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Influence of nickel during the thermal degradation of pine cone shell. Study of the environmental implications

A.I. Almendros, M. Calero*, A. Ronda, M.A. Martín-Lara, G. Blázquez

Department of Chemical Engineering, University of Granada, 18071 Granada Spain

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Thermal valorization of heavy metal impregnated biomass has grown up as a researching field during the last few years; however the use of these contaminated wastes as fuel still presents several economic and technical drawbacks. Specially, insertion of nickel metal into the biomass during an impregnation stage with aqueous solutions of nickel salts, promotes wide dispersion of the precursor inside the lignocellulosic matrix and impacts on good results with respect to the reduction of tars. Therefore, the catalytic effect of the nickel during the thermal decomposition of an impregnated pine cone shell is investigated in this work. The effects of the heating rate and the atmosphere on the thermal decomposition of the natural solid show that an increase in heating rate produces a shifting of the curves at higher temperatures without significant change of its shape. Three distinct stages of mass loss are presented during degradation process for the different reaction atmospheres; however, the temperature ranges in which the stages are performed are different. Moreover, an increase in the thermal stability of nickel-loaded pine cone shell in the early stages is observed. The results obtained by mean method of Coasts-Redfern show that the function that could represent the thermal degradation mechanism associated with the major step of degradation of the pine cone shell is the reaction of nth order, being the third, fourth or fifth order the most regular order. About the environmental implications, the residual waste is lower for nickel-loaded biomass. Moreover, the nickel remains mainly in the ashes, therefore, the nickel content in these ashes may be recovered, or ashes distribute to any subsequent application.

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1. Introduction

In the last decades, with the concern of the energy community, agricultural and forestry wastes had started being considered as valuable feedstock for energy transformation. Nowadays, the conversion of agricultural by-products and wood into bio-fuels is largely concerned in many countries (Li et al., 2016). This is an important subject not only from a waste treatment perspective but also from the recovery aspect of energy. The need for sustainability, energy security and the need to address global warming will limit the use of fossil fuels for power generation in the future. Alternative (renewable) energy technologies have emerged and are currently under investigation. Among these, biomass has a large potential to contribute towards this future renewable energy resources and extensive research is underway for converting it into energy and chemicals (Almendros et al., 2015).

One application for these agroindustrial wastes is for adsorption process, but once the adsorbent is exhausted, a metal loaded solid without any value is generated as waste (Mata et al., 2010). Although desorption and reutilization of the material in adsorption–desorption cycles could help in reducing these residues, any alternative is studied for the final exhausted waste. In this point, a detailed study about the influence of the metal during thermal processes will let us to use these metal-loaded wastes to produce energy. Thus, thermal processes could be applied as an alternative for the final disposal of the exhausted adsorbent.

The pine cone shell is produced in great quantities in the Mediterranean area, and it has no market value. Only Andalusia has a surface of stone pine cultivated, around 200,000 ha, which leads a pine cone production nearly to 55,200 tons (Almendros et al., 2015).

The main use of the pine cone production is picking the pine nuts (a fruit with a high economic value), however, the pine cone

* Corresponding author.
E-mail addresses: anaalmendrosm@correo.ugr.es (A.I. Almendros), mcaleroh@ugr.es (M. Calero), alirg@ugr.es (A. Ronda), marianml@ugr.es (M.A. Martín-Lara), gblazque@ugr.es (G. Blázquez).

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shell remains available as a waste product without any important industrial application. Its use is limited to domestic oven for heating systems or as adsorbent to remove heavy metals (Hansen et al., 2010; Ofomaja and Naidoo, 2011; Blázquez et al., 2012). However, the amount destined to this application is low and it is normally incinerated or dumped to the field without control. Therefore, the study of other alternative uses, also taking into account a possible metal-loaded material and their derived environmental concerns are extremely important.

Although several researchers have studied pyrolysis of pine cone shell (Font et al., 2009), there are not studies about the effects of metal on the mechanism of thermal decomposition of pine cone shell in an inert environment. Thus, it is necessary to study the behavior of components of biomass when it is metal loaded and to compare with that of the raw materials because interaction between metal and waste could be appear.

Mu et al., 2015 studied the interaction between biomass wastes and paper sludge and they observed that materials presented a synergistic effect on the thermal decomposition (Mu et al., 2015). Therefore, it is essential to investigate the pyrolysis behaviors and the interactions between pine cone shell and metal in a previous step by TGA.

From the studies of other authors, some conclusions were obtained for the behavior of biomass during the pyrolysis tests. In general, an increase in heating rate results in a shifting of the curves at higher temperatures without significant change of its shape. These results were obtained by Celebi and Karatepe (2015) in their study of the thermal decomposition of hazelnut shell or Lai et al. (2012) in their study of the thermal decomposition of municipal solid waste under atmospheres of N_2, CO_2 and CO_2/N_2.

Moreover, in an inert atmosphere, the decomposition of the biomass can be divided in four stages: (1) the first stage is between approximately 50 and 175 °C, corresponds to moisture loss, and volatile compounds; (2) the second stage between 200 and 300 °C, due to the less stable constituents of the biomass; (3) the third stage between 300 and 400 °C, attributes to the degradation of cellulose and (4) the fourth step in temperature range from 400 to 800 °C, corresponds to the conversion of lignin. Similar ranges associated with these thermal degradation temperatures have been found by several researchers on thermogravimetric analysis of different lignocellulosic wastes, as Caballero et al. (1997) for the olive stone; Xiaoli et al. (2013) for the poplar wood sawdust; Celebi and Karatepe (2015) for the hallzenut shells or Gómez et al. (2016) for some relevant biomasses in the Mediterranean basin. In oxidizing atmospheres a new stage of combustion is clearly differentiated as obtained Yurdakul and Atimtay (2009) during the investigation of combustion kinetics of wood samples and Fang et al. (2013) when obtained a weighted average global process model based on two stage kinetic scheme for biomass combustion. Changes in the distribution of products obtained in thermal degradation of diverse materials due to the presence of various elements already have been discussed by many authors in previous studies (Jun et al., 2006; Fu et al., 2008; Nowakowski and Jones, 2008; Lu et al., 2009; Patwardhan et al., 2010). That is, the samples treated with metals decompose faster at lower temperature, suggesting the hypothesis that the metals catalyze the degradation of hemicellulose and cellulose (Jakab et al., 1997; Blasi et al., 2007; Bru et al., 2007; Nowakowski and Jones, 2008). Finally, the application of the model of first or nth order reaction was supported by several authors (Damartzis et al., 2011; Slopiecka et al., 2012; Ceylan and Topçu, 2014; Baroni et al., 2016).

This work analyses the possibility of utilization of Ni-loaded pine cone shell as a source of renewable energy comparing its characteristics as those of raw biomass. Concretely, in the first step, a Ni-loaded PCS (Ni-PCS) was obtained after a previous contact step with a Ni(II) solution. Then, experiments were carried out for the raw and Ni-PCS samples at three heating rates and in three different atmospheres in a thermobalance. Afterward, experimental data were fitted to different methods to evaluate the kinetic parameters and results were compared between raw and Ni-loaded PCS. Finally, environmental implications of the use of Ni-PCS for energy purposes were analyzed to close the work. This study would be helpful in effective design and operation of thermochemical conversion units fed by raw or metal loaded pine cone shell.

2. Experimental section

2.1. Material

The pine cone shell (PCS) was provided by the company Carsan Biofuels SL, located in Padul, Granada. PCS was ground and sieved, using the fraction with a particle size less than 1.00 mm. The main physicochemical characteristics of PCS were determined and published in a previous work (Almendros et al., 2015).

The Ni-loaded PCS (Ni-PCS) was obtained after a previous contact step with a Ni(II) solution. Raw PCS was soaked in a solution with an initial concentration of Ni(II) of 200 mg/L until its exhaustion. Then the PCS was separated and dried in an oven at 40 °C during 24 h. The content of Ni(II) was determined by an Atomic Absorption Spectrometry Instrument (AAnalyst 200, Perkin-Elmer).

2.2. Experimental procedure

Thermogravimetric experiments were performed using a thermal decomposition thermobalance (Perkin-Elmer model 6000 STA).

Eighteen experiments were carried out for the raw and Ni-PCS at three heating rates (5, 10 and 20 °C/min) and in three different reaction atmospheres (N_2, N_2:O_2 9:1 (10% O_2) and N_2:O_2 4:1 (20% O_2)). The weight of the used sample was approximately 40 mg, the total gas flow was 20 mL/min and the temperature range from 30 to 800 °C. Experiments were performed in duplicate to test the reliability of the data.

Ashes and major elements were analyzed by ICP (Inductively Coupled Plasma Spectrophotometer) with a previous acid digestion of the sample according to standard UNE-EN 13656.

2.3. Kinetic evaluation by using model-free methods and Coast-Redfern

Model-free methods allow the evaluation of the kinetic parameters of thermal decomposition without the need to select a particular type of reaction (Biagini et al., 2008). Flynn-Wall-Ozawa (FWO), Kissinguer-Akahira-Sinose (KAS) and Friedman (FR) methods have been selected in this work because they have been applied successfully in other investigations to describe kinetics of thermal decomposition of similar lignocellulosic solid wastes (López et al., 2013; Chen et al., 2015; Arenales-Rivera et al., 2016; Huang et al., 2016). The main equations of these methods are described in Table 1.

From the results and following Coast-Redfern method, the reaction mechanism which governs the degradation process in the different intervals tested will be one for which the activation energy values are closest to the values obtained using the methods of FWO, KAS and FR.

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