





Article

Impact of the Addition of Pyrolysed Forestry Waste to the Coking Process on the Resulting Green Biocoke

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Abstract: The suitability of the charcoal obtained from woody biomass pyrolysis in a continuous screw reactor at 573, 773, 973, 1173 K temperature profile as fuel and reducing agent in metallurgical applications has been evaluated, in order to reduce the CO₂ emissions in these processes. On the one hand, a comparative study between charcoal and commercial reducers has been carried out. On the other hand, different proportions of this charcoal have been added to an industrial coking coal blend and carbonized together in a semi-pilot movable wall oven, to study the influence in the plastic and mechanical properties of the produced biocoke. The charcoal obtained fulfills the requirements to be used as fuel and reducer in non-ferrous processes where no mechanical strength is required, like rotary kilns, in substitution of fossil reducers. Its higher heating value (>32 MJ kg⁻¹) is in the range or over those of fossil coals, with the advantage of not containing polluting elements (S, N) and having less ash. The addition of up to 0.9 wt.% almost does not affect the quality of the biocoke; but the addition of ≥2 wt.% degrades the biocoke mechanical and plastic properties below the demanded requirements. Moreover, biocoke reactivity seems independent of the amount of charcoal added.

Keywords: pinus radiata woodchips; pyrolysis; charcoal; coking process; biocoke



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1. Introduction

The raw material used in the cokemaking process usually consists of a blend of different properties coals whose characteristics and price fit the best with the technical and economic needs of the blast furnace (BF) industry. The partial substitution of these coals by additives such as biomass is an option that has been studied as a way to reduce the need for this fossil fuel and consequently CO₂ emissions [1–4].

A priori, the addition of carbonized biomass to the coking coal blend to produce biocoke (i.e., coke partially produced with a renewable source of carbon), seems a viable option to reduce the CO₂ emissions [5,6]. On the one hand, its chemical composition is similar or even sometimes better than that of coal: the fixed carbon content is similar or greater than that of coal [7,8] and the content of sulfur and phosphorus in its ash, which are undesired alloying elements in the BF, are lower [6,9,10]. On the other hand, the reactivity of the charcoal is very high due to its high surface area and its porosity [11], which favors the transformation of the carbon into CO, and therefore a greater conversion of the metal oxides to pure metal, which improves the performance of the process.

However, in the case of coke, one of the most weakening agents of its mechanical resistance is its reactivity [12]. Menendez et al. [13] confirmed that there is an inversely proportional relationship between both, which shows that, especially in the case of BF, it is not appropriate to operate with high reactivity cokes. High reactivity can cause shrinkage of coke particles in the interior of the BF due to the loss of mechanical strength produced

by chemical and abrasion phenomena, impoverishing the process performance due to the loss of permeability of the coke bed by occlusion. In addition, the development of metallurgical techniques such as tuyere injection lessens the importance of the reductant and fuel functions of coke [14,15]; therefore, it is increasingly regarded to limit the reactivity of coke in order to minimize its use.

The problem with adding charcoal to a coal blend (CB) is that charcoal is not a coking coal and depending on the amount added and how well it interacts with the forming biocoke, it might have a significant impact on its characteristics. This occurs because charcoal is an inert material during the plastic phase of the coking process, it remains solid, which leads to poorer quality of biocokes [16]. Several factors have been proved to reduce these negative effects, for example a higher density, higher carbonization degree and bigger particle size of the charcoal used [4]. Some authors [17,18] have experimented with coal replacement by charcoal between 2–10% in cokemaking, stating that no important degradation of final biocoke's mechanical strength took place, achieving 1–5% CO₂ net emissions reduction. New discoveries such as using dense and demineralized charcoal and coking enhancers are seen as a way to further optimize this technique [19,20].

In recent years, the literature is getting a deeper understanding of the pyrolysis process concerning the influence of the type of biomass and the operating parameters (pyrolysis temperature, heating rate, residence time) on the properties of the charcoal obtained [6,10,21–24]. One of the conclusions reached in these investigations is that if high enough temperatures (973–1273 K) are used together with slow heating rate (slow pyrolysis), a solid product chemically similar to metallurgical coke can be obtained [25–28].

The authors have published recently a series of data about the slow pyrolysis of waste woody from *pinus radiata* in a screw reactor at different temperature profiles, 573, 573, 573, 573 K; 573, 773, 773, 773 K; 573, 773, 973, 973 K and 573, 773, 973, 1173 K. In this study it was reported that the solid yield decreased with the temperature from 53.8 wt.% at 3573, 573, 573, 573 K to 22.5 wt.% at 573, 773, 973, 1173 K, observing a strong reduction up to 573, 773, 773, 773 K [29].

In this paper, the usefulness of the charcoal obtained at 573, 773, 973, 1173 K in the previous referenced work [29] as reducing agent in steelmaking operations is presented. For this, on the one hand, a comparative of the charcoal with industrial reducing agents for applications that do not require of a high mechanical strength, such as rotary kilns, has been carried out. On the other hand, the quality of biocokes produced by mixing and coking mixtures of different proportions of charcoal and a commercial coking coal blend has been studied. The reason why 1173 K charcoal was selected is because its composition is the closest to that of the conventional coke; it presents more than 90 wt.% fixed carbon, more than 99 wt.% (daf basis) elemental carbon and less than 6 wt.% volatiles [29]. Therefore, it is expected that this charcoal presents the best characteristics to blend it with the CB in a carbonization process.

2. Materials and Methods

2.1. Raw Materials

The sample pyrolyzed was waste woody biomass of *pinus radiata* (*insignis* pine) coming from forestry activities carried out in Biscay, in the north of Spain, which was provided by a Spanish company devoted to bioenergy installations for heating. This specie was selected due to its abundance in the territory of Biscay and, in consequence, it is one of the most consumed by such company, to produce and supply wood chip fuel for thermal domestic heating. A description of the harvesting and preparation of the sample is detailed in a previous work published by the authors [30]. For the biocoke production, a commercial blend of coals (CB) used in industry for coking purposes was mixed with the charcoal obtained in the pyrolysis experiments at 573, 773, 973, 1173 K temperature profile.

Table 1 shows the results from proximate and elemental analysis of the biomass sample and of the CB, along with the higher heating value (HHV). It can be observed that most of the biomass sample consist on volatiles (79.1 wt.%), the moisture content is about 11 wt.%

and the ash content is quite low (0.7 wt.%). Regarding the elemental composition, carbon (47.8 wt.%), hydrogen (7.6 wt.%) and oxygen (most of the “others” fraction) are the main elements [29]. The composition of this biomass is quite similar to that reported by other authors for pine [30–32]. The HHV of the biomass sample is relatively low, as is usual in fresh biomass, due to its higher oxygen and moisture content.

Table 1. Chemical analysis of the initial biomass used for the pyrolysis experiments and the coal blend.

Analysis	Biomass	Coal Blend
Moisture (wt.% as received)	10.6	-
Proximate analysis (wt.% dry basis)		
Volatile matter	79.1	23.2
Ash	0.7	9.3
Fixed carbon ¹	20.2	67.6
Elemental analysis (wt.% dry and ash free basis)		
Carbon	47.8	89.7
Hydrogen	7.6	4.9
Nitrogen	0.0	1.2
Sulphur	0.0	0.7
Others ^{1,2}	44.6	3.5
H/C ratio	1.9	0.7
HHV (MJ kg ⁻¹ as received)	16.4	-

¹ by difference; ² mainly oxygen.

Regarding the CB, it presents high fixed carbon (67.6 wt.%) and elemental carbon (89.7 wt.%) content, low volatiles (23.2 wt.%) and an ash content of 9.3 wt.%.

2.2. Pyrolysis Experiments: Charcoal Production

The pyrolysis experiments were carried out using a laboratory scale continuous screw reactor (Process Integral Development Eng & Tech SL, Madrid, Spain), which splits into four individual heating zones (T_1 , T_2 , T_3 and T_4) and where the pyrolysis process took place, connected to a second reactor, where the pyrolysis vapors obtained were thermally treated to promote further cracking. The installation also includes a condensation section for the separation of condensable vapors and non-condensable gases. A more detailed description of this pyrolysis installation is shown in previous works published by the authors [28,29].

The charcoal selected in this research, attending to its characteristics, to produce biocoke was that one obtained at 573, 773, 973, 1173 K temperature profile, with a secondary vapor treatment step at 1073 K.

2.3. Carbonization Experiments

Mixtures of CB with amounts of up to 5 wt.% of the charcoal selected were prepared and carbonized at 1373 K in a semi-pilot movable wall oven of approximately 17 kg capacity in the Instituto Nacional del Carbón (INCAR) (Oviedo, Spain), to study the influence on the mechanical and chemical properties of the biocoke produced. A detailed description of the semi-pilot movable wall oven used for this study and the carbonization process is shown in a previous work published by the authors [8,33]. The duration of the coking was approximately 4 h, which corresponds to the time needed for the center of the coal to reach 1223 K plus 15 min of soaking time. The mixtures of CB and charcoal were carbonized with a dry bulk density of $782 \pm 5 \text{ kg/m}^3$ and the moisture of the charge was fixed at 4.5–5 wt.%. The produced biocoke was then refrigerated with water and left at room temperature for a whole day, and after it was characterized.

2.4. Characterization of the Biomass, Charcoal and Coal Blend Samples

The initial biomass, pyrolysis charcoal obtained and coal blend characterizations included proximate analysis determined by thermogravimetric analysis (LECO TGA-500) (LECO, St. Joseph, MI, USA) according to D3173-85, D3175-89 and D3174-82 ASTM standards, elemental composition (LECO TruSpec CHNS) (LECO, St. Joseph, MI, USA) complying the ASTM D5373 standard, and higher heating value (LECO AC-500 automatic calorimetric bomb) (LECO, St. Joseph, MI, USA), according to the ASTM D3286 standard.

The reactivity to CO₂ at 1173 K was determined using a METTLER TOLEDO TGA/SDTA851 thermobalance (METTER TOLEDO, Columbus, OH, USA), inspired in the ASTM D5341-99 standard. This parameter predicts how a metallurgical reducer would behave in CO₂ atmosphere and how much carbon would turn into CO following the Boudouard reaction ($C + CO_2 \leftrightarrow 2 CO$). A 10 mg sample is placed in a crucible that rests on a balance inside the furnace and heated up to 1173 K in an inert atmosphere of N₂; the gas is then switched to CO₂ just for 5 min and finally the sample is cooled down in N₂ gas again. The reactivity is determined dividing weight loss between the initial biomass weights.

The particle size distributions of the pyrolysis charcoal and CB were carried out by sieving 100 g of sample with a series of sieves in the range between 5–0.09 mm mesh sizes.

With respect to the textural characterization of the charcoal, true density and CO₂ adsorption measurements were determined. The real density was calculated in a Micromeritics Accupyc 1330 Pycnometer (Micromeritics Instrument Corporation, Norcross, GA, USA). The physical CO₂ adsorption was performed at 0 °C in a Quantachrome Nova 4200e apparatus (Quantachrome Inc, Boynton Beach, FL, USA). The micropores volume was determined taking account the isotherms previously obtained and applying the Dubinin-Radushkevich (DR) equation [34].

The inorganic matter composition of the charcoal and CB was analysed by X-ray fluorescence (XRF) in an SRS 3000 Bruker spectrometer (Bruker, Billerica, MA, USA) in accordance with the ASTM D4326-04 standard procedure. The 19 elements determined are: Si, Al, Fe, Mn, Ca, Mg, Na, K, P, Ti, S, Zn, Sr, Pb, Cr, Ni, Zr, Cu and Re.

2.5. Characterization of the Produced Biocokes

The Gieseler plastometer test was applied to mixtures of charcoal samples and a commercial coal blend. With this technique, the variation of the coal blend fluidity due to the addition of the charcoal was determined. To perform this test, a R.B. Automazione PL 2000 Gieseler plastometer (R.B. Automazione, Genova, Italy) complying with the ASTM D2639-74 standard was used [8,33]. The parameters that define the plastic behavior of a certain material derived from this test were: (i) softening temperature (T_s), when the stirrer reaches a certain speed (1 dial division per minute (ddpm)); (ii) the temperature of maximum fluidity (T_f), when the stirrer reaches maximum velocity; (iii) resolidification temperature (T_r), when the stirrer stops (0 ddpm); (iv) plastic range, ($\Delta T = T_r - T_s$), which is defined as the difference between the resolidification and softening temperatures; and (v) maximum fluidity (F_{max}), expressed as dial divisions per minute (ddpm).

The characterization of the produced biocokes consisted on a first cold mechanical strength test in a rotary drum. From the resulting biocoke, those particles with a size >15 mm were then dried, sieved to a particle size between 19 and 22.4 mm and the coke reactivity index and coke strength after reaction tests were consequently performed.

The cold mechanical strength of the biocokes was determined by the Japanese Industrial Standards (JIS) test (JIS K2151 standard procedure). The tests were performed introducing a sample of 10 kg of cold biocoke in a 1.5 m long and 1.5 m diameter rotary drum that rotates at 15 rpm for ten min. After the test, the biocoke was sieved and both JIS drum indexes, DI150/15 and DI150/5, were calculated from the amount of coke with a particle size >15 mm and <5 mm, respectively. In the case of DI150/5, the higher the value, the poorer the quality of the coke.

Coke reactivity index (CRI) was assessed by means of the NSC (Nippon Steel Corporation, Tokio, Japan) test (ASTM D5341 standard procedure). The CRI index is based on

the Boudouard reaction ($C(s) + CO_2(g) \leftrightarrow 2CO(g)$) and represents the loss of weight of the sample after reaction with CO_2 and it is expressed as a percent of the initial sample mass. Coke mechanical strength after reaction (CSR) was calculated by means of the NSC (Nipon Steel Corporation) test (ASTM D5341 standard procedure). The CSR represents the percentage of partially reacted coke (from CRI) that remains on a 9.5 mm sieve after 600 revolutions in a standardized drum. A good quality metallurgical coke must fulfill a $CRI \leq 30$ and a $CSR \geq 60$.

3. Results and Discussion

In order to test the usefulness of the obtained charcoal by biomass pyrolysis at 573, 773, 973, 1173 K temperature profile, to be used instead of reducing agents in metallurgical applications, on the one hand, its chemical properties and textural characteristics were compared with those of the commercial carbonaceous solid reducing agents. On the other hand, the quality of the biocokes formed by mixing and carbonizing together of charcoal in different proportions and an industrial coking coal blend (CB) was studied. In a previous research published by the authors [29] the textural characteristics of this charcoal were presented. Likewise, the influence of the original particulate size fraction (45–2000 μm) and of that grounded to 90–125 μm of the 1173 K charcoal on the combustion behavior of such charcoal under conditions that simulates tuyere injection operations in a blast furnace ironmaking process were studied. One of the conclusions was referred to that 1173 K charcoal conversion is higher than that of pulverized coal used in industrial applications, only for high injection rates, what are values typically used in industry [29].

3.1. Comparison of Charcoal with Commercial Reducing Agents

The charcoal obtained was compared with three commercial reducing agents used in the Zn recycling Waelz process such as metallurgical coke, petroleum coke and anthracite, provided by Befesa Zinc Aser, S.A. (Erandio-Biscay, Spain). For this, it has been taken account the characterization of these reducers carried out by the authors in a previous study [25], following the same procedures used in the case of pyrolysis solid (Section 2.4).

Table 2 presents the characterization of the three commercial reducers [25] and the charcoal derived from *pinus radiata* by pyrolysis at 573, 773, 973, 1173 K temperature profile. For better analysis of the results, the specifications that Befesa Zn Aser SA requires from their providers are included in brackets in the table. In order to more fairly compare the properties of the reducers and the charcoal, the proximate and elemental analysis of all the samples are presented in dry basis, regardless of the moisture content; in case of commercial reducers these data have been calculated considering that the maximum allowable moisture required by Befesa is 20 wt.%.

As it can be seen, the charcoal obtained presents more than 90 wt.% fixed carbon, less than 6 wt.% volatiles, very low ash content (3 wt.%) and moisture content rather low (1 wt.%). Concerning the elemental composition, it has more than 96 wt.% (dry basis) elemental carbon. Similar results have been reported by Agirre et al. [26], who stated that charcoals suitable for metallurgical use should present volatile matter lower than 10 wt.%. Griessacher et al. [27] also concluded that fixed carbon contents should be greater than 80–85 wt.%. The charcoal obtained is a good fuel due to its high HHV ($>32 \text{ MJ kg}^{-1}$), in the range of that petroleum coke (33.6 MJ kg^{-1}), or even over that of the metallurgical coke and anthracite used in this work (26.0 and 25.5 MJ kg^{-1} , respectively), with the advantage of not containing polluting elements (S, N), and having less ash contents.

Comparing the results (as received/produced basis) of the reducers and the charcoal, the following advantages of the charcoal can be mentioned: it has much lower moisture content than any of the commercial reducers and significantly lower ash content than the metallurgical coke and the anthracite. It also presents significantly lower sulfur content and higher fixed and elemental carbon contents than any of the commercial reducers. The only somewhat critical aspect of the charcoal is that it has a volatiles content that does not

meet the specifications of metallurgical coke, although it does meet the petroleum coke and anthracite specifications.

If the results on a dry basis are compared, it can be seen that the fixed carbon and elemental carbon contents of the commercial reducers are lower than that of the charcoal. Therefore, it can be concluded that as far as composition is concerned, pinus radiata charcoal obtained at 573, 773, 973, 1173 K can replace certain commercial reducers in reduction processes in rotary kilns with the great advantage of having much lower ash and sulfur contents.

Table 2. Chemical analysis of the commercial reducers [25] and charcoal.

Analysis	Metallurgical Coke	Petroleum Coke	Anthracite	Charcoal
Proximate analysis (wt.% as received/as produced basis)				
Moisture	11.4 (<20)	6.4 (<20)	18.0 (<20)	1.0
Volatile matter	3.5 (<7.0)	9.4 (<15.0)	5.9 (<7.0)	5.4
Ash	11.0 (<20.0)	1.8 (<20.0)	9.2 (<20.0)	3.0
Fixed carbon ¹	74.1	82.2	66.9	90.6
HHV (MJ kg ⁻¹ as produced basis)	26.0	33.6	25.5	32.3
Proximate analysis (wt.% dry basis)				
Volatile matter	3.9 (<8.75)	10.1 (<18.75)	7.2 (<8.75)	5.5
Ash	12.5 (<20)	2.0 (<20)	11.2 (<20)	3.0
Fixed carbon ¹	83.6	87.9	81.6	91.5
Elemental analysis (wt.% dry basis)				
Carbon	85.7	83.6	88.5	96.1
Hydrogen	0.5	2.8	0.6	0.2
Nitrogen	1.0	1.3	1.0	0.1
Sulfur	0.9 (<3.75)	5.6 (<3.75)	0.6 (<3.75)	0.0
Others ^{1,2}	0.8	4.9	0.0	0.6

¹ by difference; ² mainly oxygen.

With respect to the reactivity to CO₂, charcoal has higher reactivity (23.3%) than that of anthracite and metallurgical coke, whose reactivity values (determined following the same method described in Section 2.4) are around 6% and 2%, respectively.

A comparison between the textural characteristics of the three commercial reducers and the charcoal obtained at 573, 773, 973, 1173 K temperature profile is presented in Table 3.

Table 3. Textural characteristics of the commercial reducers [25] and charcoal.

Characteristic	Metallurgical Coke	Petroleum Coke	Anthracite	Charcoal
True density (g cm ⁻³)	1.916	1.389	1.793	1.798
Micropore volume (cm ³ g ⁻¹)	0.01	0.07	0.05	0.410
Surface area (m ² g ⁻¹)	24	156	122	491

It can be observed that charcoal has a true density, comparable to those of metallurgical coke and anthracite, and higher than that of petroleum coke. This fact can be attributed to the lower ash and the higher micropore volume in the case of petroleum coke (1.8 wt.% and 0.07 cm³ g⁻¹, respectively). Concerning to the surface area, the charcoal surface area is much greater than those of reducers; therefore, it can be expected that charcoal could have a higher reactivity.

3.2. Production of Biocoke Formed by Mixing Charcoal with a Coking Coal Blend

3.2.1. Comparison between Charcoal and Coking Coal Blend

The particle size distributions of the charcoal sample and CB are shown in Table 4. The particle size of the charcoal responds to logistical criteria, such as the limitations imposed by the configuration and dimensions of the laboratory scale continuous screw reactor used itself. With respect to the CB, it is a commercial coal blend typically used in industrial applications for coking purpose and its particle size is similar to the one used in the industry. As it can be seen, 32.3 wt.% of the particles in the charcoal are below 0.5 mm, most of the particles of the sample (39.0 wt.%) between 0.5 and 1 mm, and 28.6 wt.% of the particles between 1 and 2 mm. Compared to charcoal, the CB particle size distribution is wider, most of the particles are below 0.5 mm (40.4 wt.%) but both 0.5–1 mm and 1–2 mm fractions of the coal blend are smaller (23.3 and 15.8 wt.%, respectively) than that of charcoal, while 20.5 wt.% of the CB sample particle are over 2 mm.

Table 4. Particle size distribution (wt.%) of the charcoal and the coking coal blend.

Particle Size	Charcoal	Coal Blend
>5 mm	0.0	5.0
4–5 mm	0.0	2.1
3–4 mm	0.0	4.9
2–3 mm	0.1	8.5
1–2 mm	28.6	15.8
0.5–1 mm	39.0	23.3
<0.5 mm	32.3	40.4

An important factor that may have an effect on the quality of the biocokes produced with additives such as charcoal is the modification of the coke ash chemistry. To illustrate it, the ratio between the basic oxides and acidic oxides, known as the alkalinity index (*AI*), was calculated with the Equation (1).

$$AI = Ash \cdot \frac{Fe_2O_3 + CaO + Na_2O + K_2O + MgO}{Al_2O_3 + SiO_2} \quad (1)$$

The content and composition of the 1173 K charcoal ash and the CB ash, as well as *AI* are shown in Table 5. It can be observed that in contrast to the CB, biomass charcoal presents a higher amount of calcium, potassium, and, to some extent, magnesium and phosphorus, while the former contains mainly silicon and aluminum. On the one hand, both calcium and potassium have been proven to be detrimental to the blast furnace operation [35,36]. These two metals are responsible for catalyzing the Boudouard reaction; hence, they increase the reactivity of the charcoal to CO₂ [37]. This may be of interest when using it as a reducing agent in certain processes such as the reduction in rotary kilns, but not for BF cokes since it weakens the porous structure of the coke bed, which might cause the collapse of the coke bed. On the other hand, the CB sample contains three times the amount of ash present in the charcoal (9.3 wt.% and 3.0 wt.%, respectively), which is not convenient as far as calorific value, reactor maintenance and slag overproduction reasons is concerned [3]. The composition of the ash in the CB is also more acidic, which would require the use of a greater amount of flux in the blast furnace operation to increase the basicity of the resulting slag. Therefore, though the composition of the charcoal ash is worse than that of the CB, the addition of charcoal to the coking blend will give as a result the reduction of the total amount of ash in the biocoke, and this may compensate the worse composition of the charcoal ash.

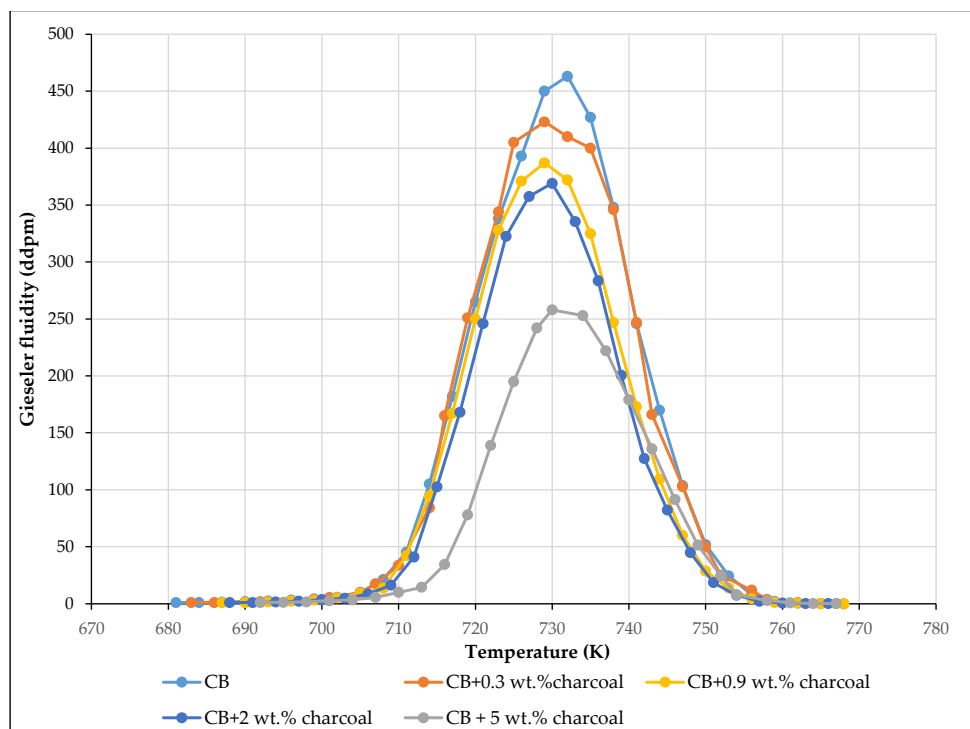
Table 5. Content (wt.% dry basis), composition (wt.%) and alkalinity index (AI) of ash of charcoal and coal blend.

Sample	Ash	SiO ₂	Al ₂ O ₃	CaO	K ₂ O	Fe ₂ O ₃	MgO	P ₂ O ₅	SO ₃	TiO ₂	Na ₂ O	MnO	Rest	AI
Charcoal	3.0	32.6	8.4	25.5	14.2	3.9	5.1	4.4	2.3	0.4	1.2	1.1	0.8	0.9
Coal blend	9.3	54.9	29.1	2.0	2.9	5.8	0.8	0.8	1.2	1.7	0.5	0.1	0.3	1.3

3.2.2. Biocokes Prepared with Different Charcoal Charges

To test the influence of the amount of charcoal added to the CB for biocoke produced in its mechanical, plastic and chemical properties, four different mixtures of pyrolysis charcoal and CB were carbonized: 0.3 wt.%, 0.9 wt.%, 2 wt.% and 5 wt.% of charcoal plus the CB. In addition, a blank coke was produced through the carbonization of the CB.

Figure 1 shows the results obtained in the Gieseler plasticity test plastometer of the mixtures prepared. As it can be seen, the temperature of maximum fluidity (T_f) is almost independent from the amount of charcoal introduced in the mixture (727–732 K). However, the maximum fluidity reached (F_{max}) clearly decreases when charcoal is added to the CB; the fluidity obtained for raw coal blend is 463 ddpm, but if 0.9 wt.% charcoal is introduced to the mixture the fluidity is reduced to 398 ddpm, decreasing to a value of 258 ddpm for 5 wt.% charcoal addition. Other authors have also experienced similar trends [38–40].

**Figure 1.** Gieseler fluidity curves of the coal blend-charcoal mixtures.

The loss of Gieseler maximum fluidity (%) when different proportions of charcoal has been added to CB is observed in Figure 2. Montiano et al. carried out a research about the influence of the addition of biomass, pine sawdust among others, to industrial coal blends, [38]. Comparing the data from this study and the ones in this work, it can be said that the effect of charcoal on coal fluidity is less deleterious than the addition of pine sawdust without any thermal treatment. The results obtained in the present research work show that the addition of 2 wt.% of charcoal produces a reduction of around 20% of the Gieseler maximum fluidity, whereas the addition of 2 wt.% of pine sawdust almost doubles that reduction [38]. This result confirms the importance of the chemical effect in the development of coal fluidity as it stated Montiano et al. in another work about the

effect of the addition of pine sawdust on the thermoplastic properties of a coal [41]. In this way, the presence of highly oxygenated compounds increases the reactivity of the system producing a greater reduction in the fluidity. In the case of charcoal, only the physical effect associated to the adsorption of coal devolatilization products is present and as a consequence a lower reduction in fluidity is observed. It can be concluded that the addition of charcoal instead of pine sawdust without thermal treatment, in the same proportions, has the advantage of a greater reduction of CO₂ emissions, since charcoal is embedded to a greater extent in the biocoke formed during the coking process due to its lower volatile matter content; charcoal should be better embedded since the loss of fluidity is less than in case of sawdust for the same proportions.

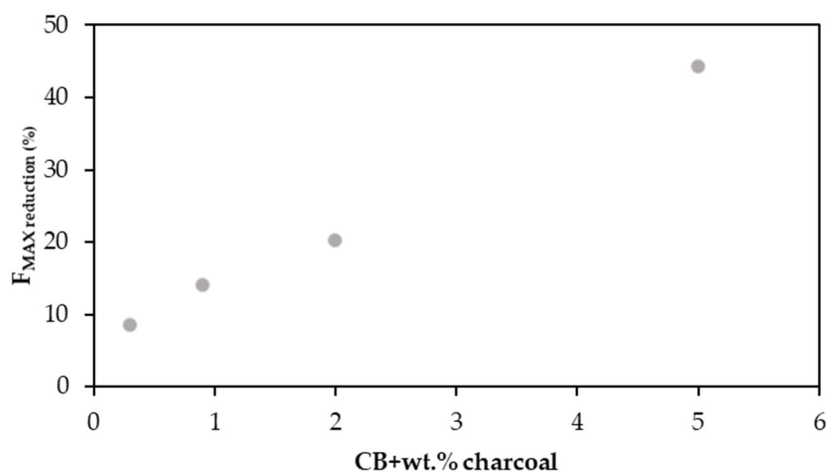


Figure 2. Variation of Gieseler maximum fluidity of the coal blend-charcoal mixtures.

An important parameter that affects biocoke rheology is the amount of charcoal added to the CB, the different nature of charcoal lessens coal fluidity, which alters biocoke formation phenomena and hence its final structure.

The results of the cold mechanical strength (JIS K2151), the coke reactivity index (CRI) and the coke strength after reaction (CSR) of the biocokes formed are presented in Figure 3. Contrary to what happened in the plasticity tests, adding up to 0.9 wt.% charcoal to the CB does not alter much the mechanical strength nor its reactivity. The DI150/15 and DI150/5 indexes are around 75–78 and 19–17, respectively, the CRI stays stable in 26–27 and the CSR shows a little difference reducing from 63 without charcoal addition to 58, with 0.9 wt.% charcoal addition. Considering that a good coke should fulfill a CRI lower than 30 and a CSR higher than 60, and that the CSR of the CB is 63 (only three points over the criteria of quality), it can be stated that both options (0.3 wt.% and 0.9 wt.% charcoal) produce a biocoke good enough to be used by the metallurgical industry.

When 2 wt.% of charcoal is added to the blend, the changes are more pronounced and the quality of the product is worsened, the DI150/15 index is reduced from 76 to 66 and the CSR from 63 down to 56. Finally, in the case of 5 wt.% charcoal, there is no results for CSR nor CRI because the pieces of biocoke obtained from the JIS cold mechanical strength test were too small as it can be seen from the high DI150/5 value (53.8, which means a very low mechanical strength). Consequently, there were not enough biocoke pieces of 19 to 22.4 mm size to enable these tests according to the NSC test. Regarding the reactivity, the CRI seems to be independent of the amount of charcoal in the mixture because even when adding 2 wt.% of charcoal the value is almost the same to the one obtained for the CB coke (26).

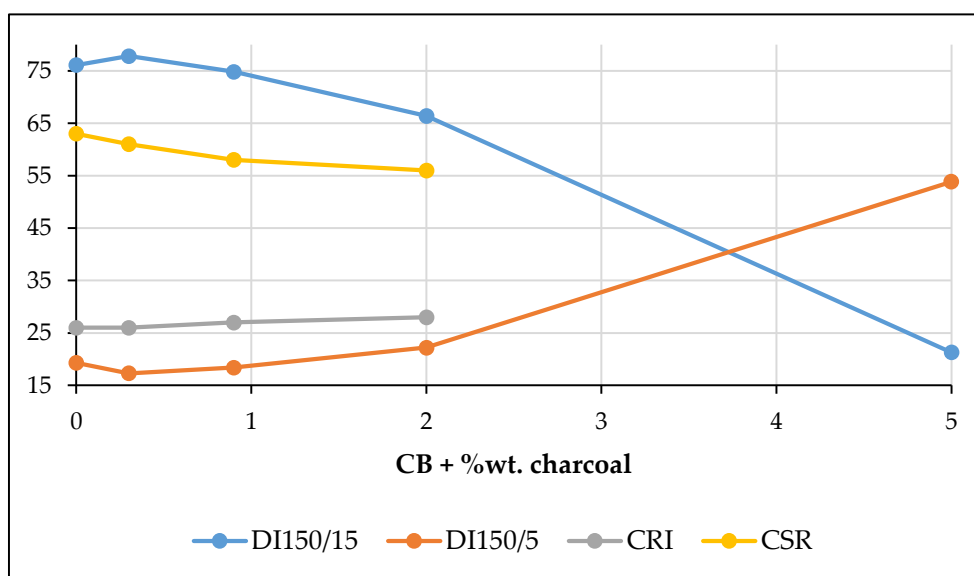


Figure 3. Biocoke cold mechanical strength (DI150/15 and DI150/5), reactivity (CRI) and mechanical strength after reaction (CSR).

The reduction of the mechanical strength is a consequence of the nature of the charcoal as a non-coking coal. Montiano et al. [38] observed through thermal decomposition that negligible interaction took place between industrial coal blend and biomass during heating. According to Matsumura et al. [42] when charcoal and coking coal are carbonized together an interface between the charcoal and the coke can be observed; this separation is due to the contraction of cokes on cooling which causes defects that deteriorates its mechanical properties.

In consequence, by decreasing the area of contact between the charcoal and coke, either by densification of charcoal prior to the blending or by using bigger particle size charcoal, there would be less interface and the number of defects would decrease to such a level, as would have negligible effect on coke strength. Matsumura et al. [42] proposed a lower limit of the particle size between 3 mm and 10 mm, which is bigger than the charcoal sample used in these experiments. Flores et al. [39] also confirmed the influence of particle size in biocoke production with charcoals, reporting that the most suitable particle size to maximize coke quality, in terms of reactivity to CO_2 and mechanical strength, is not evident. According to Suopajarvi et al. [2], even 5–10 wt.% of charcoal can be added depending on particle size and other parameters. Nonetheless it was also concluded that on the one hand, big charcoal particle size was not convenient in the biocoke since due to the higher reactivity of charcoal particles, they are the first ones gasified inside the blast furnace creating holes that weaken the coke structure; and on the other hand, smaller sizes are more favorable for appropriate mechanical strength, since they are better embedded into the coke structure.

Many references in the literature agree with the increase of biocoke reactivity with the amount of charcoal added [17,18,43], contrary to what happens in this work. In this case, CRI seems independent of the charcoal share, even when the charcoal porosity is several times greater than that of the coke; the Dubinin–Radushkevich pore area obtained for the selected charcoal, which is $492 \text{ m}^2 \text{ g}^{-1}$ (Table 3), is much higher than that obtained for the biocoke produced from the coal blend, which is $61 \text{ m}^2 \text{ g}^{-1}$. Ng [17] heated up biocokes samples with different charcoal content (0–5 wt.%) up to 1273 K in a TGA and observed that the higher gasification kinetics increased in samples containing higher amount of charcoal. Ueki et al. [40] reported that the lower volatile matter content of charcoal obtained from the pyrolysis of biomass obtained at temperatures over 773 K improves biocokes mechanical strength compared to raw biomass. Babich et al. [44] showed that depending on the biomass pyrolysis temperature, the coke microstructure is changed, enabling a

higher share of biomass products in the coal blend, at least up to 5 wt.%. Therefore, further experimentation is needed in order to determine the influence of parameters such as biomass pyrolysis peak temperature, particle size and the amount of charcoal in the mixture to produce biocokes with acceptable mechanical properties.

An alternative approach to biomass use for biocoke production was experimented by Montiano et al. [8], who prepared briquettes of biomass and non-coking coal using coal tars as binder, carbonized them mixed with coking coal blends and managed to prepare good quality biocokes adding up to 15 wt.% briquettes to the mixture.

4. Conclusions

In this study, the suitability of the charcoal produced by pyrolysis of pinus radiata waste chips in a continuous auger reactor at high temperatures (573, 773, 973, 1173 K) with a vapor's thermal treatment step (1073 K) as reducing agent in steel making operations has been evaluated, in order to reduce CO₂ emissions.

The charcoal obtained can be used, on the one hand, as a good quality renewable solid fuel with neutral CO₂ emissions to replace fossil reducers; its higher heating value is in the range or over those of conventional fossil coals and has the advantage of not containing polluting elements (S, N) and having less ash content. On the other hand, the charcoal can be used as fuel and reducer in non-ferrous processes where no strength is required, like rotary kilns, in substitution of fossil reducers typically used in such processes, as metallurgical coke, petroleum coke and anthracite, with the advantage that charcoal has less sulfur and ash contents.

Comparing the charcoal obtained at 1173 K with coking coal blend, charcoal contains less ash than the coal blend, but the metal elements (Ca, K and Na) in its ash are detrimental to its performance in the ironmaking process because they act as catalyst. The addition of charcoal to a coking coal blend for biocoke production, clearly affects the carbonization process. The charcoal can be added in proportions up to 0.9 wt.%, to produce good quality biocokes, both the cold mechanical strength and the mechanical strength after reaction of the resulting biocokes are good enough to meet quality criteria to be used in blast furnaces. However, when adding 2% or more, the mechanical properties of the biocoke are too much degraded. Nevertheless, the addition of up to 5 wt.% of charcoal does not affect the biocoke reactivity.

In any case, the results obtained in this work are encouraging and will help to set up the most appropriate conditions in which biochar would be added to industrial coking blend coals in order to produce acceptable levels of coke quality in future research.

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