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Avoiding tar formation in biocoke production from waste biomass



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ABSTRACT

This paper focuses in avoiding tar formation and in optimizing pyrolysis gas (maximizing H₂ and CO) in the production of biocoke from waste lignocellulosic biomass. In order to obtain metallurgical grade biochar (biocoke) slow heating rate and high temperature are required. Under such conditions useless pyrolysis liquids, mainly composed of water together with some heavy-sticky tars, are obtained. In order to make biocoke a cost-effective process it is necessary to optimize pyrolysis vapors avoiding tar formation and maximizing the amount and quality of both coke and gases. With this objective, in this work different heating rates (3–20 °C min⁻¹) and catalysts (zeolite, Ni/CeO₂–Al₂O₃) have been tested in a two step pyrolysis process. Olive tree cuttings have been pyrolyzed in a 3.5 L batch reactor at 750 °C and the vapors generated have been thermally and catalytically treated at 900 °C in a second tubular reactor. About 25 wt.% biocoke useful as reducing agent in certain metallurgical processes, ≈57 wt.% gases with near 50 vol.% H₂, and no tar production has been achieved when a heating rate of 3 °C min⁻¹ and the homemade Ni/CeO₂–Al₂O₃ catalyst were used.

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1. Introduction

The metallurgical industry is a great consumer of energy. It mainly uses fossil fuels (coal or crude oil) for the production of both energy and the reducing agent (coke) that is necessary for the metallurgical process. It has been estimated that this industry is responsible for about 7.8% of the carbon dioxide (CO₂) of worldwide emissions [1]. The production of coke from biomass (charcoal or biochar) would significantly contribute to the reduction of CO₂ net emissions.

Biomass energy is an alternative energy produced from renewable resources. Valuable products such as biochar and bio-oil can be obtained by pyrolysis/carbonization of biomass

sources. Biochar and bio-oil products are usually used as alternative fuels to fossil-based fuels, however, biochar can also be utilized as carbon source for producing different carbon materials, and bio-oil can be used as chemical feedstock for valuable chemicals.

Most of the published works about biomass pyrolysis focus on bio-oils and therefore have been carried out at moderate temperatures and with high heating rates (fast pyrolysis) [e.g. [2–4]]. On the contrary, there are fewer publications focused on biochar and most of them pay limited attention to bio-oils and gases.

Recent studies about pyrolysis of biomass have demonstrated that obtaining a metallurgical grade biochar from biomass is not easy. The characteristics of the biochar and the

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liquids and gases obtained by pyrolysis depend very much on the operating conditions used. Fast pyrolysis and moderate temperatures maximize the yield of liquids [5], but produce a poor quality biochar, while slow heating rates and high temperatures promote the quantity and quality of biochar [6].

The objective of this work was to obtain a metallurgical grade biochar from waste biomass and at the same time optimize the pyrolysis gas quality (maximizing H₂ and CO), so that the pyrolysis gas can be used for the production of energy or H₂, or as a reducing agent.

In a previous work carried out by the authors [7] two step pyrolysis experiments were carried out: a first 750 °C pyrolysis step followed by a second thermal and catalytic pyrolysis vapors upgrading step, which was carried out at different temperatures (from 600 to 900 °C). The best results were obtained when 900 °C and Ni/CeO₂–Al₂O₃ catalyst were used in the second reactor. A 46 wt.% reduction of tars, a 53 vol.% increase of H₂ and a 30 vol.% reduction of CO₂ compared to those obtained in one step pyrolysis, was achieved. Therefore, the present study was carried out using 750 °C in the first reactor and 900 °C in the second one.

Even though the previous work showed that the results were very much enhanced by the second catalytic step, a significant amount of tars was still produced. Therefore, the objective of the present work was to eliminate completely or to avoid the formation of tars. With this aim the effect of two decisive parameters (heating rate and catalysts) was investigated.

The heating rate of the first pyrolysis step was varied between 20 °C min⁻¹ (maximum heating rate achievable with the pyrolysis installation used) and 3 °C min⁻¹; lower heating rates were not investigated since it implied excessively long-lasting experiments.

The effect of two catalysts, commercial HZSM5 zeolite and a homemade ceria modified alumina supported catalyst (Ni/CeO₂–Al₂O₃) was explored. The catalysts were placed in the second reactor for upgrading the vapors generated in the first pyrolysis reactor.

2. Materials and methods

2.1. Materials

Olive tree cuttings from Extremadura (Spain) was the biomass used for this study. Extremadura has 271,050 ha of olive groves, a 10.5% of the total olive surface of Spain [8]. One hectare of olive grove generates three tons of pruning residues [9], which means that only in Extremadura 813,150 tons/year of branches and leaves are generated, most of which are left on the ground or illegally burnt giving rise to greenhouse gases.

The biomass used for the pyrolysis experiments was ground in a RESTCH SM 2000 cutting mill with a 10 mm sieve. 100 g of this biomass were placed into the reactor in each experiment. A small amount of such biomass was further ground to a particle size <2 mm in order to obtain an homogeneous sample which could be analyzed and characterized following the procedures indicated in Section 2.4. The biomass characterization results are presented in Table 1. It can be seen that the moisture content of the olive tree cuttings sample is about 9 wt.%, the ash content is quite low (2.1 wt.%), and the “others” content, which is mainly the oxygen that forms part of the chemical molecular structure of the plant (cellulose + lignin), is very high (45.4 wt.%). As a matter of fact, taking as reference cellulose chemical formula (C₆H₁₀O₅) oxygen should be near 50 wt.% which is quite similar to the oxygen content determined in the elemental analysis in this work.

2.2. Experimental procedure

The experiments carried out in this study, were performed using two reactors connected in series and a vapors condensation and gas–liquid separation unit. The flow sheet of the experimental setup used in the experiments is presented in Fig. 1.

The first reactor is a 3.5 L non-stirred batch reactor where pyrolysis of 100 g of biomass takes place. During the experiments, the reactor was heated at the desired heating rate to 750 °C and maintained there for 30 min. The thermocouple which measures and controls the process is placed in the middle of the pyrolysis reactor chamber. This implies that although the reactor is an unstirred one and biomass has a low thermal conductivity, it is guaranteed that the whole biomass sample reaches at least the preset temperature.

The second reactor is a vertical tubular one, where the pyrolysis vapors are treated at 900 °C either with or without catalyst. This reactor is a 309 stainless steel tube, 1 inch in diameter and 50 cm long. The tubular reactor is loaded at the bottom with a charcoal bed, followed by the catalyst monolith. The charcoal bed is used in order to resemble a continuous process in which the pyrolysis vapors would be in contact with the pyrolysis solid (charcoal) which would be being produced continuously. The authors have evaluated the effect of the char bed itself in preliminary experimental tests, and have observed that fewer liquids and more gases are yielded, and more hydrogen is produced with than without charcoal. However, such results should not only be attributed to the effect of the char, but also to the fact that when no char is used, the vapors flow more quickly through the empty reactor and so remain less time at high temperature, and in contact

Table 1 – Proximate analysis as received (ar) basis (wt.%), elemental analysis dry and ash free (daf) basis (wt.%) and higher heating value as received basis (HHV) (MJ kg⁻¹) of the biomass sample pyrolyzed.

Proximate analysis (ar basis)				Elemental analysis (daf basis)					H/C atomic ratio	(ar basis)
Moisture	Volatiles	Ash	Fixed carbon	C	H	N	S	Others ^a		HHV
8.8	74.3	2.1	14.8	49.4	6.2	0.3	<1	43.1	1.5	16.1

^a By difference.

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