INFLUENCE OF BIOMASS ON METALLURGICAL COKE QUALITY

M.G. Montiano, E. Díaz-Faes, C. Barriocanal*, R. Alvarez

Instituto Nacional del Carbón, INCAR-CSIC, Apartado 73, 33080 Oviedo. Spain

*Corresponding author. Tel: +34 985 11 90 90; Fax:+34 985 29 76 62; e.mail address: carmenbr@incar.csic.es

ABSTRACT

Two industrial coal blends used in cokemaking were subjected to tests in order to assess the influence of waste sawdust (SC2 from chestnut and SP1 from pine) on the quality of the coke produced. The biomass was added in quantities of up to 5 wt.%. It was observed that biomass produced a substantial decrease in the plastic properties of the industrial coal blend, with reductions in Gieseler maximum fluidity of around 50 % for 3 wt.% additions of the two different sawdusts. Carbonizations with sawdust additions ranging from 0.75 to 5 wt.% were carried out in a movable wall oven of 17 kg capacity. The bulk density of the charge was observed to decrease with increasing amounts of sawdust with negative consequences on the quality of the cokes produced. Mechanical strength was determined by means of the JIS test. Coke reactivity and post-reaction strength (CRI/CSR indices) were also assessed. The amount of sawdust added was low to prevent any deterioration in coke quality. The advantage of using biomass in coking blends should be seen as a possible way to reduce costs and CO₂ emissions and to incorporate alternative raw materials in coke production.

Keywords: waste sawdust, carbonization, coke, recycling.

1. Introduction

Integrated steel works generate a large amount of CO₂ due to their use of fossil fuels either as a reductant or as a fuel. It has been estimated that its contribution to total anthropogenic CO₂ emissions is about 6.5 % [1-4]. It has been proposed that fossil fuel be replaced by reductants which are more environmentally friendly. Biomass is a biological material derived from living organisms and, in the context of biomass for energy purposes, the term is often used to refer to any plant based material. Thus, wood and wood wastes, agricultural crops and their waste products are all considered as biomass. Biomass is considered to be carbon neutral because it takes carbon out of the atmosphere while it is growing and returns it as it is burned. If managed on a sustainable basis, new biomass can be replanted as part of a continuous program so that it is taking up CO₂ from the atmosphere at the same time as it is being released from the combustion of the previous harvest. In this way a closed carbon cycle with no net increase in atmospheric CO₂ levels is maintained.

Taken into account the importance of the thermoplastic properties of a coal for the development of the coke structure and for its final properties, the effect of the addition of biomass on coal thermoplastic properties has been investigated and it was found out that it leads to a reduction in maximum fluidity using a Gieseler plastometer [5]. High-temperature small-amplitude oscillatory-shear (SAOS) rheometry has been applied to evaluate the fluidity of biomass and its blends with coal as a function of time [6]. In agreement with the results obtained by Gieseler plastometry, the authors observed a detrimental effect on coal plasticity with the addition of biomass. Consequently, the effect of heating rate was studied to determine whether high heating rates might help to maintain the fluidity of the coal/biomass blends and so reduce the detrimental effect of biomass addition on the fluidity of the coal.

The interactions between coal and biomass during co-processing have been studied thoroughly in the literature [7-12]. Some authors in studying the devolatilization behaviour of blends of biomass and coal found that no interaction occurs under inert conditions and the yields of pyrolysis products is related to the amount of biomass and coal in the initial blend [7-10]. On the other hand other authors observed the existence of interactions between coal

and biomass when considering co-combustion [11] and co-pyrolysis of biomass and lignite [12]

Various possibilities for the inclusion of biomass in the iron and steel industry have been proposed [13-16]. Char produced from biomass can be used as reductant in blast furnaces either blended with metallurgical coke or alone in small blast furnaces. Another possibility is to use this char as a fuel in the blast furnace as a substitute for coal and oil. Some authors have reported the use of babassu charcoal as a replacement for metallurgical coke since it has a very low sulphur and phosphorous contents [13]. Carbonization of the entire babassu coconut would also avoid the problem associated with granulometry. Furthermore the use of charcoal in coal blends to produce metallurgical coke would be another way to reduce the level of greenhouse gas emissions produced in steelmaking [14,15]. The effect of the particle size of the charcoal on the quality of the resulting metallurgical cokes has already been studied and it was found that there is a relationship between the strength of the cokes and the size of the charcoal [15,16].

In light of these problems, the main aim of the present work was to study the effect of the addition of waste sawdust to industrial coal blends on coke mechanical strength and reactivity to CO₂.

2. Experimental

2.1. Materials

Two industrial coal blends (B3 and B4) which contain more than six different coals each with volatile matter content ranging from 33 to 14 wt% db were used. In addition, chestnut sawdust waste (SC2) and a pine sawdust waste (SP1) were selected as raw materials for the experiments.

The sawdust wastes were obtained from the furniture and flooring industry. The same sawdusts have already been studied [5] in relation to their effect on the development of thermoplastic properties of a coal with high fluidity and high volatile matter content. Proximate analyses were performed following the ISO-562 and ISO-1171 standard

procedures for volatile matter and ash content, respectively. The elemental analysis was determined by means of a LECO CHN-2000 for C, H and N, and a LECO S-144 DR for sulphur. Oxygen was determined on a LECO VTF-900. The inorganic matter composition of each sample was analysed by X-Ray fluorescence (XRF) in a SRS 3000 Bruker spectrometer in accordance with the ASTM D4326-04 standard.

2.2. Thermogravimetric analysis (TG/DTG).

The TG/DTG analysis of the raw materials was carried out using a TA Instruments SDT 2960 thermoanalyser. 10-15 mg samples with a particle size of < 0.212 mm were heated to $1000\text{ }^{\circ}\text{C}$ at a rate of $3\text{ }^{\circ}\text{C}/\text{min}$ under a nitrogen flow of $100\text{ ml}/\text{min}$. From the data obtained from the thermogravimetric analysis (TG), the volatile matter evolved up to a specific temperature (VMT) and the derivative of the weight loss curve (DTG curve) were calculated. T_{max} , the temperature of maximum volatile matter evolution was also obtained from the TG/DTG curves.

2.3. Assessment of coal thermoplastic properties

The thermoplastic properties of the industrial coal blend B4 and its mixtures with 0.75, 1.5, 2.25 and 3 wt% of the two sawdusts were measured by means of the Gieseler test (ASTM D2639-74). Only one of the industrial coal blends was studied assuming the same results for both, especially in view of the results obtained in a previous work [5]. The sample was heated at a heating rate of $3\text{ }^{\circ}\text{C}$ to a final temperature of $550\text{ }^{\circ}\text{C}$. The parameters measured in this test were: (i) softening temperature, T_s ; (ii) the temperature of maximum fluidity, T_f ; (iii) resolidification temperature, T_r ; (iv) plastic range, $T_r - T_s$, defined as the difference between the resolidification and softening temperatures; and (v) maximum fluidity, MF, expressed as dial divisions per minute (ddpm).

2.4. Carbonization experiments and coke quality evaluation

Carbonization tests were carried out in a movable wall oven of approximately 17 kg capacity (MWO17) [17,18]. The dimensions of the oven are 250 mm L x 165 mm W x 790 mm H. A load cell was mounted on the movable wall to measure the force exerted on it during carbonization. A programmable controller was used to regulate the oven temperature. The temperature at the centre of the coal charge was monitored by means of a thermocouple

connected to a PC. The coal was charged when the oven reached 1100 °C. The temperature of the wall was kept constant at 1100 °C throughout the test. The coke was pushed 15 min after the centre of the charge had reached 950 °C. The coking time was around 3.5 hours which gives a coking rate of 0.39 mm/min. The moisture of the charge was maintained at 5 wt%.

The cold mechanical strength of the cokes produced was assessed by the JIS test (JIS K2151 standard procedure). After the test, the coke was sieved and two indices were determined: the DI150/15 index was calculated from the amount of coke with a particle size greater than 15 mm and the DI150/5 index from the percentage of coke with a particle size lower than 5 mm. Consequently, the higher the DI150/15 and the lower the DI150/5, the better the quality of the coke. Coke reactivity and mechanical strength after reaction were assessed by means of the NSC test (ASTM D5341 standard procedure). Two indices were derived from this test i.e. the CRI index representing the loss of weight and the CSR index representing the percentage of partially-reacted coke remaining on a 9.5 mm sieve after 600 revolutions. The relationship between the CSR values obtained in the MWO of 17 kg capacity and those obtained in a 300 kg MWO has been explained elsewhere [19].

2.5. Optical microscopy and porosity of cokes

Samples with a particle size of 0.6-1.18 mm were mounted in resin for optical microscopy examination. The samples were then smoothed using silicon-carbide papers before being polished with fine alumina. To assess coke textural composition, the polished surfaces were examined using a polarising microscope fitted with crossed polars and a full-wave retarder plate. Optical appearance at 250 points on the cokes' polished surface was evaluated using the classification developed by Patrick [20].

The true density (ρ_{He}) of the cokes was measured by means of helium pycnometry in a Micromeritics Accupyc 1330 Pycnometer. Their apparent density ($\rho_{\text{H}_2\text{O}}$) was determined by water displacement using a 300 g coke sample with a particle size of 19–22.4 mm. From the true and apparent densities, porosity ($\epsilon_{\text{H}_2\text{O}}$) was calculated by means of the following equation [21]:

$$\varepsilon_{H_2O} (\%) = \left(1 - \frac{\rho_{H_2O} (g/cm^3)}{\rho_{He} (g/cm^3)} \right) \cdot 100 \quad (1)$$

3. Results and discussion

3.1. Characteristics of the raw materials

The main characteristics of the two industrial blends (B3 and B4) and the two sawdusts (SC2, SP1) are presented in Table 1. The blends have slightly different volatile matter contents (23.0 vs 26.2 wt.% db), but a very similar carbon content (approx. 82 wt% db). The C/H and C/O atomic ratios are similar for both industrial coal blends. The waste chestnut sawdust presents a lower volatile matter content and a higher ash content and C/H ratio than the pine sawdust. Both wastes present very high oxygen contents with consequently low C/O atomic ratios. Particle size distribution is a very important property in relation to coking as it influences the bulk density of the charge in the oven. The particle size distribution of the additives used in coking is also very important for ascertaining their influence on the quality of the resultant coke. It is generally accepted that coke breeze with a fine particle size does not cause any deterioration in the M10 index [22]. However, with coarser particle sizes the M10 is impaired. In the case of M40 there is an optimum size below and above which a deterioration in the M40 index occurs. The effect of particle size of the biomass used as additive on the quality of the cokes produced has been studied [16]. For biomass formed by compression at room temperature to a size larger than 10 mm, addition up to be increased to 1.5% was allowed. In the present research work, the particle size of the sawdust used was maintained as received and SP1 was finer than SC2.

3.2. Influence of sawdust on coal thermoplastic properties.

In a previous paper, the influence of three types of sawdust on coal thermoplastic properties was studied and it was found that 2 wt.% addition of this type of biomass produces a reduction in fluidity between 40% and 50 % depending on the sawdust and the type of coal [6]. In the present research work an industrial coal blend was used as base for the additions. Figure 1 shows the variation of the Gieseler fluidity in the industrial blend B4 and its mixtures with the two sawdusts studied (SP1 and SC2). A reduction in the maximum value of the curve is evident but the shape of the curve of the mixtures is similar to that of the B4 on its

own. The effect of the two sawdusts -SC2 and SP1- is similar and the addition of 3 wt% produces a reduction of around 50% in Maximum Fluidity in both cases. The result of the addition of sawdust to an industrial coal blend was similar to what was found previously with an individual coal [5]. When infusible materials are used the plastic range usually decreases because the softening temperature increases [23,24]. In contrast, the addition of asphalts, pitches or tars lowers the softening temperature, whereas the resolidification temperature does not change, and so the plastic range increases [23,25]. In the present case there is no significant variation in the plastic range as a result of the addition of sawdust, whereas the reduction in the fluidity of the blends is related to the amount of sawdust in the blend. Similar results were found when sawdust was added to a high fluidity coal [5]. The experimental data were adjusted to the logarithmic equation shown in Figure 2. The Figure includes the data of the variation of the fluidity obtained in a previous research work when a high fluidity and high volatile matter content coal was used. It appears that the industrial blend B4 is less affected by the sawdust than the individual coal. This could be due to the fact that B4 is composed of a high number of coals of different rank which could help to compensate the deleterious effect of the sawdust.

3.3. *Thermogravimetric analysis*

The thermal behaviour of the sawdusts, the industrial coal blends and the mixtures of the industrial coal blends with sawdusts is shown in Figures 3 and 4. The coke/char yield depends on the volatile matter content of the material. The large difference between the mass residues from the coal and biomass has been attributed [10] to the polymers that constitute the structure of the biomass which are linked through ether bonds. These types of bonds are less resistant to heat than those in the coal structure which are aromatic C=C. The thermal decomposition of the sawdusts shows three different stages: the first corresponding to the decomposition of hemicellulose in the temperature range of 200-300 °C; the second corresponding to the decomposition of cellulose in the temperature range of 275-350 °C; and the last one corresponding to the decomposition of lignin. The lignin decomposes over a broad temperature range between 280 and 500 °C with the maximum rate of decomposition

occurring at around 400 °C [26-28]. Whereas hemicellulose and cellulose present a high devolatilization rate over a narrow temperature range, the thermal decomposition of lignin takes place over a wider temperature range that commences at a lower temperature than cellulose. The devolatilization curves for the two waste sawdusts show that in the case of SP1 the decomposition of the hemicellulose appears as a shoulder in the derivative of the mass loss curve (DTG). The profile of the TG curves in the case of coal blends is similar, since the process of mass loss is a single step-process. The curves that represent the rate of volatile matter evolution for B3 and B4 also show that as the volatile matter content increases, the maximum rate of evolution of volatile matter increases. Table 2 contains a summary of the decomposition steps and their characteristic temperatures during the thermal treatment of the sawdusts and the industrial coal blends.

The differences related to the coke yield, which depends on the volatile matter content of the coal blends are worth noting. For single coals, the coke yield, and thus coal rank, is related to the temperature of maximum release of volatile matter (T_{max}) and to the DTG_{max} [29]. It can be seen that the higher the volatile matter content of the coal, the higher the DTG_{max} and the lower the T_{max} . The variation with rank of the macromolecular structure of the coals is the explanation for this behaviour. As coal rank increases for bituminous coals, so does the degree of aromaticity, the size of the lamella that forms part of its structure and the height of the stacking. In addition, the heteroatom content diminishes. All of these factors contribute to the increase in temperature during the decomposition process.

The industrial coal blends lost most of their volatile matter in the 400 and 500 °C range as was observed previously for single coals, but up to 400 °C the loss of volatiles was small [29]. In contrast the two sawdusts at the same temperature lost more than 75% of their total volatile content. In the literature it has been reported that the amount of char generated with increasing amounts of biomass in co-pyrolysis with coal decreases as the biomass content in the blend increases and that there are no apparent synergistic effects between the coal and biomass during co-pyrolysis [7-10]. In the present research work, pyrolysis of mixtures of industrial coal blends with the 3 and 5 wt.% amounts of the sawdusts was carried

out in a thermobalance. The results from the tests have been included in Table 2 and the devolatilization steps can be observed in Figures 3 and 4. In the temperature range below 400 °C the thermal decomposition of the sawdusts is shown together with the devolatilization of the coal blend that occurs mainly between 400 and 500 °C. The data in Table 2 indicate quantitatively the results observed in Figures 3 and 4 i.e., the 3-stage decomposition of the blends with sawdust which is assigned to the decomposition of hemicellulose and cellulose from SC2 and SP1 whereas the third stage corresponds to the decomposition of the coal blends. The thermal decomposition of sawdust from chestnut (SC1) and pine (SP1) had been studied in a previous research paper [5]. The shape of the TG/DTG curves in both cases is very similar with differences in char yield at 1000 °C of around 2%. The greatest differences in the temperatures of the three decomposition stages correspond to the chestnut sawdust (SC1 and SC2). It should be pointed out that although both are from chestnut they were collected at different times in the same factory. Therefore small differences in composition could be responsible for differences observed.

3.4. Carbonization of industrial coal blends with sawdust as additive

Carbonizations were carried out in a 17 kg movable wall oven at INCAR-CSIC using mixtures of the two industrial blends to which the waste sawdusts are added in percentages ranging from 0.75 to 3 wt.% in the case of B4 and from 1.5 % to 5 wt.% in the case of B3. Generally speaking biomass has a low bulk density. Consequently the inclusion of biomass in coal blends should produce a reduction in the bulk density of the charge. Figure 5 shows the variation in bulk density with the addition of sawdust during the carbonizations. Two factors can be considered to have had an influence on the bulk density of the carbonization charge in the oven, i.e. moisture and particle size [22]. Since humidity was kept constant in the two blends the difference in the bulk density of the charge carbonized without the addition of sawdust must be related to the differences in the particle size of the industrial blends (Table 1).

The quality of the cokes produced was assessed by means of the JIS test. Figure 6 shows the variation of the two indices derived from this test against the amount of sawdust in

the carbonizing blend. The indices corresponding to the coke from the industrial blends without the addition of any sawdust are $DI_{150/15}=79$, $DI_{15/5}=15$ for B4 and $DI_{150/15}=73$, $DI_{150/5}=17$ for B3. It can be seen that B4 produces cokes of better quality than B3 which agrees with the higher bulk density of B4 (Figure 5) revealed in the carbonization tests. The use of the two sawdusts produces a similar decrease in the cold mechanical strength indices, although it appears that the negative effect is slightly lower in the case of SP1. The particle size distribution of the two sawdusts which is shown in Table 1 indicates that SP1 has a finer size distribution, with a weight percentage lower than 0.5 mm of 19.1 wt.% for SP1 and only 4.1 wt.% in the case of SC2. Other authors on comparing the cold mechanical strength of cokes with 1 wt.% addition of biomass of different sizes found that in the case of particle sizes of 0.4 mm and 0.8 mm, the strength of the coke had a lower value than that of the base coal [16]. In contrast when biomass with a particle size of 2 mm was used, the strength of the coke was similar to that of the coke with no addition. Neither did they observe any impairment of coke quality when compacted biomass was added in the case of particle sizes greater than 11 mm. The particle size of the biomass was not found to be decisive in the present work possibly due to the broader size distribution used (0.5 and 3 mm).

The porous structure of cokes is known to influence its mechanical strength. Indeed there is a relationship between tensile strength and porous structure [30]. In the present research work the porosity of the cokes was derived by measuring their density, the results of which are shown in Table 3. It appears that the addition of sawdust produces an increase in total porosity mainly due to the decrease in the apparent density of the material. This variation in porosity may affect the mechanical strength of the cokes. No relationship has been established between the data obtained from the mechanical strength drum test and porosity determinations. Nevertheless, it is evident that, although pores may not always act as inherent flaws or weak locations, they may act as positions of initiation of microfissures out of which flaws develop [30].

Coke quality for its use in the blast furnace is usually assessed by means of the NSC test [31]. This method is considered to represent the conditions of the coke in the blast

furnace and it is generally used by coke producers. All sixteen cokes produced were tested to determine their CRI and CSR indices. Their variation with the amount and type of sawdust is shown in Figure 7. As is well known the two indices are linearly related, in this case the correlation coefficient being $r=0.935$. From the figure it can be seen that the industrial blend B3 produces a coke with a lower quality than B4. The two sawdusts further impair the quality of the coke as the amount of sawdust increases in the blend. From the data presented in Figure 7 it is possible to compare the effects of sawdust addition to two different industrial blends. If ΔCRI is defined as $\text{CRI}(\text{pure blend}) - \text{CRI}(\text{blend} + \text{sawdust})$, then ΔCRI for B4 with 3wt% sawdust is similar to ΔCRI for B3 with 5wt% addition (4 points for SP1 and 5 points for SC2). Defining ΔCSR as in the case of CRI, then ΔCSR for B4 with 3wt% level addition is lower (5-7 points for SP1 and SC2 respectively) than ΔCSR for B3 with 5 wt% addition (greater than 10 points).

It would appear from these results that the type of biomass does not play an important role in the CRI and CSR values, seeing that the two sawdusts produce a similar trend in the variation of the two indices. Nevertheless the CSR of the blends that contain SP1 is slightly higher than that of the blends with SC2 for the same level of addition to the industrial coal blend. Other authors using charcoal as additive found that the addition of finely crushed charcoal produced an increase in CRI with a corresponding lowering of the CSR [15]. Nevertheless when a coarser particle size was added the effect was less noticeable. In the present research work, although there were some differences in the particle size distributions of the two waste sawdusts used i.e. SP1 is finer than SC2 (see Table 1), it is not possible to assign difference in the quality of the cokes produced to the different size distributions of the sawdusts. The differences observed in the modification of the reactivity of the cokes produced with the addition of both sawdusts might be due to the catalytic effect of the ashes from the biomass. The data presented in Table 1 show that SC2 contains a higher amount of ash than SP1 (1.5 vs 0.3 wt.%db). The presence of metals like Ca and Mg has also been reported to appear in biomass and such metals have been known to catalyze the reaction of coke with CO_2 [15, 32]. The higher amount of ashes in the case of SC2 would

then enhance the reactivity of the cokes towards CO_2 to a greater extent than in the case of SP1. The composition of the ashes of the cokes produced from blends of B3 with 5 wt.% of SC2 and SP1 has been determined and the results presented in Table 4. The basicity index (BI) has been calculated taking into account the ash content and the ratio of basic to acidic oxides [31]. This index is higher in the coke with SC2 addition which agrees with its greater reactivity to CO_2 .

Optical microscopy is a technique widely used to study the textural components present in cokes and their impact on the quality of cokes [20, 33-36]. The rank of the coal is known to be important for determining the extent of anisotropic development during coking. Another important factor is the fluidity of the coal under study. Because the addition of sawdust modifies the fluidity of coals, it might also have an impact on the anisotropic structure of the cokes. The size and type of optical texture is predominantly a function of the parent material, the fluidity of which plays an important role in determining textural development. In the case of high rank coals the size of the anisotropic units depends more on the structure of the coals and little structural change was observed [37].

In the present case the quantitative analysis (see Table 5) of the cokes includes the differences between their anisotropic and isotropic components together with the percentage of inerts in the coke matrix. The inclusion of the sawdust produces, on the one hand, a decrease in the anisotropic components due to the deleterious effect of the sawdust on the fluidity of the coals, and on the other, an increase in the percentage of inerts. The latter effect is due to the appearance of the sawdust under the optical microscope. Figure 8 shows microphotographs of the char produced from the sawdust SC2 which is very similar to the appearance of the organic inerts in the cokes. Modification of the optical texture might in part explain the degradation of coke quality because isotropic material is considered to be more reactive towards CO_2 than anisotropic components.

4. Conclusions

The possibility of adding waste sawdust to two industrial coal blends was studied and it was found that, as in the case of the individual coals, it produces a significant decrease in fluidity

irrespective of the type of sawdust used (in this case chestnut and pine). Thermal decomposition was also studied and it was observed that negligible or no interaction takes place between the industrial coal blend and the sawdust during heating. It was found that the bulk density of the charge decreases with the inclusion of the sawdust and that the quality of the cokes is impaired specially in the case of 5 wt.% addition which is accompanied by an increase in the porosity of the materials. The addition of sawdust, without any densification pre-treatment should be kept to a low level i.e. below 2 wt%.

Acknowledgements

The authors are grateful to the Research Fund for Coal and Steel (RFCS) for financial support (Project RFCR-CT-2010-00007). M.G.M. thanks the Government of the Principado de Asturias for the award of a predoctoral grant with funds from the PCTI-Asturias within the Severo Ochoa program. Comments by anonymous reviewers on a previous version of this paper are acknowledged.

References

- [1] Wiklund CM, Pettersson F, Saxen H. Optimal resource allocation in integrated steelmaking with biomass as auxiliary reductant in the blast furnace. *ISIJ International* 2012;52:35-44.
- [2] Norgate T, Langberg D. Environmental and economic aspects of charcoal use in steelmaking. *ISIJ International* 2009;48:587-595.
- [3] Norgate T, Haque N, Somerville M, Jahanshahi S. Biomass as a source of renewable carbon for iron and steelmaking. *ISIJ International* 2012;52:1472-1481.
- [4] Ariyama T, Murai R, Ishii J, Sato M. Reduction of CO₂ emissions from integrated steel works and its subjects for a future study. *ISIJ International* 2005;45:1371-1378.
- [5] Montiano MG, Barriocanal C, Alvarez R. Effect of the addition of waste sawdust on thermoplastic properties of a coal. *Fuel* 2013;106: 537-543.
- [6] Castro Díaz M, Zhao H, Kokonya S, Dufour A, Snape CE. The effect of biomass on fluidity development in coking blends using high-temperature SAOS rheometry. *Energy & Fuels* 2012;26:1767-1775.
- [7] Moghtaderi B, Meesri Ch, Wall TF. Pyrolytic characteristics of blended coal and woody biomass. *Fuel* 2004;83:745-750.
- [8] Nola G, Jong W, Spliethoff H. TG-FTIR characterization of coal and biomass single fuels and blends under slow heating rate conditions: Partitioning of the fuel-bound nitrogen. *Fuel Process. Technol.* 2010;91:103-115.
- [9] Lu KM, Lee WJ, Chen WH, Lin TCh. Thermogravimetric analysis and kinetics of co-pyrolysis of raw/torrefied wood and coal blends. *Applied Energy* 2013;105: 57–65.
- [10] Vuthaluru HB. Thermal behaviour of coal/biomass blends during co-pyrolysis. *Fuel Process. Technol.* 2003;85:141-155.
- [11] Wu T, Gong M, Lester E, Hall P. Characteristic and synergistic effects of co-firing of coal and carbonaceous wastes. *Fuel* 2013;104:194-200.

- [12] Zhang L, Xu S, Zhao W, Liu S. Co-pyrolysis of biomass and coal in a free fall reactor. *Fuel* 2007;86:353-359.
- [13] Emmerich FG, Luengo CA. Babassu charcoal: a sulphurless renewable thermo-reducing feedstock for steelmaking. *Biomass and Bioenergy* 1996;10:41-44.
- [14] Ng KW, MacPhee JA, Giroux L, Todoschuk T. Reactivity of bio-coke with CO₂. *Fuel Process. Technol.* 2011;92:801-804.
- [15] MacPhee JA, Gransden JF, Giroux L, Price JT. Possible CO₂ mitigation via addition of charcoal to coking coal blends. *Fuel Process. Technol.* 2009;90:16-20.
- [16] Matsumura T, Ichida M, Nagasaka T, Kato K. Carbonization behaviour of woody biomass and resulting metallurgical coke properties. *ISIJ International* 2008;48:572-577.
- [17] Montiano MG, Barriocanal C, Alvarez R. Effect of elemental composition of various additives on the modification of coal thermoplastic properties. *Proc. ICCS&T 2011. Oviedo 2011 P1.27.*
- [18] Fernández AM, Barriocanal C, Alvarez R. The effect of additives on coking pressure and coke quality. *Fuel* 2012;95:642-647.
- [19] Díaz-Faes E, Alvarez R, Barriocanal C, Díez MA. Semi-pilot scale carbonization to assess blast furnace coke quality. *Proc. ICCS&T 2011. Oviedo 2011 P1.20.*
- [20] Barriocanal C, Hanson S, Patrick JW, Walker A. The characterization of interfaces textural components in metallurgical cokes. *Fuel* 1994;73:1842-1847.
- [21] León y León CA. New perspectives in mercury porosimetry. *Advances in Colloid and Interface Science* 1998;76-77: 341-372.
- [22] Loison R, Foch P, Boyer A. *Coke quality and production*. Butterworth London 1989.
- [23] Haberbehl D, Orywal F, Beyer HD. Plastic properties of coal in Elliot MA (Ed.). *Chemistry of Coal Utilization*, 2nd supplementary volume. Wiley interscience. New York 1981.
- [24] Fernández AM, Barriocanal C, Díez MA, Alvarez R. Influence of additives of various origins on thermoplastic properties of coal. *Fuel* 2009;88:2365-2372.

- [25] Fernández AM, Barriocanal C, Díez MA, Alvarez R. Evaluation of bituminous wastes as coal fluidity enhancers. *Fuel* 2012;101:45-52.
- [26] Basu P. Biomass gasification and pyrolysis. Practical design and theory. Academic press. 2010.
- [27] Melkior T, Jacob S, Gerbaud G, Hediger S, Le Pape L, Bonnefois L, Bardet M. NMR analysis of the transformation of wood constituents by torrefaction. *Fuel* 2012;92:271-280.
- [28] Yang H, Yan R, Chen H, Lee DH, Zheng Ch. Characteristics of hemicellulose, cellulose and lignin pyrolysis. *Fuel* 2007;86:1781-1788.
- [29] Barriocanal C, Díez MA, Alvarez R, Casal MD, Canga CS. On the relationship between coal plasticity and thermogravimetric analysis. *Journal of Anal. Appl. Pyrol.* 2003;67: 23-40.
- [30] Patrick JW, Walker A. Porosity and strength of carbon materials. In Patrick JW (Ed.) *Porosity in carbons: characterization and applications*. Edward Arnold 1995.
- [31] Díez MA, Alvarez R, Barriocanal C. Coal for metallurgical coke production: predictions of coke quality and future requirements for cokemaking. *Int. J. Coal Geol.* 2002;50:389-412.
- [32] White JE, Catallo WJ, Legendre BL. Biomass pyrolysis kinetics: A comparative critical review with relevant agricultural residue case studies. *Journal of Analytical and Applied Pyrolysis* 2011;91:1-33.
- [33] Marsh H, Clarke DE. Mechanism of formation of structure within metallurgical coke and its effect on coke properties. *Erdöl und Kohle- Ergdas* 1986;39:113-122.
- [34] Patrick JW, Reynolds MJ, Shaw FH. Influence of carbonization conditions on the development of different types of optical anisotropy in cokes. *Carbon* 1975;12:509-514.
- [35] Patrick JW, Reynolds MJ, Shaw FH. Optical anisotropy of carbonized coking- and caking-coal vitrains. *Fuel* 1979;58:501-509.

- [36] Barranco R, Patrick JW, Snape C, Thompson A. Impact of low-cost filler material on coke quality. *Fuel* 2007;86:2179-2185.
- [37] Moreland A, Patrick JW, Walker A. Optical anisotropy in cokes from high-rank coals. *Fuel* 1988;67:730-732.

Table 1. Main characteristics of the raw materials used.

	B3	B4	SC2	SP1
VM (wt.% db) ^a	23.0	26.2	76.8	85.3
Ash (wt.%db)	8.5	7.8	1.5	0.3
C (wt.%db)	82.1	82.4	56.1	53.3
H (wt.%db)	4.7	4.9	5.2	6.6
N (wt.%db)	1.9	1.9	0.5	0.5
S (wt.%db)	0.51	0.62	0.02	0.00
O (wt.%db)	2.3	2.4	36.7	39.2
C/H ^b	1.45	1.40	0.89	0.67
C/O ^b	46.9	45.0	1.82	0.81
Particle size distribution (wt.%)				
>3 mm (wt.%)	20.4	26.6	1.0	0.2
2-3 mm (wt.%)	9.8	10.6	4.5	1.3
1-2 mm (wt.%)	16.6	17.0	24.6	19.8
0.5-1 mm (wt.%)	16.6	15.3	65.8	59.6
<0.5 mm (wt.%)	36.6	30.5	4.1	19.1

a: Volatile matter. b: atomic ratio.

Table 2. Parameters derived from the thermogravimetric analysis performed at 3°C/min.

	B3	B4	SC2	SP1	B3+5SC2	B3+5SP1	B4+3SC2	B4+3SP1
VM400 ^a	9.9	11.5	76.8	86.9	19.4	24.3	17.6	21.3
VM400-500 ^a	46.6	49.2	7.1	5.6	42.6	40.0	48.7	46.3
VM500-750 ^a	31.0	27.9	8.1	4.2	29.4	27.4	26.7	25.0
DTGmax1 (%min ⁻¹) ^b	-	-	1.24	1.63	0.070	0.134	0.066	0.083
Tmax1 (°C) ^c	-	-	271	298	260	302	265	294
DTGmax2 (%min ⁻¹) ^b	-	-	3.14	3.77	0.167	0.248	0.129	0.200
Tmax2 (°C) ^c	-	-	310	342	310	343	308	346
DTGmax3 (%min ⁻¹) ^b	0.49	0.60	0.32	0.26	0.466	0.470	0.585	0.556
Tmax3 (°C) ^c	464	460	378	405	469	465	461	465
CY (%) ^d	74.5	71.5	20.0	14.8	73.4	71.6	71.6	71.2

^aVMT: volatile matter evolved up to a specific temperature (T) or in a specific temperature range and normalized to 100 %.

^b DTGmax: Rate of maximum volatile matter evolution.

^c Tmax: Temperature of maximum volatile matter evolution.

^d CY: Coke yield at 1000 °C.

Table 3. Pore characteristics of the cokes produced.

	ρ_{He} (g/cm ³)	$\rho_{\text{H}_2\text{O}}$ (g/cm ³)	$\epsilon_{\text{H}_2\text{O}}$ (%)
B4	1.861	0.894	52
B4+3SC2	1.878	0.847	55
B4+3SP1	1.882	0.882	53
B3	1.893	0.942	50
B3+5SC2	1.884	0.869	54
B3+5SP1	1.904	0.868	54

ρ_{He} : true density. $\rho_{\text{H}_2\text{O}}$: apparent density. $\epsilon_{\text{H}_2\text{O}}$: porosity.

Table 4. Oxide composition and basicity index.

	SiO ₂ (wt. %)	Al ₂ O ₃ (wt. %)	Fe ₂ O ₃ (wt. %)	MnO (wt. %)	MgO (wt. %)	CaO (wt. %)	Na ₂ O (wt. %)	K ₂ O (wt. %)	TiO ₂ (wt. %)	P ₂ O ₅ (wt. %)	BI*
B3+5SP1	50.12	32.25	7.52	0.06	0.89	2.35	0.61	1.15	1.82	1.15	1.79
B3+5SC2	50.60	32.37	7.50	0.05	0.85	2.33	0.56	1.04	1.81	1.11	1.88

*BI=Ashx(Fe₂O₃+ MgO+ CaO+ Na₂O+ K₂O)/(SiO₂+ Al₂O₃)

Table 5. Quantitative analysis of the optical texture of the cokes.

	Anisotropic components (vol%)	Isotropic components (vol%)	Large inert (vol%)	Small inert (vol %)
B3	70	2	22	6
B3+5SC2	61	5	26	8
B3+5SP1	60	6	25	9

Figure 1. Gieseler curves of the industrial blend B4 with various amounts of sawdusts SP1 and SC2.

Figure 2. Variation of the Gieseler fluidity of the mixtures of blend B4 with sawdust with respect to that of B4. PW SC1, PW SP1 and PW SR1 correspond to data from ref. 5.

Figure 3. Thermogravimetric curves corresponding to the industrial coal blend B3 and the mixtures with sawdusts SP1 and SC2.

Figure 4. Thermogravimetric curves corresponding to the industrial coal blend B4 and the mixtures with sawdusts SP1 and SC2.

Figure 5. Variation of bulk density of the charge in the coking oven with SC2 addition.

Figure 6. Variation of the JIS indices with the amount of sawdust added to the industrial coal blends B3 and B4.

Figure 7. Variation of the CRI and CSR indices of the cokes containing various amounts of sawdust.

Figure 8. Microphotographs of the char obtained at 900 °C from SC2 and of the cokes from the industrial coal blend B3 and their blends with 5wt% of SC2 and SP1. Magnification: x50.