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Research paper

# Influence of temperature and residence time in the pyrolysis of woody biomass waste in a continuous screw reactor

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ABSTRACT

The aim of this paper is to study the influence of temperature and residence time in the quality of the charcoal obtained in the pyrolysis of biomass waste, in order to be used as a reducing agent in metallurgical applications. Woody biomass waste (*pinus pinaster*) coming from forest activities carried out in the north of Spain has been pyrolyzed in a laboratory scale screw continuous reactor connected to a second reactor where the pyrolysis vapors have been thermally treated to promote further cracking, with the aim of diminishing tars and improving the composition of the gas phase.

Both the peak temperature and the exposition time at peak temperature have an impact in the pyrolysis fractions yields and composition, however it is at 1173 K where the bigger changes occur both in pyrolysis products yield and composition. In all cases the solids obtained (charcoal) fulfill the requirements to perform as metallurgical reducers. The higher the peak temperature the greater the charcoal quality but the lower the pyrolysis solid yield since secondary pyrolysis reactions consume charcoal. The pyrolysis gases obtained are valuable products rich in CO (22–35 vol%) and hydrogen (35–50 vol%); on the contrary, the pyrolysis liquids obtained are mainly worthless products composed of water and some aromatic compounds (e.g. naphthalene, fluorene & antrhacene).



## 1. Introduction

Carbon is an essential element in the production of steel and many other pyrometallurgical processes [1,2], mainly because it can simultaneously act as versatile fuel and metallurgical reducer. The most common sources of carbon for these processes are mineral coals and carbonized heavy petroleum fractions, that mostly are converted into coke, the form in which carbon is commonly used in the metallurgical industry [1–3]. The production of coke from these materials, along with the massive amount of energy and carbon this process requires, causes the production of steel to be one of the activities that contributes most to climate change; in fact, the iron and steel industry is responsible for approximately 6.7% of total world $CO_2$ emissions [4]. Looking forward to reducing the environmental impact generated, many producers are developing new cleaner technologies. One of the most recognized and successful of them is the implementation of woody biomass derived charcoal in the blast furnace steel fabrication process [5–7]. This has been achieved successfully in some blast furnaces in Brazil [8] that manage dedicated eucalyptus plantations to produce charcoal that is afterwards utilized as a reducing agent partially substituting coal coke and reducing green house gas emissions in terms of reforestation, wood carbonization and charcoal utilization [9,10].

Biomass presents many advantages compared to conventional fossil fuels: it is a sustainable and renewable energy and chemicals source, it is easily available for many countries, and it presents a neutral carbon balance, which means that, theoretically, all the carbon dioxide produced from its exploitation has already been consumed during the biomass growth. Amongst all the biomass types accessible for industrial scale use, woody biomass coming from forestry waste is an interesting alternative to reduce operating costs and carbon emissions while also a solution for the environmental and health problems caused when organic waste is neglected [11]. There is a great potential in the use of woody biomass though is a resource relatively unexploited, Skytte et al. [12] reported that there is a $4 \cdot 10^{18}$ J $year^{-1}$ woody biomass

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potential in Europe (almost $2 \cdot 10^6$ km$^2$ of forest area [13]), which represents almost 45% of the total biomass (woody and non woody) potential in the same region, and just $2 \cdot 10^{18}$ J year$^{-1}$ of that total biomass potential is being used.

Due to the chemical nature of biomass, pyrolysis has been proved to be a suitable technique to transform biomass waste into more useful materials [14]. When pyrolyzed, woody biomass yields three main products: a carbon-rich solid called charcoal, an organic liquid known as bio-oil usually formed by an aqueous phase and dense tars and a gas mixture composed of carbon oxides, light hydrocarbons and hydrogen [15–17]. The amount and quality of each of these fractions depends on the pyrolysis operating parameters such as presence of catalyst [15], heating rate [16], peak temperature [18], residence time [19] and so forth [20,21]. According to the literature, three different processes are distinguished: flash, fast and slow pyrolysis [22], hence depending on which product is the objective of the process, one of these techniques are selected.

Most of the literature about biomass pyrolysis is focused on fast low temperature pyrolysis [23,24], which aims to maximize the production of bio-oils and its quality. High carbon and hydrogen containing upgraded bio-oils were obtained by Bhattacharya et al. [25] by performing continuous pyrolysis in an auger reactor at around 773 K with wood/plastic blends samples. Other authors have also achieved good quality liquids from continuous pyrolysis of biomass in an auger reactor, Thangalazhy-Gopakumar et al. [26] converted pine wood chips into bio-oils at low temperatures (673–773 K), Veses et al. [27] used different Mg and Ca based catalyst to enhance the liquid product in a low temperature (723 K) continuous pyrolysis process. In practice though, it is rather difficult to make use of bio-oils, since they are a complex and corrosive mixture of products with rather low higher heating value (HHV), and high oxygen and water contents. Nonetheless, charcoal can be useful in many different applications [28]. In fact, recent research [17,20,29] indicates that high temperatures (973–1073 K) slow pyrolysis can perform a solid product similar to metallurgical coke, and between the different technologies available screw reactors are very promising both in results and industrial aspects. Puy et al. [30] used an auger screw reactor at temperatures as high as 1073 K with two species of pinewood chips to determine the influence of different operating parameters. Fassinou et al. [31] also studied the influences of temperature, biomass flow rate and residence time in pyrolysis of *pinus pinaster* in a continuous auger screw reactor and concluded that temperature is the main parameter driving the reaction, followed by the residence time. The novelty of the work presented in this paper is that the screw reactor operated at higher temperatures (1173 K) and that to enhance the gas yield and its composition a second cracking step immediately after the main pyrolysis process was used, which the authors have proven is a good measure to decrease liquids converting them into valuable gases such as synthesis gas and light hydrocarbons [15,16].

This paper focuses on the optimization of the woody biomass pyrolysis process in order to produce a solid (charcoal) useful as reducing agent in metallurgical applications and at the same time maximize the production of high value gases by thermal treating of pyrolysis vapors in order to reduce bio-oils. The pyrolysis tests consist of two steps, a first slow pyrolysis reaction of the biomass carried out in an auger screw continuous reactor followed by a second step where the pyrolysis vapors are thermally treated to promote further cracking with the aim of diminishing tars and improving the composition of the gas phase. The achievement of these goals implies an important step towards a more sustainable and overall more economically interesting process of production of metallurgical reducers derived from biomass charcoal.

## 2. Material and methods

### 2.1. Preparation of the samples

The sample pyrolyzed was waste woody biomass of *Pinus pinaster* (maritime pine) coming from forest thinning carried out in Biscay (43°19′ N, 2°52′ W), in the north of Spain. The harvested pine trunks (26 years old) were stripped from their bark, and chipped to produce fuel of the appropriate size for boilers and separated into different fractions. The biomass waste used in the experiments consisted in a rejected fraction of smaller size not suitable for boilers (<6 cm). To prepare the samples for the experiments, a portion of the rejected biomass was first taken by the quartering method in order to obtain homogenous and representative samples, spread out on a clean surface and dried under room conditions for several days until equilibrium moisture was reached. Finally the biomass was sieved in order to obtain a sample of homogenous size particles (0.5–2 mm, which represented more than 60 wt% of the dried biomass) which was the feed to the reactor.

Table 1 shows the composition of the biomass sample pyrolyzed. It can be seen that the moisture content of the sample is about 11 wt%, the ash content is quite low (1.2 wt%) and the "others" content (mainly the oxygen [30,31] that forms part of the chemical structure of the biomass -cellulose and lignine-), is high (34.8 wt%). It has been reported that the main constituents of woody biomass are cellulose (mainly glucanes), hemicellulose (xylanes and arabinanes), lignin and the extractives, which consist in primary metabolites (sugar, fats, amino acids and carboxylic acids) and more complex secondary metabolites [32]. The constituent composition presented in this paper is in agreement with this statement and is quite similar to that reported by other authors for pine [31,33].

### 2.2. Pyrolysis experiments

The pyrolysis experiments were carried with a practical approach, using a laboratory scale continuous pyrolysis plant that resembles a potential industrial plant. The pyrolysis plant consists of two reactors connected in series: a pyrolysis reactor and a vapors treatment reactor. The schematic drawing of the experimental unit with its main components is shown in Fig. 1. Firstly 500 g of biomass are placed into a 3 dm$^3$ feeding hopper, the hopper is

**Table 1**
Initial sample chemical analysis.

| | |
|---|---|
| **Proximate analysis (wt%)** | |
| Moisture | 10.8 |
| Volatiles | 64.4 |
| Ash | 1.2 |
| Fixed carbon[a] | 23.6 |
| **Elemental analysis (wt% daf basis)** | |
| C | 57.7 |
| H | 7.2 |
| N | 0.3 |
| Others[b] | 34.8 |
| **Constituents analysis (wt% daf basis)** | |
| Extractives | 7 |
| Glucan | 27.2 |
| Xylan | 16.6 |
| Arabinan | 0.2 |
| Lignin | 49 |
| **HHV (MJ kg$^{-1}$)** | 15.7 |

daf: dry ash free basis.
[a] By difference (100-M-VM-A).
[b] By difference (100-C-H-N).

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