate on a) sulfur and b) carbon content in the ashes of the briquettes prepared with (M2+S)6, 33.

Figura 1. Influencia de la velocidad de calentamiento en el contenido de a) azufre y b) carbono en las cenizas de las briquetas preparadas con (M2+S)6, 33.

The evolution of both sulfur a) and carbon b) is analogous for the heating rates of 20 and 30 ºC/min. However, the 10º C/min rate is quite different from the previous ones both at the beginning and throughout the combustion, showing a slower combustion.

At the beginning, the sulfur content in the solid is lower at the heating rate of 10 ºC/min than at the other rates due to a lower production of SO_2 and therefore a lower retention, this goes on until after 72 min the sulfur values are similar for the three heating rate. On the other hand, the largest decreases in carbon tend to start at the highest temperature reached in each heating rate; for sulfur content, the maximum temperatures reached in each heating rate and the beginning of a greater retention are also similar. The evolution of carbon exhibits, also clearly, the delay and the greater duration of the combustion of the briquette for the heating rate, 10 ºC/min and zero carbon content is reached at 80 min, while for the highest rate, 30 ºC/min, it is necessary a duration of 52 min.

Calcium addition

Briquettes with the formulation described in the previous section have been used with the addition of calcium in the form of limestone. In this case, the effect of the three different heating rates has also been studied. As an example, Figure 2 shows the evolution of sulfur a) and carbon b) content of briquettes with and without added calcium when combustion is carried out at a heating rate of 10 ºC/min and 30 ºC/min.

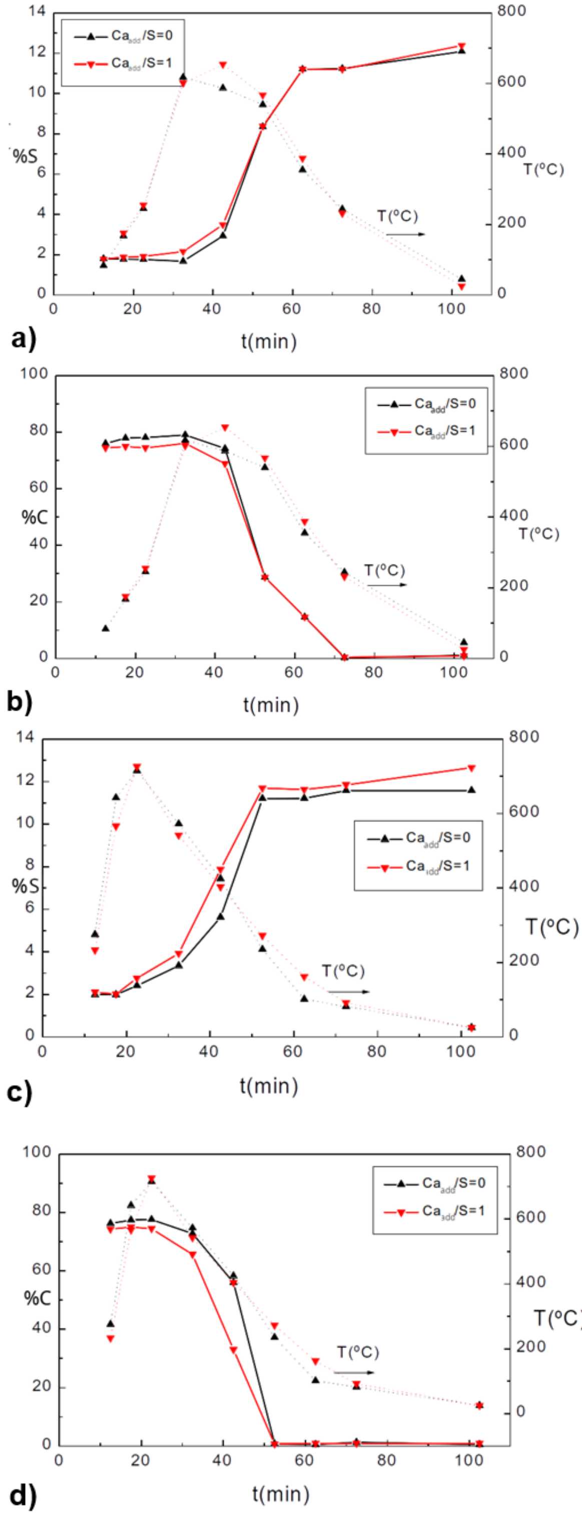


Figure 2. Influence of the addition of calcium on the content of a) sulfur and b) carbon in the ashes of the briquettes prepared with (M2+S)6, 33 burned with heating rates of 10 ºC/min; c) Influence of the addition of calcium on the c) sulfur and d) carbon content of the ashes of the briquettes prepared with (M2+S)6, 33 burned with heating rates of 30 ºC/min.

Figura 2. Influencia de la adición de calcio en el contenido de a) azufre y b) carbono de las cenizas de las briquetas preparadas con (M2+S)6, 33 quemadas con velocidas de calentamiento de 10 ºC/min; c) Influencia de la adición de calcio en el contenido de c) azufre y d) carbono de las cenizas de las briquetas preparadas con (M2+S)6, 33 quemadas con velocidas de calentamiento de 30 ºC/min.

The evolutions of the two elements are almost coincident for both the briquettes without calcium and with calcium. In the case of sulfur, the briquette with calcium presents, at the beginning and at the end of combustion, a slightly higher content than the briquette without calcium. The evolution of carbon (%) indicates a higher content of it in the briquette without calcium until 60 min of combustion, after 80 min the carbon content is zero for the two briquettes; it seems that briquettes with calcium burn slightly faster than those without calcium. Similar results were obtained when the heating rate was 20 ºC/min. The evolution of carbon content also indicates that the briquette with calcium begins to burn a little earlier than those that do not contain calcium. Finally, when the heating rate was 30 ºC/min, the final sulfur content in the solid is the highest of the three rates tested, indicating a higher sulfur retention produced because the calcium additive is available earlier.

The photograph reported in Figure 3 depicts the physical appearance of briquettes prepared with co-carbonized (M2+S)6, 33, and extracted from the combustion chamber at the indicated times and temperatures.

a)

b)

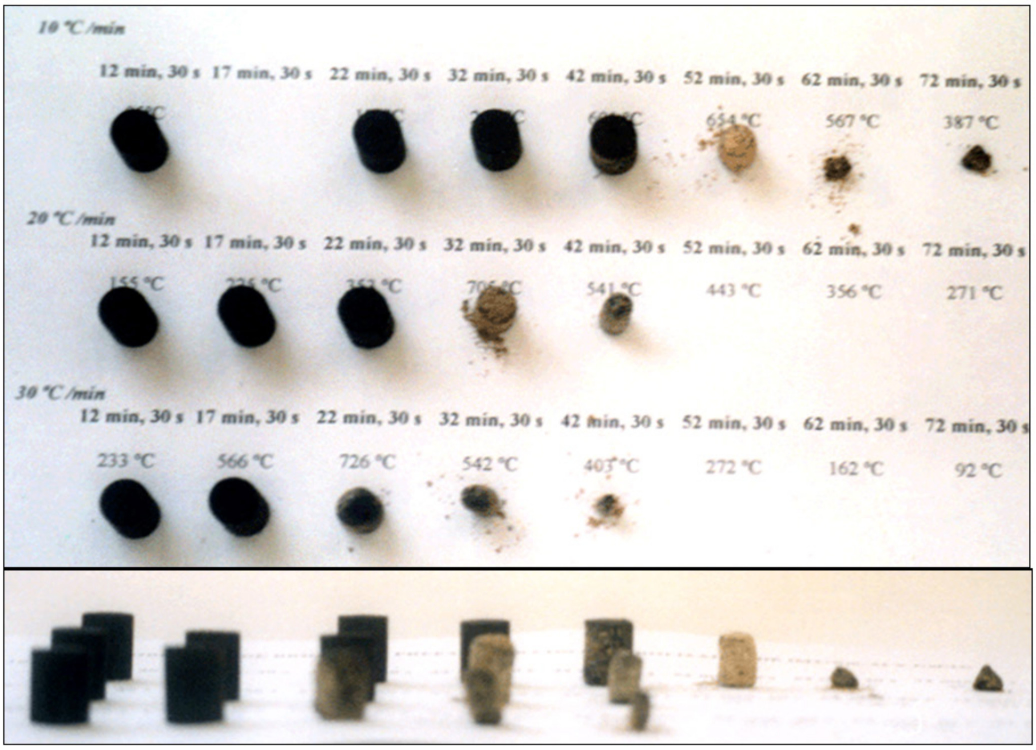


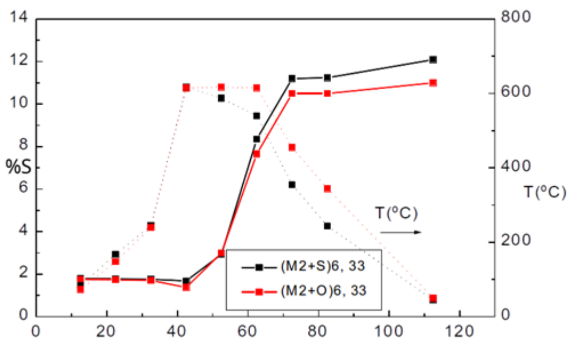
Figure 3. Photograph of the briquettes prepared with (M2+S)6, 33 burned in the combustion chamber.

Figura 3. Fotografía de las briquetas preparadas con (M2+S)6, 33 quemadas en la cámara de combustión.

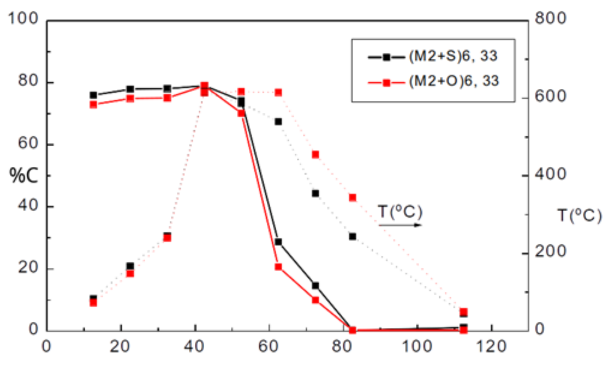
The ashes are formed as the temperature increases; the size of the briquettes decreases due to the release of the volatiles and they mantain their external appearance until they lose it due to manipulation after the experiment.

Biomass

The type of biomass used, sawdust or olive pits, on the carbon and sulfur content of the co-carbonized coal and biomass with 33% coal has been studied when the briquettes begin to burn at a heating rate of 10ºC/min (Figure 4).



a)



b)

Figure 4. Influence of biomass, sawdust (S) and olive pits (O), on the content of a) sulfur and b) carbon in the combustion ashes with a heating rate of 10 ºC/min of the briquettes prepared with a carbon content of 33%.

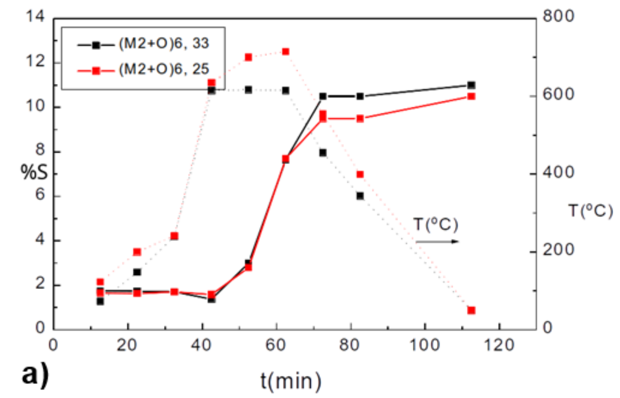
Figura 4. Influencia de la biomasa, serrín (S) y huesos de oliva (O), en el contenido de a) azufre y b) carbono de las cenizas de combustión con velocidad de calentamiento de 10 ºC/min de las briquetas preparadas con un contenido de carbón del 33 %.

The maximum temperatures reached by the two briquettes show that the one prepared with sawdust presents remarkably lower temperatures for the same moment of combustion. Figure 4 a) shows that the evolution of the sulfur content in the solids of both briquettes is analogous up to 600º C, later the briquette with sawdust maintains a higher sulfur content until the end of combustion. The evolution of the carbon content can be seen in Figure 4 b), showing that this content is lower in the briquette with olive stones, which indicates that it begins to burn earlier. For the two briquettes, zero carbon content is reached at 82 min, a time that indicates a long and complete combustion. This result highlights the good quality of these briquettes and even more considering their shape and weight.

Coal/biomass ratio

In this section, it can be followed the effect of different contents of co-pyrolyzed coal, 33 and 25%, with co-carbonized olive pits in briquettes burned at a heating rate of 10 ºC/min.

The evolution of the sulfur content in the solid is observed in Figure 5 a), and the carbon content of the briquettes prepared with co-carbonized M2 coal and olive pits with two ratio of coal carbonized at 600 ºC of temperature, 33 and 25%, (M2+O)6, 33 and (M2+O)6, 25, and burned with heating rate of 10 ºC/min is depicted in Figure 5 b).



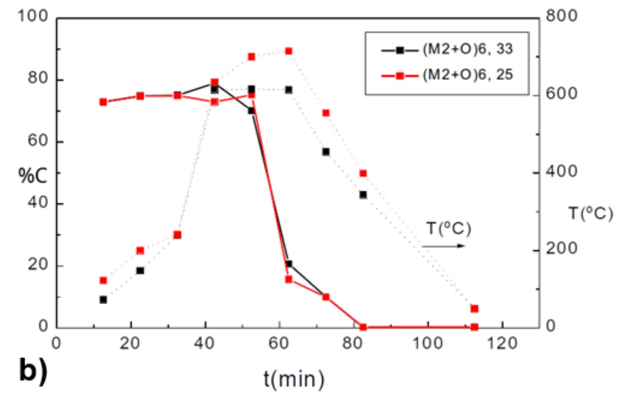


Figure 5. Influence of the carbon to biomass ratio on the a) sulfur and b) carbon content of the combustion ashes with a heating rate of 10 ºC/min.

Figura 5. Influencia de la proporción carbón a biomasa en el contenido de a) azufre y b) carbono de las cenizas de combustión con una velocidad de calentamientos de 10 ºC/min.

Figure 5 a) shows the evolution of the temperature and sulfur content of the solids during combustion. With regard to the former, it can be seen that the briquettes with 25% coal begin to heat up earlier and that once the ignition has started, these briquettes reach much higher temperatures than those with 33% coal. The evolution of the sulfur content is very similar for the two briquettes up to 70-75 min of combustion, later the sulfur increases in the briquette with higher content of co-carbonized coal. The carbon evolution presented in Figure 5 b) indicates that there are no notable differences between the two briquettes under these experimental conditions.

Visually, it was observed that the briquettes prepared with 33 and 25% coal. The greater amount of biomass in the co-carbonized, (M2+O)6, 25, the earlier combustion observed by the formation of ashes.

Sulfur retention

The retained sulfur has been estimated by applying the expression (6) to the materials involved in combustion with the materials obtained in the previous runs.

$$\%S_{retained} = S_{ash} / S_{initial} \times 100 \qquad (6)$$

The results obtained with the selected molasses briquettes are indicated in Table 1.

Table 1. Sulfur retained in the ashes of the briquettes burned in the combustion chamber

Tabla 1. Azufre retenido en las cenizas de las briquetas quemadas en la cámara de combustión

Carbonized material	Ca_{added}/S	Heating rate (ºC/min)	$S_{retained}$ (%)
(M2+S) 6, 33	0	10	73,84
(M2+S) 6, 33	0	20	70,06
(M2+S) 6, 33	0	30	70,73
(M2+S) 6, 33	1	10	89,14
(M2+S) 6, 33	1	20	86,40
(M2+S) 6, 33	1	30	91,08
(M2+O) 6, 33	0	10	93,58
(M2+O) 6, 25	0	10	98,99

This table shows that there are no relevant differences in sulfur retention depending on the heating rate. The best value for briquettes prepared with limestone is obtained with the highest heating rate, 30 ºC/min, because the calcium additive is available soon to fix the sulfur in the ashes.

The briquettes prepared with co-carbonized of (M2+O)6, 33 present higher retentions than those calculated for the briquettes prepared with the co-carbonized of (M2+S)6, 33. There is a 27% of difference between them. In addition, it also improves sulfur retention of the briquettes prepared with a higher relative proportion of biomass, (M2+O)6, 25, due, in part, to the low initial sulfur content.

4. Conclusions

Sulfur emissions have been reduced by increasing the relative amount of biomass in the carbonized material and with the presence of added calcium. Briquettes prepared with co-carbonized are more reactive than those containing only coal carbonized because the biomass promotes ignition and burning speed.

Combustion of briquettes prepared with molasses and co-carbonized of coal and olive pits is not fast and the SO_2 emissions remain the longest in the case of burning briquettes with molasses.

Briquettes containing calcium and 50-33% of coal achieve the highest retention.

The combustion of the selected briquettes showed an excellent duration, between 40 and 50 min, taking into account their shape and size. They burned uniformly starting from the outermost layer and evolving depending on the diffusion of oxygen to the interior. These briquettes were burned without smoke and, in general, without flame, reaching almost zero carbon values in the ashes, which makes them suitable for domestic use.

SO_2 emissions were reduced by decreasing the relative amount of coal in the cocarbonized material, obtaining materials with low volatile and sulfur content. Retentions of 99% of sulfur were achieved for briquettes prepared with co-carbonized of coal and olive pits and molasses as a binder.

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