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## INFLUENCE OF PYROLYSIS CONDITIONS AND THE NATURE OF THE WOOD ON THE QUALITY OF CHARCOAL AS A REDUCING AGENT

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### Abstract

The production of charcoal for metallurgical applications requires careful selection of the wood and control of the pyrolysis conditions to ensure acceptable charcoal quality. The main properties of charcoal to be considered are density, mechanical strength, and reactivity. In this study, charcoal was produced from two types of wood commonly used in the industry, *Eucalyptus globulus* (eucalyptus) and *Picea abies* (spruce), in a pilot scale pyrolysis fixed bed reactor at three temperatures (500, 650 and 800 °C) and two solid residence times (0 and 90 min). The yields, composition, apparent density, true density, porosity, carbon structural ordering, friability, compressive strength and CO<sub>2</sub> reactivity of the resulting charcoals were analyzed. A new method to test compressive strength was applied to a charcoal bed. Our results show that the nature of the wood has a much greater impact on these values than the pyrolysis operating conditions. Wood apparent density is not a good indicator of the mechanical behavior of charcoal. Despite its higher density, eucalyptus charcoal showed lower mechanical stability than spruce charcoal independently of the pyrolysis conditions. When the final pyrolysis temperature was increased, the mechanical strength, porosity of the charcoal increased and CO<sub>2</sub> reactivity decreased. The impact of solid

residence time during pyrolysis on the charcoal properties was negligible except for CO<sub>2</sub> reactivity, which decreased with an increase in residence time.

### **Highlights**

- Spruce and eucalyptus were pyrolyzed in a pilot reactor under varying conditions
- The potential of charcoals as reducing agents was investigated
- Compressive strength, friability, and reactivity of charcoals were measured
- Correlation between charcoal mechanical properties & wood/char density is discussed

### **Keywords**

*Charcoal, Reducing agent, Mechanical strength, Compressive strength, Friability, Reactivity*

## **1. Introduction**

Reducing greenhouse gas (GHG) emissions is vital in the context of climate change. Metallurgical processes mainly use fossil reducing agents like coal/coke or petroleum coke that result in high emissions of fossil CO<sub>2</sub> gases [1,2]. For industry, finding alternatives is becoming increasingly urgent. One promising alternative way to reduce the fossil CO<sub>2</sub> emissions from those particular processes is using charcoal made from woody biomass as a complement or as a substitute reducing agent [1-3]. Unlike fossil coal, charcoal can be produced locally at low cost using available local resources or dedicated plantations [4], thereby ensuring the self-sufficiency of producers who currently depend on imported coal. What is more, using charcoal improves the quality of the metal as its sulfur and ash contents are less than those of fossil reducers [5,6]. In the case of silicon, which requires high Si purity, charcoal makes it possible to obtain a silicon that better meets the chemical specifications for polysilicon applications in the photovoltaic industry [7].

In fact, charcoal was used in numerous metallurgical processes until the end of the 19th century, when it was replaced gradually by coal thanks to its availability and low price. Today facilities are optimized for coal/coke, and replacing coal by charcoal and charcoal's specific properties create

operational problems and reduces the plants' performance [6,8-10]. Depending on the application, charcoal needs to be produced with the specific physical and chemical properties required by the process concerned. In this paper, we focus on two different applications: ironmaking and silicon production. For ironmaking purposes, blast furnaces (BF) are the most widely used technology. There are several possible ways to use charcoal in BF [2,10]: - to replace the top charged coke, - to replace the pulverized reducers (coal, oil, gas), or - to replace the coal in the ore sintering process. In this study, we investigated the use of charcoal as an alternative to the top charged reducer, which has three functions: (1) it acts as a reducing agent by generating the CO needed for the reactions, (2) it provides energy for the process and (3) serves as a support medium for the burden material [9,10]. Submerged arc furnaces (SAF) are the most commonly used for silicon production. In this process, the reducing agent (usually coal) is mixed with the ores that need to be reduced and smelted together. The main role of the reducing agent is to capture the SiO gas generated in the lower part of the SAF and that is flowing upward within the burden [11,12].

The main disadvantage of using charcoal as a substitute in these processes is its low density and low mechanical stability compared with fossil reducers [13-18]. A low density reducer limits the fixed carbon available in the furnace for the carbothermic reactions, thereby reducing productivity and increasing specific energy consumption. Additionally, the transport, handling, and storage of a low density reducers is more constraining [15]. Regarding mechanical stability, the production of fines due to charcoal friability during transport and handling is problematic when they are introduced inside the furnace. Fines reduce the permeability of the burden bed to the reacting gas thereby adversely affecting the efficiency of the process the conduct of operations. A reducer with high compressive strength is essential in fixed processes: compaction of the bed has a negative effect on the reduction reactions by limiting bed permeability, which, in turn, causes problems for process control by increasing pressure drop and channeling [17,19-21]. Charcoal has higher reactivity toward reacting gas than fossil reducers [22-24]. In BF, this is problematic, as low reactivity toward CO<sub>2</sub> is required to support the rapid consumption of the burden material and ensure efficient reduction of the iron ores [17,23]. Conversely, for silicon production, the aim is high reactivity towards SiO gas. If the reducing agent is not sufficiently reactive, the SiO gas

flows out of the process without reacting, thereby reducing the silicon yield and increasing specific energy consumption [12,22]. To sum up, the main criteria to consider for even partial replacement of fossil reducers by charcoal are its density, mechanical strength and reactivity. Our work concerns the influence of charcoal production parameters on these properties.

For charcoal production, wood pyrolysis at a low heating rate is preferable, as it is known to optimize solid yield. Many studies have been conducted to explain the impact of pyrolysis parameters on charcoal yield and properties [25,26]. Increasing the final pyrolysis temperature and solid residence time reduces charcoal yield and increases the fixed carbon content. It also reduces the CO<sub>2</sub> reactivity of the resulting charcoal. Very little is known about charcoal SiO reactivity, some authors [24,27] suggest it follows the same trend as CO<sub>2</sub> reactivity. Charcoal density, and hence porosity, depends primarily on the parent woody biomass and decreases with increasing pyrolysis temperature. However some authors reported a slight increase in this property above 500 – 600 °C [15,28,29]. Reports in the literature are not consistent concerning the impact of the pyrolysis conditions and of the nature of the wood on the mechanical properties of the charcoal, and today there are no standard references available to which industry can refer [16,26]. The mechanical stability of charcoal is generally said to increase with the apparent density of the precursor wood, and hence with charcoal density [16,26,29,30]. Charcoal compressive strength decreases with increasing pyrolysis temperature, and according to most authors, starts to increase again at temperatures above 500- 600 °C [21,28,29]. However, a recent study reported a decrease in charcoal compressive strength up to 750 °C [31]. Regarding the influence of pyrolysis parameters on charcoal friability, only two studies considered a wide range of temperature and their findings are contradictory. Oliveira, et al. [32] reported an increase in charcoal friability at temperatures ranging from 300 to 500 °C, followed by a decrease up to 700 °C, whereas Coutinho and Ferraz [33] reported that charcoal friability increased continuously from 400 to 1000 °C. To our knowledge, no study has been conducted on the effect of solid residence time at final pyrolysis temperature on the mechanical properties of charcoal. Likewise, studies on charcoal compressive strength have always been carried out using static compression tests on monolithic wood particles, which cannot be compared with to the

behavior of the charcoal bed bulk in industrial processes, and no studies have been performed on a charcoal bed, as we propose here.

The majority of studies on the use of charcoal as a reducing agent concerned ironmaking applications and focused on increasing charcoal yield, fixed carbon content and apparent density, and on reducing CO<sub>2</sub> reactivity. Charcoal's mechanical strength has rarely been investigated together with these criteria. Moreover, studies on charcoal production for other metallurgical applications are rare. For some applications, silicon production for example, both high reactivity and high mechanical strength are needed. These criteria are difficult to obtain as an increase in the final temperature and in the solid residence time may reduce reactivity while increasing the mechanical strength of the charcoal. Consequently a compromise has to be sought while optimizing the pyrolysis parameters.

The overall aim of this study was thus to investigate how industrial process parameters (temperature, solid residence time), the nature of the wood and their interactions affect the quality of charcoal as a reducing agent to identify the most suitable parameters for charcoal production for ironmaking and for silicon production. To that end, two woody biomasses of different nature were selected: *Eucalyptus globulus* (hardwood) and *Picea abies* (softwood). They were pyrolyzed in a pilot scale reactor at three temperatures (500, 650 and 800 °C) and two solid residence times at final temperature (0 and 90 min). The potential use of charcoal as a reducing agent for this application is discussed based on measurement of yields, densities, porosity, carbon structural ordering, compressive strength, and friability and CO<sub>2</sub> reactivity.

This paper provides new insights into the impact of charcoal production on metallurgical processes. Our results support research on modeling charcoal behavior, at the same time as providing practical information for operators.

## 2. Material and methods

### 2.1. Raw material: selection and preparation of the biomass

Two woody biomasses were used in this study: *Eucalyptus globulus* as a hardwood and *Picea abies* (spruce) as a softwood. They were produced in Spain and Finland, respectively. The samples were received in the form of planks (without bark) and cut into 32x28x25 mm cubes.

**Table 1** lists the chemical characteristics and density of the two feedstocks. Proximate analyses were conducted using standard methods NF EN ISO 18134-3, NF EN ISO 18123 and NF EN ISO 18122. Ultimate analyses were conducted according to NF EN ISO 16948 with a Vario Macro Cube elemental analyzer. Wood extractive content was determined using Soxhlet extraction according to TAPPI 204 om-88, but substituting ethanol/benzene for ethanol/toluene. Lignin content was estimated by summing soluble and insoluble lignin according to TAPPI 222 om-02. Insoluble lignin was determined using the Klason method and soluble lignin was determined by spectrophotometry. Holocellulose content was determined by difference, based on extractive-free wood.

Apparent density was determined by measuring each dimension of ten cubic samples to the closest 0.1 mm with a caliper and their mass after drying at 105 °C for 12 hours. Density was computed as a proportion of weight and volume.

The results of proximate and ultimate analysis of spruce and eucalyptus were quite similar. The ash content of spruce wood was two times higher than that of eucalyptus. The extractive contents of the two biomasses were similar. Concerning the other constituents, spruce had higher lignin content and lower holocellulose content than eucalyptus. The apparent density of the spruce wood was 405 kg.m<sup>-3</sup>, twice lower than that of eucalyptus which was 891 kg.m<sup>-3</sup>. These values are in agreement with those in the literature [34,35].

### 2.2. Pyrolysis experiment: charcoal production

Pyrolysis experiments were conducted in an externally heated fixed bed reactor designed to produce batches of homogenous charcoal with dimensions similar to those used in the metallurgical industry (between 20 and 40 mm) [21,36]. The reactor (**Fig.1**) consisted of a refractory stainless steel tube

(1) (937 mm in height, 264 mm i.d.), inside of which a removable refractory stainless steel basket (2) (670 mm height, 252 mm i.d.) was placed. The basket volume was about 30 L, corresponding to a mass of about 5 kg of spruce wood and 12 kg of eucalyptus wood. The system was heated by a tubular resistance furnace (3) (20 kW power) with three independent heating zones, to facilitate homogeneous heating of the wood bed. Nitrogen was preheated and injected continuously into the reactor through a steel coil (4) to inert the atmosphere and sweep away the volatile vapors. Particular attention was paid to the homogeneous distribution of the flow of nitrogen in the reactor. The nitrogen flow rate was controlled by a mass flow meter set at 1 L/min. The pyrolysis gases exited the reactor from the top and from there went to a flare burner. During cooling, the steel coil was bypassed to allow nitrogen to flow at 30 L/min without being preheated. The cooling of the reactor was boosted by convection that forced air between the reactor and the heating elements. The pilot was instrumented equipped with 10 lateral temperature probes. Four temperature probes ( $T_1$  to  $T_4$ ) with three thermocouples each, and one with one thermocouple ( $T_5$ ), were placed inside the bed, arranged vertically along the reactor to monitor temperature radially and vertically on the whole length of the bed. Two thermocouples ( $T_0$  and  $T_6$ ) controlled the temperature of the gases at the entrance and the exit of the reactor. One was placed near the nitrogen inlet and the second above the bed in the upper part of the reactor. Three thermocouples ( $T_7$  to  $T_9$ ) were used to control the temperature of the three independent heating zones.

The wood samples were oven dried for at least 12 hours, then pyrolyzed at 500, 650 and 800 °C for 0 and 90 min solid residence time at peak temperature. The resistance heating rate was set to 2.5 °C/min. Preliminary studies showed that the heating rate inside the bed is controlled by the exothermic pyrolysis reactions between 250 and 450 °C and was around 5 °C/min close to the wall of the reactor (B) and around 10 °C/min in the center (C) as presented in **Fig. 2**. Above 500 °C, the heating rate of the bed was the same as the heating rate of the resistance. This heating rate was chosen because it allows the reactor to reach a temperature of 450 °C at exactly the same time as the biomass, thus ensuring homogeneous temperature distribution in the bed and well-controlled solid residence time. Each test was conducted twice.



## 2.3. Charcoal characterization

### 2.3.1. Charcoal yields, chemical analysis, densities, and structural ordering

The charcoal yield  $Y_{char}$  (%) was determined by mass difference between the dried biomass before pyrolysis and that of the resulting charcoal. Charcoal proximate analyses were carried out according to the standard NF EN 1860 and ultimate analyses according to ASTM D5373. The fixed carbon yield  $Y_{fix}$  was determined using the definition proposed by Antal, et al. [30]:

$$Y_{fix} (\%) = Y_{char} \cdot \left( \frac{C_{fix,char}}{100 - Ash_{wood}} \right) \quad (1)$$

where  $Y_{char}$  (%) is the charcoal yield,  $C_{fix,char}$  (%) is the fixed carbon content of the charcoal and  $Ash_{wood}$  (%) is the ash content of the parent wood. The apparent density  $D_{app}$  (g.cm<sup>-3</sup>) of charcoal samples was measured according to the ASTM D2395. The volume of 16 representative samples, collected over the entire length and width of the reactor, was determined by water immersion. A specific scale based on Archimedes' principle was used to precisely measure the volume of water displaced. Apparent density was computed as a proportion of dried mass and volume. Charcoal true density  $D_{true}$  (g.cm<sup>-3</sup>) was determined on dried charcoal powder (< 500 μm) by helium displacement using a Micrometrics AccuPyc II 1340 pycnometer for four runs with 40 iterations. The standard deviation between the runs was less than 0.01 g.cm<sup>-3</sup>. Apparent density accounts for the solid structure, all the pores, and surface irregularities, while true density is based on the solid carbon structure, i.e. the pore walls of the charcoal particles, and any pores that are not accessible to the analysis gas. Porosity  $P$  was thus calculated from the difference in densities [37]:

$$P (\%) = \frac{D_{true} - D_{app}}{D_{true}} \times 100 \quad (2)$$

Raman spectroscopy was used to study the changes in the carbon structure of the charcoal with the pyrolysis conditions. This technique provides information on the 'average structural composition' of the chars and thus makes it possible to compare different charcoals [38]. Raman spectra of the charcoals were recorded with a Horiba Jobin Yvon Labram BX40 spectrometer at an excitation wavelength of 532 nm. An attenuator was used so the power of the laser did not modify the sample. The samples were crushed (<

200  $\mu\text{m}$ ) and homogenized before analysis. The Raman spectra were recorded at nine locations on the sample. Mean values and relative standard deviations were calculated for the different parameters while taking the heterogeneity of the charcoal sample into account. For disordered carbons, the Raman spectrum is thought to be the combination of several bands corresponding to different carbonaceous structures [38-40]. In the present study, the spectra were deconvolved into eight main bands (**Table 2**) as proposed by Elmay, et al. [39], assuming a Gaussian shape for the different bands. The ratio of the D band to G band intensity,  $I_D/I_G$  (peak area ratio), was used to investigate changes in the structure of the charcoal as a function of the pyrolysis parameters.

### 2.3.2. Compressive strength of charcoal: bed compression

Compressive strength is used to evaluate the ability of charcoal to withstand mechanical stress during transport and handling as well as the stress existing in the burden of the furnace [29].

The test consisted in measuring the brittleness of charcoal bed. It is based on a protocol developed by the Wood Panels and Energy Laboratory (LAPEM) of the department of Forest Engineering of the Federal University of Viçosa, (Minas Gerais, Brazil), with adaptations. The test is based first on the breakage of charcoal samples controlled in size by a compressive load, and second on the subsequent analysis of the size distribution of the samples. A vibrating sieve was used to determine charcoal size distribution according to standard ISO 1953 to ensure good repeatability of the tests. The quantity of fine particles produced by sieving was negligible compared to the initial mass of the sample ( $< 1.5\%$ ) and to the fines produced by the compression and friability tests.

As shown in **Fig. 3**, charcoal with a particle size ranging from 22.4 to 32 mm, was placed in a cylindrical cell with an internal diameter of 285 mm. The dimensions of the cell versus the dimensions of the piece of charcoal made it possible to disregard edge effects. The cell was placed in a universal testing machine (ADAMEL Lhomargy DY 36 - DY36D MTS) and force was applied by a piston with a diameter of 275 mm at a constant speed of 0.05 mm/s with a maximum pressure of  $2 \text{ kg}\cdot\text{cm}^{-2}$ . The piston was mounted on a ball joint to ensure the forces were uniformly applied to the surface of the bed. For each biomass, a

volume of around 5 L of charcoal was used; this corresponded to a mass of about 1000 g for eucalyptus charcoal and of 500 g for spruce charcoal. The charcoal bed comprised three layers of particles.

After compression, the charcoal was sieved through a column of sieves and the mass of the different fractions was measured. Compressive strength is assessed by the stability index  $S$ , an indicator of the capacity of charcoal to resist breakage. It is the percentage of charcoal retained in a given sieve relative to the initial mass and is defined as follows:

$$S (\%) = \frac{m_r}{m_i} \times 100 \quad (3)$$

where  $m_i$  (g) is the initial mass of charcoal before compression and  $m_r$  (g) is the mass of charcoal after sieving retained by the mesh sieve concerned.

In this study, we arbitrarily used the charcoal retained by the 18 mm mesh sieve to calculate the  $S$  index. The data provided for each experiment is the average of two tests.

This test is not the same as the standard static compression test on a single particle. For the standard test, the surface of the charcoal particle should be flat and parallel where the load is applied and be free of voids and cracks [29]. Consequently, the standard test is not suitable to determine the compressive strength of charcoal produced in industrial reactors in which the particles are irregular in shape and contain cracks. An additional advantage of our test is that it analyzes the behavior of a charcoal bed that is similar to those used in industrial conditions.

### 2.3.3. Friability

Friability reflects the ability of the charcoal to produce fine particles (fines) due to the combined action of abrasion and shocks, particularly during handling and transport [28].

As there is no standard method to assess this property in charcoal, we chose to use the drum test as described by Oliveira, et al. [28], with adaptations. This procedure has already been used by other authors [17,33] even though there were some differences in the setting. Our experimental setup comprised a rotating drum (diameter 300 mm and length 250 mm) fixed on a horizontal axis. A metal plate welded to the internal surface of the drum facilitates mixing and impacts between the particles of charcoal. A sample

of charcoal with a mass of around 150 g between 26.5 and 32 mm in size was placed in the drum and subjected to shocks and abrasion at 30 rpm for 15 min. After the test, the charcoal was sieved through a column of sieves and the mass of the different fractions produced was measured.

Friability is defined by the friability index  $F$ , which gives an idea of the quantity of fines potentially produced by the charcoal. It is calculated as the percentage of charcoal passing through a given sieve:

$$F (\%) = \frac{m_i - m_r}{m_i} \times 100 \quad (4)$$

where  $m_i$  (g) is the initial mass of charcoal before it is placed in the drum and  $m_r$  (g) is the mass of the charcoal after sieving that is retained by the mesh sieve concerned.

In this study, charcoal that passed through a 6.3 mm mesh sieve was qualified as fines. This corresponds to the size of the fine particles that have to be avoided in the silicon production process [19]. The data provided for each experiment is the average of two tests.

#### 2.4. CO<sub>2</sub> Reactivity experiments

Reactivity is a key factor in every process involving thermochemical conversion. It depends to a great extent on the temperature and the composition of the reactive atmosphere. There is no standard to determine the reactivity of charcoal. One of the most common techniques used is the determination of CO<sub>2</sub> reactivity by thermogravimetric analysis. CO<sub>2</sub> reactivity characterizes the rate of reduction of charcoal according to the Boudouard reaction as follows:



The CO<sub>2</sub> reactivity of the samples was tested using a macro-thermogravimetric reactor (**Fig. 4**) consisting of a ceramic tube (1) (1110 mm in height, 75 mm i.d.), placed in an electrical furnace (2). The three independently controlled heating zones made sure the temperature was uniform throughout the reactor.

The gas was preheated in a 2 m long coiled tube (3) located in the upper heated part of the reactor and the flow rate was controlled by mass flow meters (M<sub>1</sub> and M<sub>2</sub>).

The experiment consisted in gasifying charcoal particles at atmospheric pressure, under well-controlled temperature and reacting gas conditions. A post-pyrolysis stage is required before gasification to prepare

the charcoal for reduction. The reactor was first heated to 900 °C for each experiment. Around 120 mg of sample (< 500 µm) was carefully spread on the sample holder (4), which had an internal diameter of 47 mm, to form a mono layer. The sample was raised from the bottom of the reactor to the desired position to reach 900 °C in 30 s and maintained under a 5 NI/min N<sub>2</sub> flow for 10 min to release all remaining volatile matter. As the residence time before reaction is very short, thermal deactivation phenomena are considered to be negligible. The sample mass was measured and recorded continuously. When constant mass was reached, the N<sub>2</sub> flow was replaced by a 5 NI/min CO<sub>2</sub> flow. As gasification occurred, the mass of the char progressively decreased until constant mass - which corresponds to ash content - was reached. Conversion *X* during gasification is calculated as follows:

$$X = \frac{m_i - m_t}{m_i - m_{ash}} \quad (6)$$

where, *m<sub>i</sub>* (g), *m<sub>t</sub>* (g) and *m<sub>ash</sub>* (g) are respectively the initial mass (after devolatilization), the mass at time *t* and the mass of ash. All experimental data presented in the following are the average of at least two replications. The deviation is less than 10%, which is quite acceptable given the heterogeneity of the sample and the accuracy of the equipment. The representative reactivity value is the average reactivity between two degrees of conversion. In this study, it was chosen to consider the reactivity between 0 and 50% *R<sub>0-50</sub>* (mg.(g.min)<sup>-1</sup>) and reactivity between 20 and 80% *R<sub>20-80</sub>* (mg.(g.min)<sup>-1</sup>) of the conversion rate of charcoal.

### 3. Results and discussion

Once produced under varying pyrolysis conditions, the yields, composition, apparent and true density, porosity, structural ordering, mechanical strength (compressive strength and friability) and CO<sub>2</sub> reactivity of the charcoals made from spruce and eucalyptus were characterized.

#### 3.1. Charcoal yields and composition

The results of the ultimate and proximate analysis of the charcoal produced under different operating conditions are presented in **Table 3**. The compositions of the resulting charcoals were independent of the wood species, whatever the pyrolysis temperature or solid residence time used. The

fixed carbon in the two biomasses ranged from 80.5% to 98.1%: it increased with pyrolysis temperature inversely to volatile matters content. The longer the solid residence time, the higher the carbon content due to the larger quantity of volatile matter being released. Nevertheless, this increase was less pronounced at high temperatures. For example, the fixed carbon content of eucalyptus charcoal increased from 80.9% to 86.8% when prepared at 500 °C, with 0 and 90 min residence time, respectively, and by less than 1% when prepared at 800 °C.

The effects of pyrolysis temperature and solid residence time on the yield of charcoal from the two biomasses are shown in **Fig 5**. The eucalyptus charcoal yield was about 6 - 8% higher than spruce charcoal yield whatever the pyrolysis conditions. The difference in charcoal yield from the two different biomasses produced in the same conditions is often explained by their lignin content. However, in our study, the charcoal yield from eucalyptus was higher despite having a lower lignin content than spruce. This can be explained by the very high density of eucalyptus compared to spruce. The high density of eucalyptus prevents volatile matters from migrating to the surface of the wood and consequently enhances the formation of secondary charcoal [41,42].

The charcoal yield decreased with increasing pyrolysis temperature. From 500 to 800 °C, eucalyptus charcoal yield decreased from 33.8% to 28.1% and spruce charcoal from 31.7% to 26.1%, when the solid residence time at the final temperature was zero minutes. The charcoal yield also decreased with increasing solid residence time. At 500 °C, the eucalyptus charcoal yield decreased from 33.8% to 32.0% when the residence time increased to 90 min; and at 800 °C, from 28.1% to 27.5%. At 500 °C, the spruce charcoal yield decreased from 31.7% to 29.3%, and at 800 °C, from 26.1% to 25.3%.

**Fig. 6** shows the fixed carbon yields for the two charcoals produced under different pyrolysis conditions. This value is particularly important as it provides information on the real yield of carbon that is available to react with ores in the process. It will impact the profitability of the whole process.

It can be seen that, in our operating conditions, they are independent of the pyrolysis temperature and the solid residence time. The fixed carbon yield was about 25% for spruce and 27% for eucalyptus.

**Table 3** shows that the fixed carbon content increased when temperature increased from 500 to 650 °C or by increasing solid residence time at a low temperature. These operating conditions allow the fixed carbon content to reach 85-90%, which is required for metallurgical applications [9,26].

### *3.2. Influence of the pyrolysis parameters on the density and porosity of the two charcoals*

The true and apparent density of the charcoals produced under different operating conditions, as well as their porosity, are listed in **Table 4**. True density increased from around 1.4 g.cm<sup>-3</sup> to 1.8 g.cm<sup>-3</sup> in both charcoals and was independent of the nature of the wood. The increase in true density with increasing temperature from 500 to 800 °C is caused by the conversion of low-density disordered carbon to higher-density turbostratic carbon, approaching the graphite structure that has a true density of 2.25 g.cm<sup>-3</sup> [43-45]. An increase in solid residence time promotes this phenomenon for pyrolysis temperature higher than 500 °C.

Charcoal apparent density values were widely scattered in the measurements attributed to wood heterogeneity, accentuated by the fact that wood pieces came from different trees of the same species. Nevertheless, charcoal apparent density is obviously highly dependent on that of the parent wood. Consequently, eucalyptus charcoal presented average higher apparent density (400 kg.m<sup>-3</sup>) than spruce charcoal (200 kg.m<sup>-3</sup>). The density of the resulting charcoal was 50 - 60% lower than that of the parent eucalyptus wood, and about 35 – 50% for spruce. This reduction in density is due to a general opening of the macrostructure of the charcoal caused by the release of the volatiles [25,26].

These results suggest a slight increase in charcoal apparent density with an increase in temperature from 500 to 800 °C in both species, although the standard deviation is high. Eucalyptus charcoal apparent density increased from 0.362 to 0.448 g.cm<sup>-3</sup>, and that of spruce charcoal from 0.196 to 0.258 g.cm<sup>-3</sup>.

An increase in pyrolysis temperature caused a loss of mass and an increase in charcoal porosity through the release of volatiles, but also a shrinkage of the charcoal due to condensation of the carbon crystallites, and thus reduced the volume of charcoal [15,29,46]. Competition between these phenomena resulted in a slight increase in charcoal apparent density with an increase in temperature from 500 to 800 °C. These results are in agreement with those of Blankenhorn, et al. [47] who reported an increase from

0.408 to 489 g.cm<sup>-3</sup> in the apparent density of *Prunus serotina Ehrh.* charcoal with an increase in pyrolysis temperature from 500 to 800 °C. An increase from 0.350 to 0.390 g.cm<sup>-3</sup> in the apparent density of *Eucalyptus grandis* charcoal with an increase in pyrolysis temperature from 500 to 700 °C was also reported by Oliveira, et al. [28].

Charcoal porosity depends on apparent and true densities. As shown in **Table 4**, spruce charcoal was more porous (85.4-88.0%) than eucalyptus charcoal (72.5-76.6%), because of its lower apparent density. Overall charcoal porosity increased when the pyrolysis temperature was increased from 500 to 800 °C, as its true density increased and as changes in apparent density were relatively small.

### 3.3. Influence of the pyrolysis parameters on the carbon structure of the two charcoals

No significance difference was observed in the  $I_D/I_G$  values of the two wood species in any given heat treatment (**Table 4**).

These results underline the extreme importance of pyrolysis temperature for the carbon structure. The structure of the samples obtained at low temperatures was amorphous with a low  $I_D/I_G$  ratio, between 0.6 and 0.9, for charcoals prepared at 500 °C. This was not the case for spruce charcoal prepared at 500 °C with no solid residence time, when a very wide range of  $I_D/I_G$  ratio values, (0.66 to 1.72) was observed. However, these values should be interpreted with caution. These  $I_D/I_G$  ratios are characteristic of a low level of carbonization [40]. In charcoal prepared at 800 °C, the ratios for both woods increased with an increase in the pyrolysis temperature to between 2.0 and 2.5. This increase reflects a more ordered carbon structure. The charcoals were in a carbonization phase in which the stacks of aromatic rings increase, but the defects in these stacks were not corrected. At first, a rich amorphous phase carbon was formed as the result of the destruction of the oxygenated functions, after which the amorphous phase was transformed into a faulty stack of polyaromatics corresponding to peak D. If the temperature was further increased (> 1600 °C), this phase would be organized and a decrease in the  $I_D/I_G$  ratio would be observed [40 509].

The effect of solid residence time on the carbon structure of the charcoals depends on the pyrolysis temperature. At 500 °C, there was no significant difference between the  $I_D/I_G$  ratio of the samples produced with and without solid residence time, with the exception of spruce charcoal prepared at



500 °C without solid residence time. At 650 °C, the difference between the samples produced with and without solid residence time was very pronounced and transformation was relatively slow at this temperature. At 800 °C, the difference was less pronounced, evidence for the reduced impact of residence time at this temperature, or the residence time at this temperature was too short for significant differences to be observed.

The relation between the structural ordering of the charcoals, i.e. the  $I_D/I_G$  ratio, and their true density is plotted in **Fig. 7**. As can be seen, a linear relationship was found between these parameters. As the true density of the charcoal is linked to the ordering and shrinkage of the carbon structure, this makes sense. Consequently true density seems to be a good indicator to monitor charcoal carbonization and its structural ordering in the temperature range studied.

#### *3.4. Mechanical strength of the charcoal*

In our study, two tests were designed to evaluate the bulk mechanical behavior of charcoals. The purpose of these tests was to simulate the constraints that charcoal may undergo during handling/transport and in the furnace during the industrial process.

##### *3.4.1. Compressive strength of charcoal: bed compression*

The charcoals produced were subjected to the bed compression test and then sieved to assess their mechanical stability. The stability index  $S$  was determined for each experiment as described above. A high  $S$  index is a sign of high compressive strength. The results are shown in **Fig. 8**. The nature of the wood was the most influential parameter affecting the compressive strength of the charcoal: spruce charcoal had higher compressive strength than eucalyptus charcoal whatever the pyrolysis conditions. The  $S$  index increased from 85.4 to 94.0% for spruce charcoal, and from 64.9 to 77.7% for eucalyptus charcoal. What is notable here is that the higher is the original wood density, the lower the charcoal compressive strength. This difference can be partly explained by the appearance of large cracks and voids in the eucalyptus charcoal during pyrolysis, whereas the shape of the spruce charcoal, whose density was originally lower, remained in quite regular shapes with no major defects (**Fig. 3**). Indeed, the release of volatile compounds from high density wood increased the gas pressure inside the particle, which finally ruptured the internal

macrostructure of the particle, thereby increasing its fragility. *Eucalyptus globulus* is also known to develop a high proportion of reaction wood [48,49]. The reaction wood found in hardwoods is called tension wood, it is formed in response to external constraints. Tension wood is often characterized by high tangential shrinkage during drying of wood samples causing marked degradation and cracks [48]. Thus, in the case of large particles of charcoal, like those found in industrial processes, wood apparent density is not a good indicator of compressive behavior, contrary to what is often claimed.

Moreover, the average *S* index increased significantly with an increase in the pyrolysis temperature (**Fig. 7**). An absolute increase of 10% in the *S* index was measured for spruce and of 12% for eucalyptus with an increase in temperature from 500 to 800 °C. In contrast, the solid residence time did not significantly affect the compressive strength of the charcoal in the range of temperatures tested here. The difference in the *S* index in eucalyptus charcoal prepared at 500 °C with and without solid residence time can be attributed to the random appearance of cracks during pyrolysis and consequently to subsequent differences in breakage. The increase in the *S* index with increasing temperature was linear. This increase in charcoal mechanical strength can be attributed to the combined effects of crystallite condensation and alignment, which produce a more resistant carbon structure, to the increase in the amount of fiber per unit area because of charcoal shrinkage, and to the change in porosity [16,28,29]. Our results (**Fig 9**) revealed a linear relationship between the *S* index and the true density for spruce charcoal. This suggests that charcoal compressive strength is closely linked to the ordering and density of the carbon structure. The higher the carbon ordering, the more resistant the carbon structure. Thus, charcoal true density seems to be a good indicator of the mechanical strength of a given species of charcoal produced in similar pyrolysis conditions. An increase in the *S* index was also observed with increasing apparent density of the spruce charcoal, however, the relationship was not as strong as the one for the true density. No correlation was found for eucalyptus charcoal, the large numbers of random cracks in the charcoal make these criteria irrelevant in this particular case. Our results are in agreement with those of Kumar, et al. [29], who reported a general increase in charcoal compressive strength with an increase in apparent density in acacia and eucalyptus charcoal. This was attributed to condensation of carbon microcrystallites, deposition of

pyrolytic carbon, and loss of porosity. Our results revealed an increase in porosity with increasing pyrolysis temperature in both charcoals, with no reduction in compressive strength. This suggests that the porosity of charcoal is not sufficient to explain its mechanical behavior in the temperature range studied here.

According to Oliveira, et al. [28], the decrease in the charcoal volume due to the rearrangement of the carbon structure, increases the number of fibers per unit area and consequently the mechanical strength of the charcoal. According to the same authors, any changes in the size, shape, and distribution of the porosity of the material can influence its mechanical strength. Kumar and Gupta [50] observed a decrease in the pore size of *Acacia* and *Eucalyptus* charcoal when the pyrolysis temperature was increased from 600 to 1050 °C. This reduction in pore size may increase the rigidity of charcoal and hence its compressive strength. Nevertheless, it does not seem reasonable to only use charcoal apparent density to evaluate its compressive strength, as this property depends on numerous factors.

#### 3.4.2. Friability of charcoal: drum test

The spruce and eucalyptus charcoals behaved differently when subjected to tumbling (**Fig. 10**). The bar graph shows the typical relative percentage of the different sized fragments of charcoal after tumbling for eucalyptus and spruce charcoal prepared at 500 °C with no solid residence time at final temperature.

The first bar (> 26.5 mm) corresponds to the quantity of charcoal that showed no change in size after the test. More than 70% of spruce charcoal kept its original size, whereas this was the case for only 35% of eucalyptus. Eucalyptus charcoal produced a wide range of different sized fragments because of the cracks in the charcoal, which led to breakage during the test and the production of smaller pieces. Spruce charcoal kept its shape and integrity during the test and produced mainly fine particles, which led to a slight reduction in size in 20% of the charcoal (> 22.4 mm).

The friability of charcoal is quantitatively determined by the quantity of particles < 6.3 mm produced. The friability index is represented by the last bar in **Fig. 10**. The friability indexes  $F$  for each test are shown in **Fig 11**; a high  $F$  index indicates high friability. In general, spruce charcoal is less friable

than eucalyptus charcoal. The  $F$  index ranged from 7.3 to 10.0% for spruce charcoal, and from 8.9 to 16.0% for eucalyptus. The smaller pieces of charcoal resulting from eucalyptus breakage offer more surface contact for shock and abrasion inside the drum thereby increasing the number of fines produced, and hence the friability index.

Friability decreased with increasing pyrolysis temperature. A 60% decrease in the friability of eucalyptus charcoal was observed with an increase in the pyrolysis temperature from 500 to 800 °C and a 62% decrease in spruce charcoal. **Fig. 11** shows there was a linear decrease in the  $F$  index with increasing temperature. The solid residence time had no influence on charcoal friability in either eucalyptus or spruce. As mentioned above, the difference in the results observed for eucalyptus prepared at 800 °C without and with solid residence time can be explained by the random formation of cracks during pyrolysis.

Like for the  $S$  index, a linear relationship was observed between the  $F$  index and charcoal true density for spruce charcoal (**Fig. 9**). Therefore, the decrease in friability is certainly due to the better ordering of the carbon structure with increasing pyrolysis temperature, leading to a denser and more resistant carbon structure. A general decrease in the  $F$  index was also observed with an increase in apparent density in spruce charcoal. No relation was found for eucalyptus charcoal.

Similar findings were reported by Oliveira, et al. [32] who found an increase in charcoal friability with an increase in the pyrolysis temperature from 300 to 500 °C followed by a decrease in friability with an increase from 500 to 700 °C. The opposite was observed by Coutinho and Ferraz [33], who found a linear increase in charcoal friability with an increase in pyrolysis temperature from 400 to 1000 °C.

To sum up, charcoal compressive strength and resistance to friability evolved in the same way depending on the changes in the pyrolysis parameters and appears to be controlled by the carbon structural ordering.

### 3.5. Charcoal CO<sub>2</sub> reactivity

Reactivity of the char produced was measured during isothermal gasification experiments in 100% CO<sub>2</sub>, at 900 °C. The conversion of different eucalyptus and spruce charcoals is plotted versus time in **Fig. 12**.

From this result, it is clear that eucalyptus charcoal reacts significantly more slowly than spruce charcoal. As can be seen in **Table 5**, spruce charcoal reactivity was more than three times higher than that of eucalyptus. Spruce charcoal was completely converted in the interval of 500-1000 s, whereas eucalyptus charcoal was only fully converted after 2500-3000 s. The difference in reactivity between the two species is attributed to the higher porosity of spruce charcoal, and most certainly in the difference in its porosity distribution [51,52]. Compared to hardwood, softwoods are known to produce a charcoal with a higher macro-porosity [53]. These wider pores may enhance the accessibility of the reactive gas inside the particle. The higher ash content in spruce charcoal may also contribute to the increase in reactivity because of catalytic effects [54].

The influence of pyrolysis conditions on charcoal reactivity is less important than the nature of the wood. In both charcoals, an increase in pyrolysis temperature led to a decrease in charcoal reactivity. When the temperature was increased from 500 to 800 °C with no solid residence time, the average reactivity  $R_{0-50}$  decreased from 120.81 to 96.25 mg.(g.min)<sup>-1</sup> in spruce charcoal, and from 44.03 to 33.00 mg.(g.min)<sup>-1</sup> in eucalyptus charcoal. However, this decrease was more pronounced in spruce charcoal when it was kept at the final temperature for 90 min the average reactivity  $R_{0-50}$  dropped from 109.32 to 80.34 mg.(g.min)<sup>-1</sup>. No significant influence of solid residence time on reactivity was observed in eucalyptus charcoal.

The decrease in reactivity with increasing pyrolysis temperature is caused by the higher structural ordering of the carbon matrix (as revealed by the Raman analysis), and the subsequent decrease in the number of active sites [52,55]. The residence time at final temperature is also known to have an impact on carbon matrix restructuring and hence on reactivity. When the residence time was increased from 0 to 90 min, the average reactivity  $R_{20-80}$  of spruce charcoal decreased from 90.70 to 77.41 mg.(g.min)<sup>-1</sup> at 800 °C

whereas the decrease was twice lower at 500 °C. Thus, rearrangement of the particles appears to significantly influence reactivity only at a pyrolysis temperature of 800 °C in spruce charcoal.

#### **4. Discussion - the selection of pyrolysis parameters and wood species for metallurgical applications**

Our results show that the nature of the wood is the most important criteria for the production of charcoal to be used as a reducing agent. When considering the fixed carbon yield, apparent density and ash content, eucalyptus (*Eucalyptus globulus*) is a better choice than spruce (*Picea abies*) for charcoal production, independently of the pyrolysis parameters. A minimum value of 250 kg.m<sup>-3</sup> for apparent density is generally considered for a charcoal reducer in BF and SAF [14,56], based on this criterion, spruce charcoal does not fulfill the needs of metallurgical applications. Furthermore, in silicon production where high Si purity is required, eucalyptus charcoal is more suitable as its ash content is twice lower than that of spruce charcoal.

Surprisingly, the denser charcoal produced (eucalyptus) had the lowest compressive strength and the highest friability. If the mechanical behavior is taken into account, eucalyptus charcoal may cause more operational problems than spruce charcoal. Indeed, in ironworks, because of its low mechanical strength, charcoal can only be used as a top charged reducer up to 100% in small-scale BF. In larger BF, the most common process, coke substitution, is limited to 20% [6,9,10]. However, charcoal in BF can also be tuyere injected in the form of powder up to 25% [3] or can be introduced in the sintering process up to 100% [57]. In SAF, for silicon production, the load bearing requirement is less than in BF due to the small height of the burden in the furnace [19]. Some silicon producers claim to operate with 100% charcoal as a reducing agent in medium size furnace (20 MW) [36].

Concerning reactivity, the final decision on the suitability of charcoal as a reducing agent depends on the specific characteristics of the process itself. Eucalyptus charcoal is less reactive than spruce charcoal, but charcoal from all woods is always more reactive than fossil reducers [23,24]. Thus, compared with fossil reducers, charcoal may be a good choice for use in SAF, but not for BF.

Nevertheless, the following general trends regarding the pyrolysis parameters can be considered to improve the metallurgical qualities of charcoal. No real influence of the solid residence time was observed, with the exception of fixed carbon content and reactivity. A highly carbonized product can be obtained by increasing the pyrolysis temperature to 600-700 °C. This result is in agreement with the results reported by Griessacher, et al. [18] and Weber and Quicker [26] that a suitable metallurgical charcoal can be obtained by slow pyrolysis of wood at a temperature of 700 °C. The compressive strength increases and friability decreases linearly with increasing pyrolysis temperature. Thus, high temperature pyrolysis is favorable for the production of metallurgical charcoal with high mechanical stability but also needs to be considered from the point of view of energy and operational costs.

Charcoal reactivity has to be low in the case of BF application. Therefore high pyrolysis temperatures should be preferred for the production of charcoal for ironmaking. On the other hand, for silicon production, high SiO reactivity is required from the reducing agents to guarantee the recovery of SiO. The idea of a possible relationship between CO<sub>2</sub> and SiO reactivity was mentioned by Paull and See [27] and Wang, et al. [24]. If we assume a qualitative relation between SiO reactivity and CO<sub>2</sub> reactivity, an increase in pyrolysis temperature could be unfavorable for the process. Work is currently underway to check if this relationship exists.

## **5. Conclusions**

The aim of this study was to evaluate the impact of pyrolysis conditions on the quality of charcoal for use as a reducing agent in different metallurgical processes. The influence of pyrolysis temperature, of solid residence time and of wood species was analyzed. The quality of the charcoal as a reducer was estimated by its fixed carbon yield, fixed carbon content, apparent density, compressive strength, friability, and CO<sub>2</sub> reactivity. A new compression test was developed to be applied in a real charcoal bed. The main conclusions of our works are summarized below:

- The species of wood is the parameter that has the most influence on the charcoal properties of interest for metallurgical applications. Spruce charcoal has a higher mechanical strength and CO<sub>2</sub>

reactivity, and a lower carbon fixed yield and apparent density than eucalyptus charcoal whatever the pyrolysis conditions. Lignin content is not an indicator of charcoal yield.

- The common claim that dense wood will produce charcoal with high mechanical strength (compressive strength and friability) was not confirmed when charcoal was produced from large particles in near-industrial conditions. Large cracks and voids appeared in eucalyptus charcoal during pyrolysis due to its high apparent density, leading to more brittle charcoal. Charcoal apparent density is not a good indicator to evaluate charcoal compressive strength either.

- Charcoal compressive strength and resistance to friability evolved in the same way according to the changes in the pyrolysis parameters. A strong linear relationship was found between spruce charcoal true density, and consequently its structural ordering, and its compressive strength and resistance to friability. This underlines the fact that a better ordered and denser carbon structure leads to a more resistant charcoal.

- An increase in pyrolysis temperature leads to a slight increase in charcoal apparent density and a linear increase in charcoal compressive strength as well as a linear decrease in friability, and a decrease in CO<sub>2</sub> reactivity. Solid residence time has no significant influence on mechanical strength. An increase in solid residence time reduces charcoal CO<sub>2</sub> reactivity. When high mechanical strength and high reactivity are both needed, the selection of pyrolysis parameters will require a compromise.

### **Abbreviations**

Ash = ash content

BF = blast furnace

C<sub>fix</sub> = fixed carbon content

SAF = submerged arc furnace

srt = solid residence time

T = pyrolysis temperature

VM = volatile matter content



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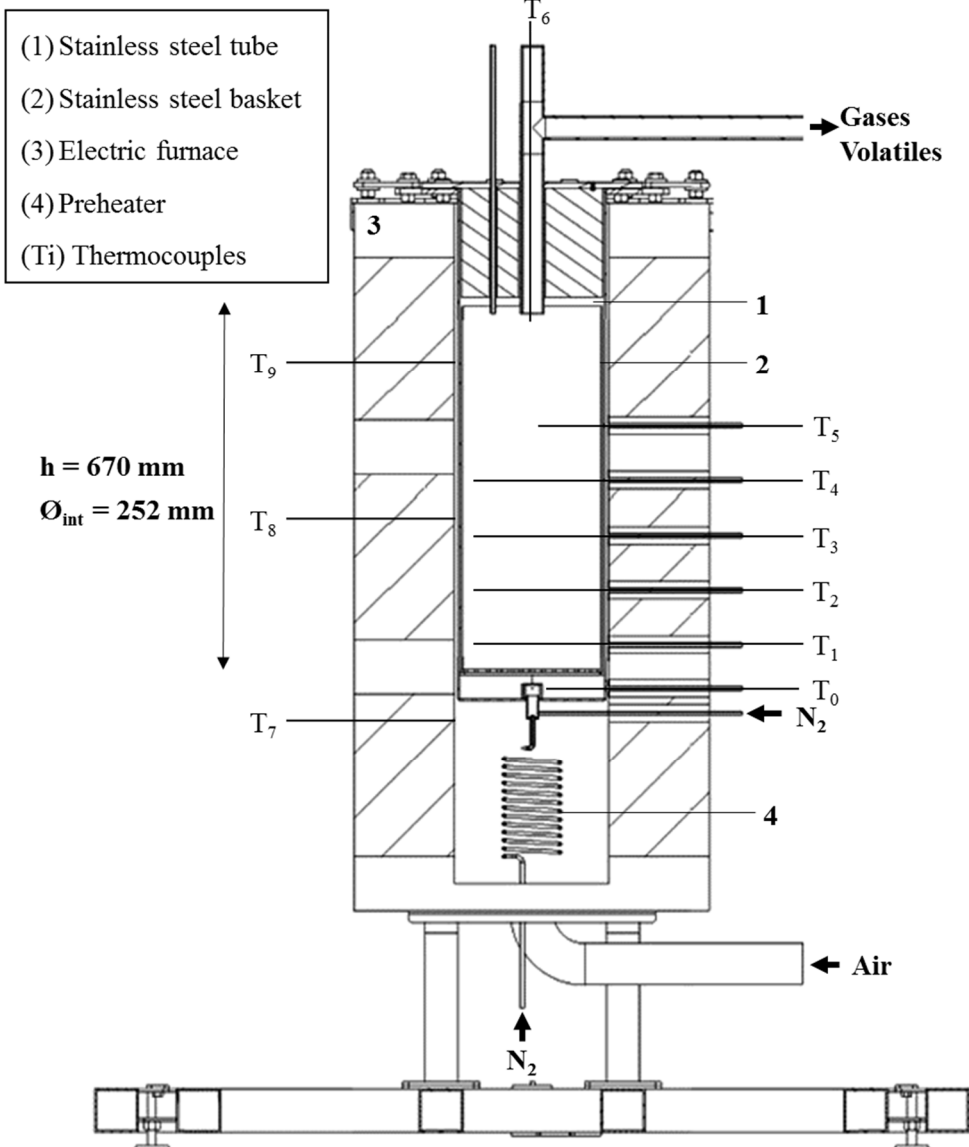
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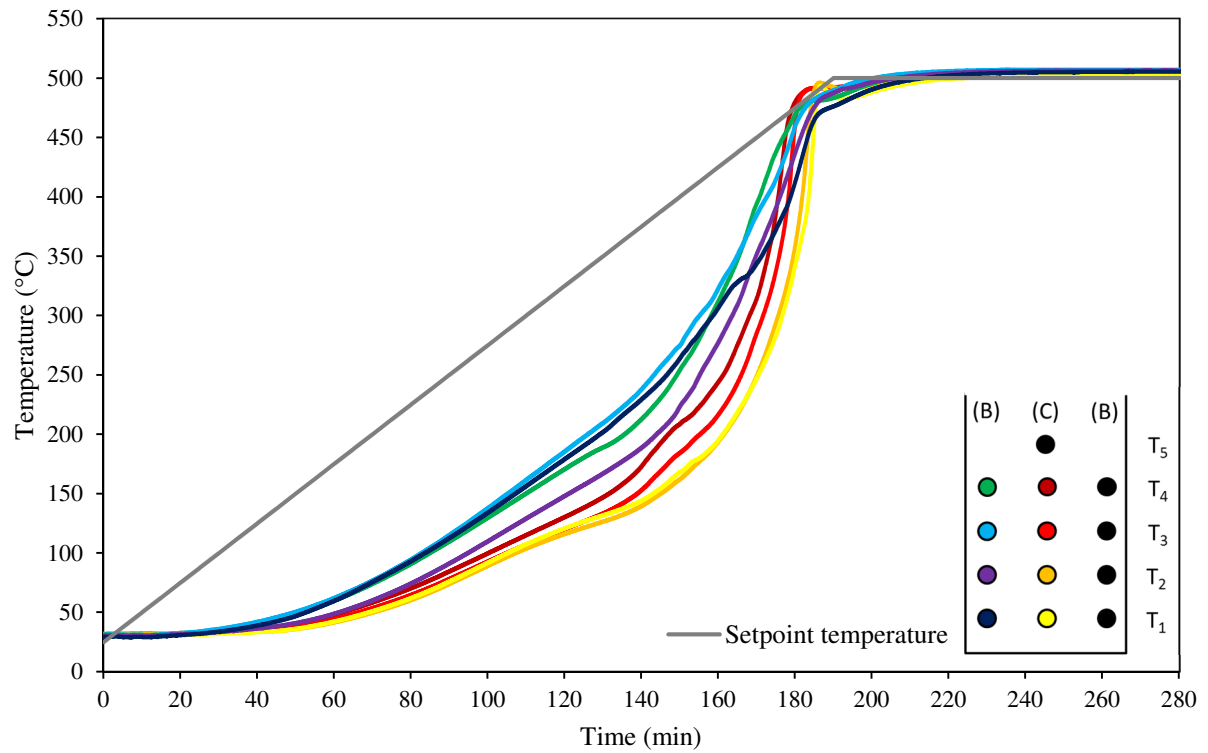
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Fig. 1. Diagram of the pyrolysis reactor.



**Fig. 2.** Temperature inside the reactor for spruce wood during pyrolysis at 500 °C for 90 min. The position of each thermocouple in the load is given by the legend sketch.



**Fig. 3.** Photographs of eucalyptus charcoal (left) and spruce charcoal (right) produced at 500 °C with 0 min solid residence time.

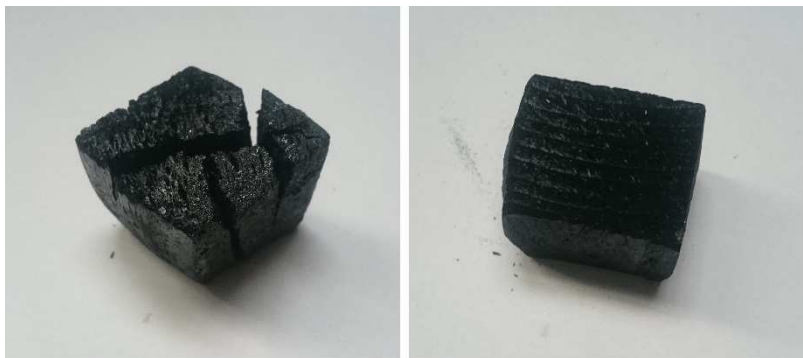
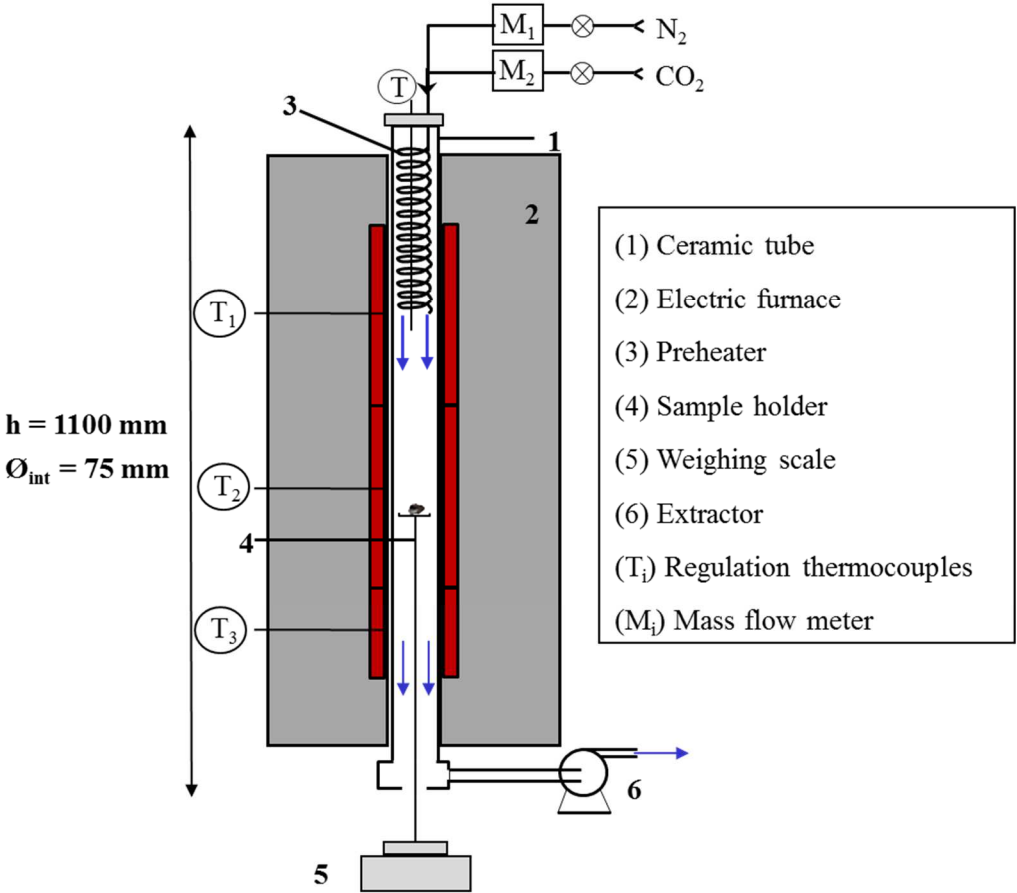
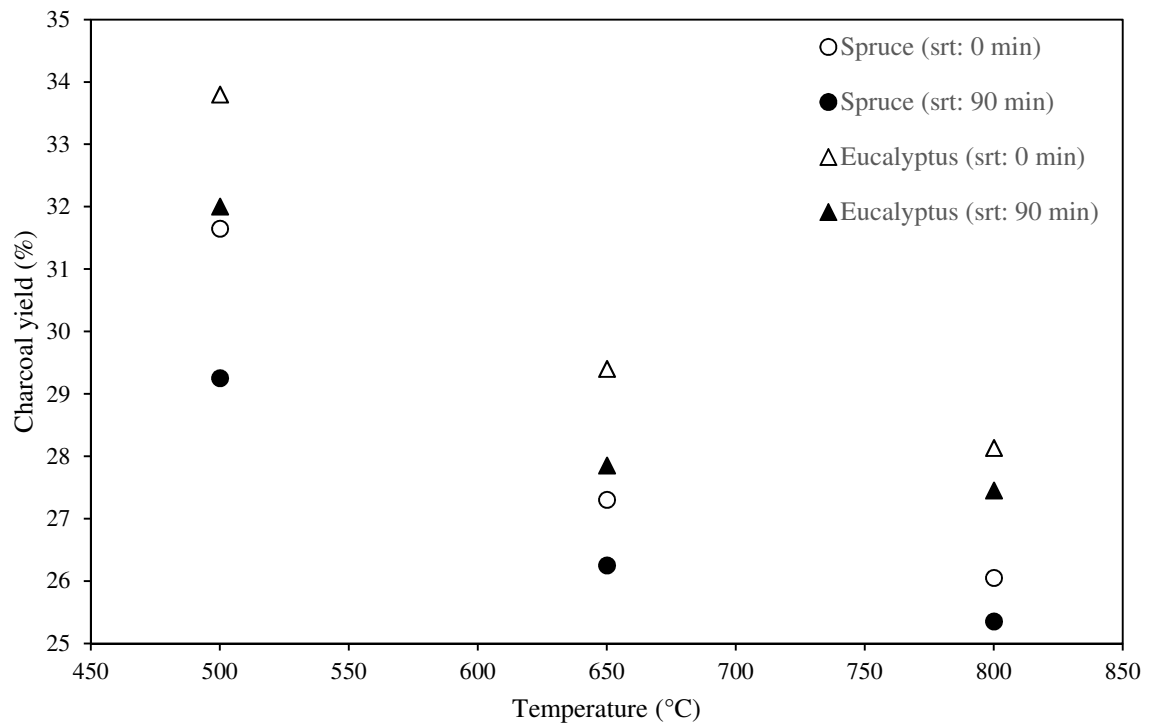


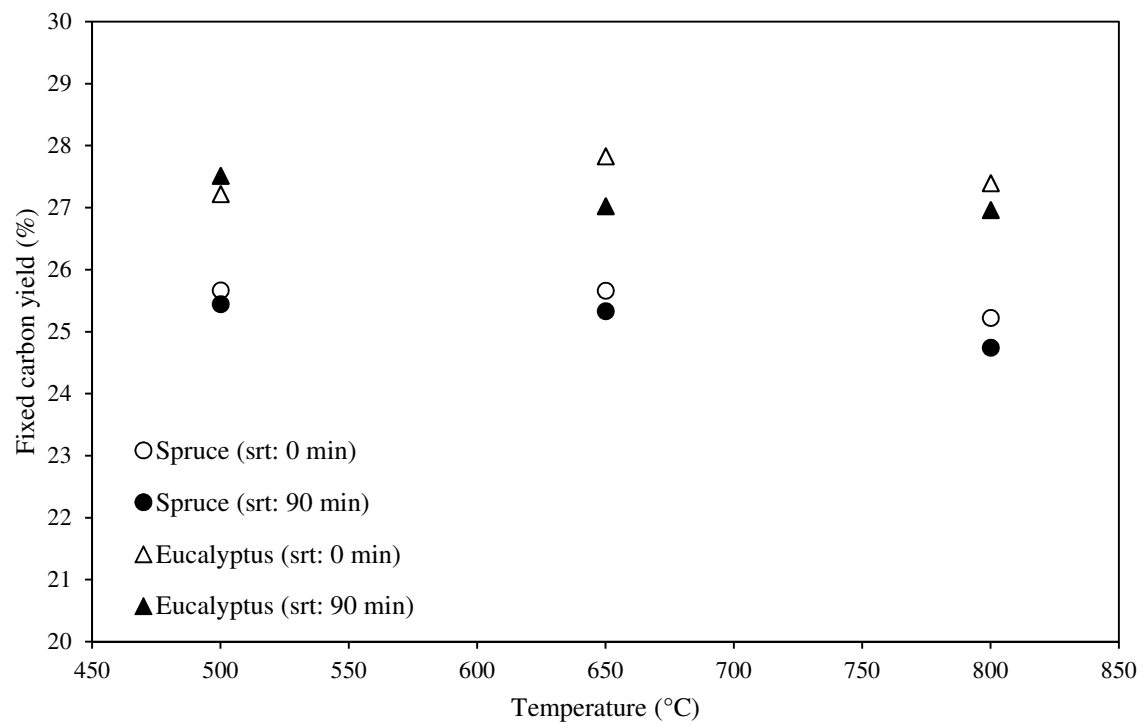
Fig. 4. Diagram of the macro-thermogravimetric reactor.



**Fig. 5.** Influence of the pyrolysis temperature and solid residence time (srt) on charcoal yield.

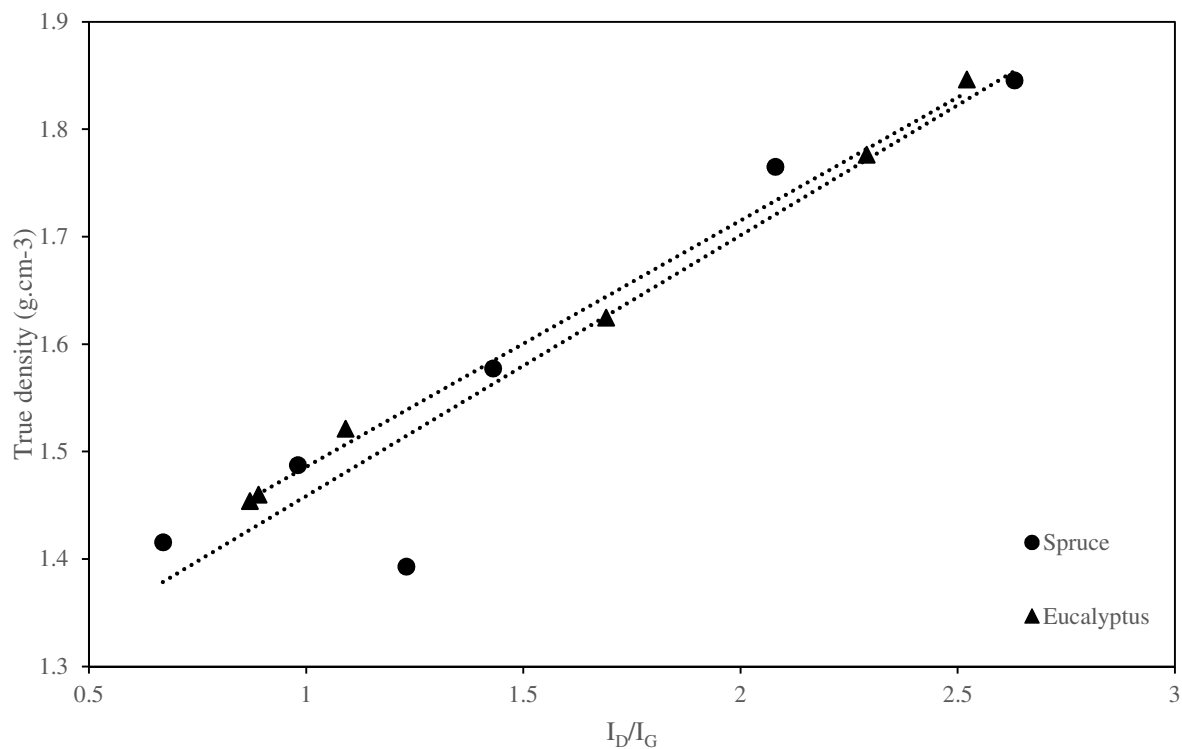


**Fig. 6.** Influence of the pyrolysis temperature and solid residence time (srt) on fixed carbon yield.

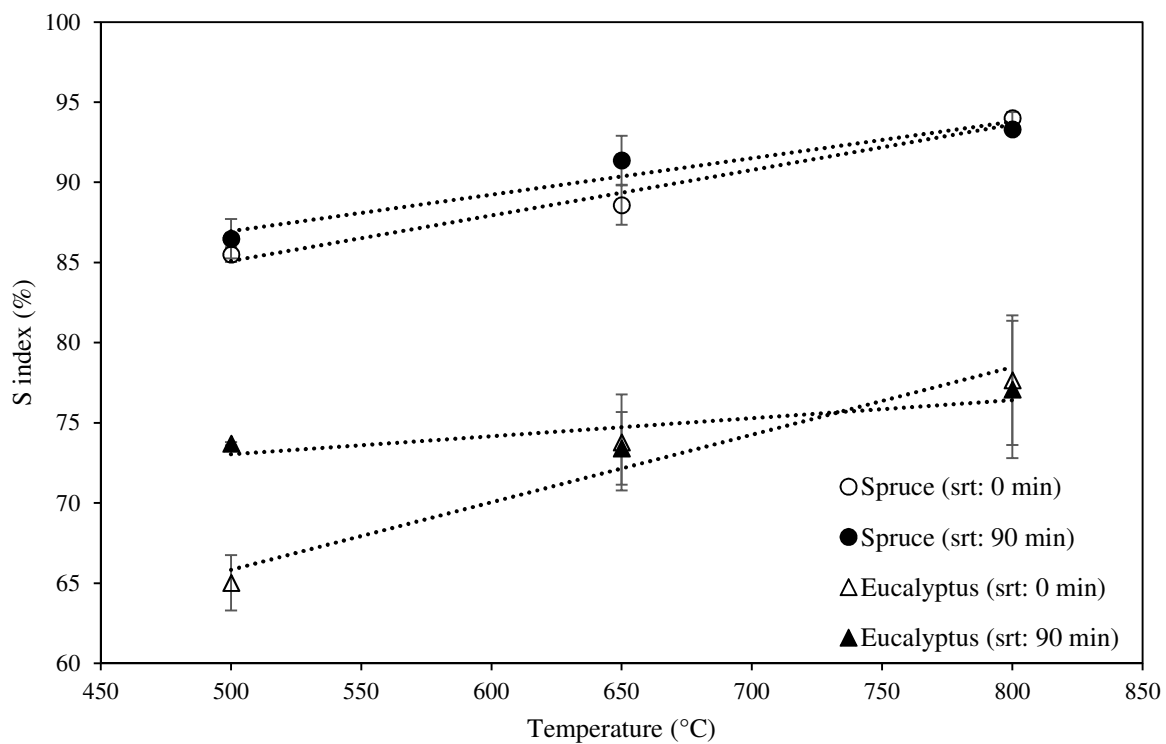




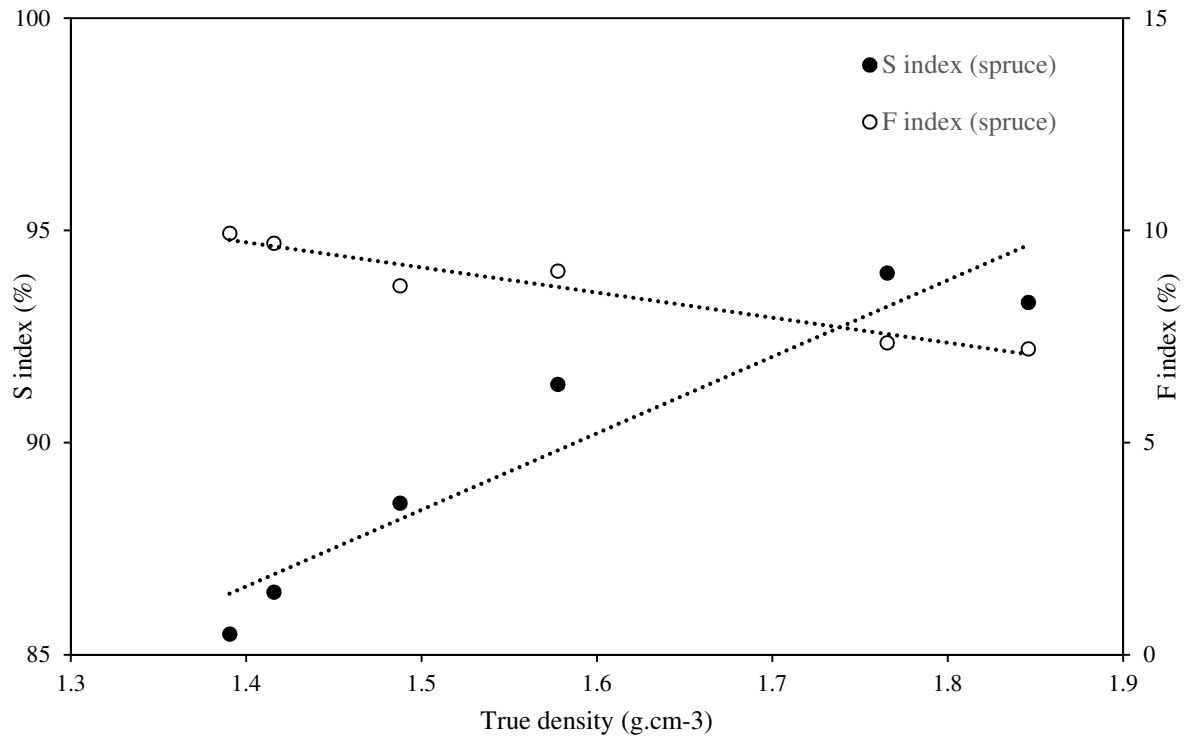
**Fig. 7.** Relationship between the  $I_D/I_G$  ratio and charcoals true density for spruce and eucalyptus.



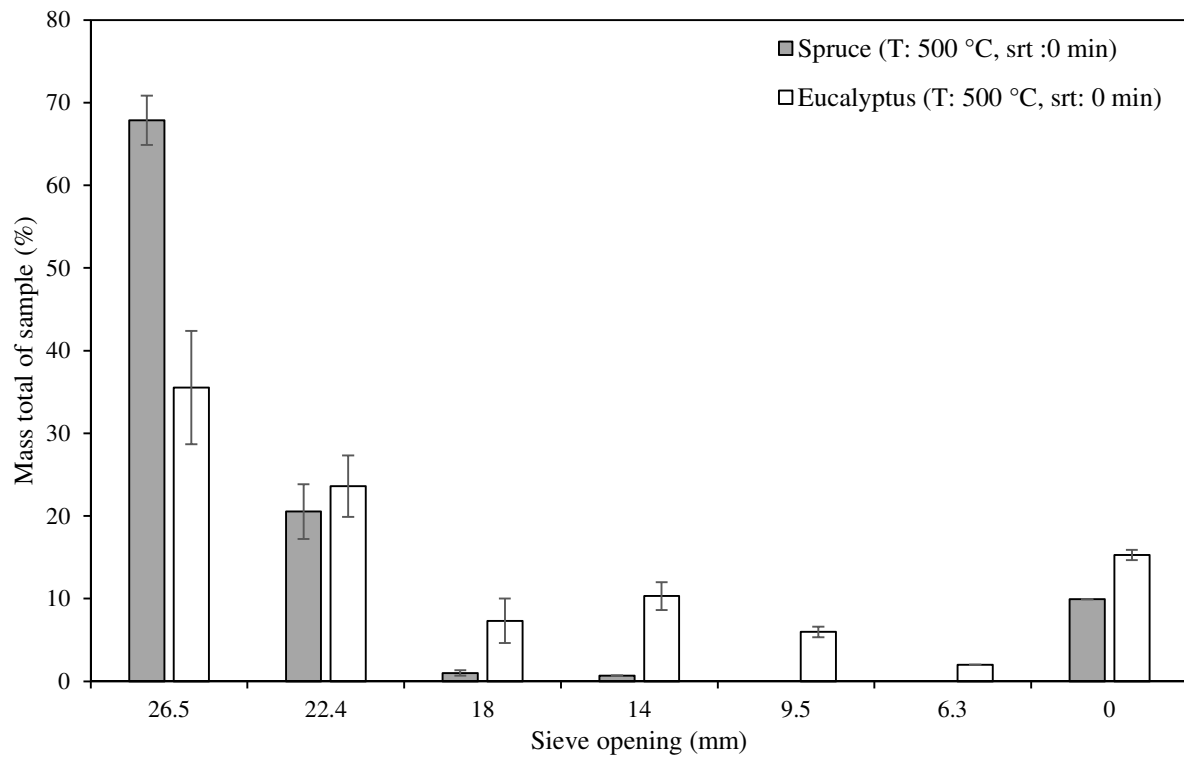
**Fig. 8.** Influence of the pyrolysis temperature and solid residence time (srt) on the S index.



**Fig. 9.** Relationship between the mechanical indexes and the true density for spruce charcoal.



**Fig. 10.** Particles size distribution after drum test for eucalyptus and spruce charcoal produced at 500°C with no solid residence time.





**Table 1**  
Chemical compositions and apparent density of feedstock.

<u>Analysis</u>		<u>Spruce</u>	<u>Eucalyptus</u>
Proximate analysis (wt.%)	Moisture <sup>a</sup>	9.3	7.9
	C <sub>fix</sub> <sup>b, c</sup>	13.6	15.4
	VM <sup>b</sup>	86.2	84.5
	Ash <sup>b</sup>	0.2	0.1
Ultimate analysis <sup>b</sup> (wt.%)	C	46.5	45.6
	H	6.5	6.3
	N	0.1	0.1
	O <sup>c</sup>	46.7	47.9
Constituents <sup>b</sup> (wt.%)	Extractives <sup>b</sup>	3.3 ± 0.2	4.2 ± 1.0
	Holocellulose <sup>c, d</sup>	68.2	75.1
	Lignin <sup>d</sup>	31.6 ± 2.3	24.8 ± 1.8
D <sub>app</sub> <sup>b</sup> (kg.m <sup>-3</sup> )		405 ± 22	891 ± 87

<sup>a</sup> as received; <sup>b</sup> dry basis; <sup>c</sup> by difference, <sup>d</sup> extractive-free

**Table 2**  
Principal band assignments of Raman spectra [39].

<u>Wavenumber (cm<sup>-1</sup>)</u>	<u>Band name</u>	<u>Assignments</u>
1160 cm <sup>-1</sup>	D2	C-O-C stretching
1260 cm <sup>-1</sup>	D1	Aromatic ether
1330 cm <sup>-1</sup>	D	Disordered structure, aromatic ring
1440 cm <sup>-1</sup>	R	CH <sub>2</sub> scissoring
1500 cm <sup>-1</sup>	S	Asymmetric aryl ring stretching, C=C stretch
1600 cm <sup>-1</sup>	G	Aromatic ring breathing
1640 cm <sup>-1</sup>	G1	Unsaturated and carbonyl structures
1700 cm <sup>-1</sup>	G2	Carbonyl group

**Table 3**  
Proximate and ultimate analysis of the charcoal obtained with different pyrolysis parameters.

<u>Sample</u>	<u>Pyrolysis parameters</u>		<u>Proximate analysis (wt.%) <sup>a</sup></u>			<u>Ultimate analysis (wt.%) <sup>a</sup></u>			
	T (°C)	srt (min)	C <sub>fix</sub> <sup>b</sup>	VM	Ash	C	H	N	O <sup>b</sup>
Spruce	500	0	80.9	18.3	0.8	83.4	3.7	0.2	12
	500	90	86.8	12.5	0.7	87.0	3.2	0.2	8.9
	650	0	93.8	5.3	0.9	92.0	2.5	0.2	4.4
	650	90	96.3	2.8	0.9	94.0	2	0.3	2.8
	800	0	96.6	2.4	0.9	93.1	1.3	0.5	4.2
	800	90	97.4	1.5	1.1	95.2	1.0	0.5	2.2
Eucalyptus	500	0	80.5	19.2	0.3	83.6	3.3	0.1	12.6
	500	90	85.9	13.8	0.3	87.0	2.9	0.2	9.6
	650	0	94.6	5.1	0.4	92.8	2.3	0.3	4.2
	650	90	97.0	2.5	0.6	94.3	1.9	0.3	3.0
	800	0	97.8	1.6	0.6	95.9	1.3	0.4	1.8
	800	90	98.1	1.4	0.5	96.4	1.0	0.5	1.6

<sup>a</sup> dry basis; <sup>b</sup> by difference

**Table 4**  
Charcoal textural and structural analysis for different pyrolysis parameters.

<u>Pyrolysis parameters</u>			<u>Apparent density<sup>a</sup></u> (g.cm <sup>-3</sup> )				<u>True density<sup>a</sup></u> (g.cm <sup>-3</sup> )	<u>Porosity</u> (%)	<u>I<sub>D</sub>/I<sub>G</sub></u>
Sample	T (°C)	srt (min)	Min	Max	Average	Standard deviation			
Spruce	500	0	0.141	0.265	0.204	0.042	1.39	85.4	1.23 ± 0.32
	500	90	0.147	0.269	0.196	0.037	1.42	86.2	0.67 ± 0.12
	650	0	0.141	0.273	0.204	0.051	1.49	86.3	0.98 ± 0.10
	650	90	0.145	0.301	0.213	0.038	1.58	86.5	1.43 ± 0.12
	800	0	0.172	0.331	0.258	0.044	1.77	85.4	2.08 ± 0.25
	800	90	0.132	0.309	0.221	0.025	1.85	88.0	2.63 ± 0.15
Eucalyptus	500	0	0.269	0.573	0.400	0.091	1.45	72.5	0.87 ± 0.04
	500	90	0.170	0.557	0.362	0.096	1.46	75.2	0.89 ± 0.06
	650	0	0.240	0.504	0.374	0.088	1.52	75.4	1.09 ± 0.22
	650	90	0.324	0.582	0.448	0.069	1.62	72.4	1.69 ± 0.16
	800	0	0.283	0.594	0.447	0.102	1.78	74.9	2.29 ± 0.20
	800	90	0.226	0.583	0.432	0.104	1.85	76.6	2.52 ± 0.25

<sup>a</sup> dry basis

**Table 5**  
Average CO<sub>2</sub> reactivity for charcoal obtained with different pyrolysis parameters.

<u>Pyrolysis parameters</u>			<u>CO<sub>2</sub> reactivity</u>	
Sample	T (°C)	srt (min)	R <sub>0-50</sub> (mg.(g.min) <sup>-1</sup> )	R <sub>20-80</sub> (mg.(g.min) <sup>-1</sup> )
Spruce	500	0	120.81 ± 3.29	103.17 ± 0.35
	500	90	109.32 ± 3.28	96.96 ± 2.82
	800	0	96.25 ± 4.03	90.70 ± 0.64
	800	90	80.34 ± 1.98	77.41 ± 1.48
Eucalyptus	500	0	44.03 ± 0.14	33.44 ± 1.19
	500	90	42.25 ± 1.12	37.18 ± 0.08
	800	0	33.00 ± 0.68	33.41 ± 0.25
	800	90	29.97 ± 0.37	29.22 ± 0.57