



# Hydrogen rich reducing gases generation in the production of charcoal from woody biomass carbonization



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## ABSTRACT

The metallurgical industry uses fossil carbonaceous materials in order to fulfill the high energetic demand of its processes, involving the emission of great amounts of CO<sub>2</sub> that contribute to the greenhouse effect. These CO<sub>2</sub> emissions can be mitigated by using biomass derived fuels and products due to their CO<sub>2</sub>-neutral condition. The objective of this paper is to study the carbonization process of woody biomass with the aim of producing a metallurgical grade charcoal and at the same time, a gas reducing agent with a high proportion of H<sub>2</sub> + CO through the thermo-catalytic treatment of the pyrolysis vapors.

The experiments were performed using two reactors connected in series. The first one was a semi-batch non stirred 3.5 L reactor swept with 1 L min<sup>-1</sup> N<sub>2</sub>, where pyrolysis took place at 750 °C. The second one, directly connected to the first reactor, was a tubular reactor where the thermal and/or catalytic treatment of the pyrolysis vapors took place at 900 °C. The sample used for the experiments was eucalyptus trunk wood and to improve the yield and quality of the pyrolysis gases, the following catalysts were tested: commercial HZSM5 zeolite, as received and modified with nickel, a commercial Ni-containing steam reforming catalyst (Katalco 57-4Q), and a homemade Ni/CeO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalyst. As a general rule, the catalysts tested had a beneficial effect in the process: they reduced liquid yields, increased gas yields, raised the H<sub>2</sub> content and decreased the CO, CO<sub>2</sub> and CH<sub>4</sub> content in the gases. The positive effect of the catalysts increased in the following order: HZSM5, Ni/HZSM5, Katalco 57-4Q and the homemade Ni/CeO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalyst.

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## 1. Introduction

The production of ferrous and non-ferrous materials is a high energy-demanding sector. Some authors claim that around 20% of the total industrial energy demand is consumed only in steel-making [1]. The energetic requirements are mainly covered by the utilization of fossil fuels (primarily coke and coal-like products), which makes the iron and steel industry be the responsible of 5–7% of the total world CO<sub>2</sub> emissions [1–3]. Taking into account that coke and coal-like products are also intensively used in the production of other metals, the impact of metallurgy on energy consumption and CO<sub>2</sub> emissions accounts currently for a very high proportion.

An alternative to reduce the high emissions of CO<sub>2</sub> coming from the metal sector is to use woody biomass-based fuels instead of fossil fuels, taking advantage of their CO<sub>2</sub>-neutral nature. These fuels can be raw biomass, torrefied biomass or charcoal coming from the slow pyrolysis/carbonization of biomass [1,4]. All these

materials have been proved in different steps of integrated steel plants, as they are able to be used in cokemaking, iron ore sintering and blast furnace [1,2,5]. In some studies, a reduction up to 31–57% in net CO<sub>2</sub> emissions has been reported [1].

Charcoal obtained from the carbonization of biomass at high temperature and long residence times is claimed to be the best material to use in steelmaking in substitution of coal and coke, mainly due to the physical and chemical similarity between them [1,6]. Therefore, although charcoal production through biomass carbonization is a millennial process [7], new researches have been carried out in the last years in modern installations in order to determine the best raw materials and operating parameters for charcoal production [8–14] and also to characterize the behavior of charcoal in the processes of steelmaking [15–17].

However, not only charcoal is produced during slow pyrolysis of biomass. When wood structures are cracked, volatiles (from now on called pyrolysis vapors) release from wood [18]. These vapors consist of a large number of different compounds that spontaneously split into two phases when cooling down, forming a mixture of organic and aqueous liquids, and a gas fraction [19,20]. In the industrial production of charcoal and the majority of research

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carried out about charcoal production, these vapors are burned [8,9,19,21]. The reason is that the liquid phase obtained after high temperature biomass carbonization is nothing like the bio-oil obtained from the fast pyrolysis, so the possibilities of using it as liquid bio-fuel or feedstock are very limited, because they are composed of water and a group of single and polycyclic aromatic compounds, known as a whole as tars [11].

One interesting option when operating under high temperature slow pyrolysis conditions is to try to convert the vapors in as much  $H_2$  and CO (syngas) as possible while they are at vapor state, reducing at the same time the quantity of tars. In this way, two products commonly used in metals manufacturing (charcoal + gas reducing agent) can be produced from biomass at the same time. The authors have been investigating this possibility from some years now [11,12,20,22]. The method consists on cracking and reforming the pyrolysis vapors by using catalysts at high temperature, taking advantage of the presence of water in pyrolysis vapors to carry out reforming ( $C_xH_y + H_2O \leftrightarrow CO/CO_2 + H_2$ ) and water gas shift reactions ( $CO + H_2O \leftrightarrow CO_2 + H_2$ ). In such experiments, nickel containing alumina-based catalysts and ZSM-5 zeolite were proved in the carbonization of olive tree cuttings, one of the main agricultural waste in Spain, obtaining up to 76 vol.% of  $H_2 + CO$  in gases and the elimination of tar compounds [22].

Now, the objective of this paper is to study the possibility of producing high quality reducing gases in the carbonization process of eucalyptus trunk wood, because eucalyptus is the most used feedstock for charcoal industrial production [18,21,23], and his charcoal has better properties than olive tree charcoal [12,24]. The goal of the research is to find a way to produce reducing gases to apply them in the industrial fabrication of charcoal, enhancing the economy of the process and at the same time reducing the emission of pollutant gases.

For the present study, a ZSM5 zeolite with and without Ni, a Ni/CeO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalyst prepared in our laboratories and a commercial steam reforming catalyst have been used. Although other type of catalysts have been used for hydrogen rich gases production in pyrolysis of biomass [25–28], Ni containing alumina and zeolites are the best used in the majority of the applications concerning biomass thermo-chemical processing [29], including the elimination of tar compounds in biomass gasification [30–33] and the reforming of bio-oils [34–38]. This kind of catalysts has been also used in the pyrolysis of biomass to enhance the properties of bio-oils [39], to eliminate pyrolysis tars [40], to produce  $H_2$ -rich gases in the co-processing of biomass and plastic waste [41] and in the reforming of pyrolysis vapors by using steam [42–43].

Concerning pyrolysis of biomass to produce metallurgical grade charcoal, there are some works about the treatment of the pyrolysis vapors to produce methane [44] and about their condensation in order to obtain some benefit from the liquid phase [45]. However, as far as the authors are concerned, there is not any published study about catalytic cracking and reforming of pyrolysis vapors for yielding reducing gases in the production of metallurgical grade charcoal. Therefore, this paper can be a new step forward the integral utilization of woody biomass in the production of feedstock materials for the steel and metal industry.

## 2. Materials and methods

### 2.1. Materials

The biomass sample used for pyrolysis experiments was eucalyptus trunks wood. This sample came from chopped pre-crushed trees, therefore the received material was very homogenous and pure (no soil, nor stones), as shown in Fig. 1.

The eucalyptus wood sample was further ground to two different particle sizes by using a cutting mill. Pieces smaller than



Fig. 1. Eucalyptus wood biomass sample as received.

10 mm were used for pyrolysis experiments. Besides, in order to have an appropriate homogeneous sample available for characterization, a small amount of biomass was also ground to <2 mm.

The proximate and ultimate analyses, together with the constituents' composition of the eucalyptus sample, are presented in Table 1. Wood is an organic material, thus the main elements of the sample are carbon, hydrogen and oxygen, this last one represents the major part of the "others" fraction. There is also a small amount of nitrogen (0.1 wt.%) in the sample. In view of the proximate analysis, it is expected that the volatile matter and moisture (81.7 wt.%) will vaporize during the pyrolysis experiment and turn into volatiles constituting both the condensable and non-condensable pyrolysis vapors. The remaining matter (fixed carbon and ashes (18.9 wt.%) will form the solid fraction.

As shown in Table 1, the main constituents of the eucalyptus sample are cellulose (mainly glucanes) and lignin. In a lesser proportion there are hemicellulose (xylanes and arabinanes) and extractives, substances like proteins or fats present in vegetable tissue that can be separated by successive treatment with solvents.

### 2.2. Experimental procedure

The pyrolysis experiments were performed using a lab-scale plant consisting of two reactors connected in series, and a vapors condensation and gas-liquid separation unit. In a typical run, 100 g of sample were introduced in the first non-stirred 3.5 L stainless steel reactor, where pyrolysis took place. The reactor was heated with a  $3\text{ }^\circ\text{C min}^{-1}$  heating rate to  $750\text{ }^\circ\text{C}$  and maintained there for 30 min (first stage). The second reactor was a vertical tubular reactor, where the pyrolysis vapors were treated at  $900\text{ }^\circ\text{C}$  (second stage). The tubular reactor was loaded with a charcoal bed, followed by the catalyst. Prior to the reaction, catalysts were reduced in situ at  $800\text{ }^\circ\text{C}$  during 4 h with a 10 vol.%  $H_2$  - 10 vol.%  $N_2$  - Ar mixture. A flow of  $1\text{ L min}^{-1}$  of  $N_2$  was fed during the experiments, in order to maintain the inert atmosphere in the process. A full description of the experimental procedure together with a picture of the installation can be found elsewhere [20,22].

The mentioned operating temperatures and heating rate were selected based on previous experience from the authors [20,22]. It has been proven by the authors that such conditions minimize tars formation and maximize the gas yield, along with a higher quality gas and solid products. The amount of solids and liquids generated after each experiment are weighed and the corresponding pyrolysis yields are calculated as weight % with respect to the initial biomass sample weight (wet biomass). The gas yield is determined by difference to 100. All the yields values presented

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