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Fast pyrolysis of eucalyptus waste in a conical spouted bed reactor

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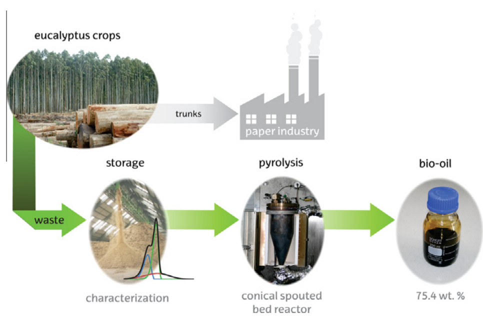
HIGHLIGHTS

- Conical spouted bed reactor is suitable for eucalyptus wastes pyrolysis.
- Higher bio-oil yield (75.4 wt.%) than with other technologies is obtained.
- Water, phenols and ketones content in bio-oil are 35, 26 and 10 wt.%, respectively.
- TG analysis is set as a methodology for determining the composition of the biomass.

GRAPHICAL ABSTRACT



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ABSTRACT

The fast pyrolysis of a forestry sector waste composed of *Eucalyptus globulus* wood, bark and leaves has been studied in a continuous bench-scale conical spouted bed reactor plant at 500 °C. A high bio-oil yield of 75.4 wt.% has been obtained, which is explained by the suitable features of this reactor for biomass fast pyrolysis. Gas and bio-oil compositions have been determined by chromatographic techniques, and the char has also been characterized. The bio-oil has a water content of 35 wt.%, and phenols and ketones are the main organic compounds, with a concentration of 26 and 10 wt.%, respectively. In addition, a kinetic study has been carried out in thermobalance using a model of three independent and parallel reactions that allows quantifying this forestry waste's content of hemicellulose, cellulose and lignin.

1. Introduction

Bio-fuel and bio-based chemical production from non-edible biomass provides an excellent opportunity for reducing the dependence on fossil fuels and mitigating the associated environmental impacts. Over the last decades, biomass conversion technologies have been directed towards the development of the biorefinery concept by means of chemical, biochemical and thermochemical processes for the production of fuels and chemicals (FitzPatrick et al., 2010). Flash pyrolysis for bio-oil production has been regarded as one of the most feasible processes on a large scale as it involves several advantages, such as simplicity and low energy requirements and capital investment (Maity, 2015). Thus, bio-oil can be produced in a delocalized way in rural areas where biomass is available and transported to centralized biorefineries for the production of fuels and chemicals as well as heat and power (Bridgwater, 2012).

Several reactor configurations such as fluidized bed, transport and circulating fluidized bed, rotating cone, ablative, auger, vacuum moving bed and spouted bed reactors have been developed and scaled-up to pilot or demonstration plants for biomass flash pyrolysis (Bridgwater, 2012). However, the industrial implementation of the biomass pyrolysis process needs to solve several challenges, with one of the most important ones being the regular supply of biomass resources that do not compete with food (Ho et al., 2014). Therefore, the use of wastes derived from the existing forest industries as feedstock for the pyrolysis process is essential

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for the development of this technology at large scale (Arbogast et al., 2012), thus reducing the costs associated with the production of a suitable feedstock, which is one of the steps with the highest energy consumption (Sanna, 2014). These waste materials are highly heterogeneous because they are composed of wood, bark, leaves, and so on, and have therefore varying properties. This feature places biomass fast pyrolysis technologies in the situation of having to face the challenge of being sufficiently versatile so as to produce high bio-oil yields with adequate properties, regardless the heterogeneity of the raw material (Carpenter et al., 2014).

Accordingly, the present paper aims at studying the pyrolysis of a waste material composed of branches and leaves coming from the cutting down of eucalyptus trees for the paper manufacturing sector. This waste material accounts for a considerable fraction of the whole tree (around 30–40 wt.%). Furthermore, eucalyptus crops are achieving an increasing importance in the European Mediterranean watershed. This eucalyptus material is highly heterogeneous, which means that its large scale exploitation requires an adequate pyrolysis technology, as well as a simple and reproducible analytical methodology to determine hemicellulose, cellulose and lignin contents. The latter is an essential tool in order to store different waste materials that give way to a regular mixture composition, with the aim of guaranteeing reproducibility in the composition of the pyrolytic products, especially that of bio-oil.

In this work, a methodology previously developed for other biomass materials (Amutio et al., 2013a) has been applied, i.e., a thermogravimetric study allowing the quantification of the chemical components (hemicellulose, cellulose and lignin) in the eucalyptus waste. Furthermore, a conical spouted bed reactor (CSBR) is proposed for the fast pyrolysis of this residual biomass as alternative to fluidized beds, given that it performs well by obtaining high bio-oil yields with several biomass materials, such as pinewood (Amutio et al., 2012) or forest shrub wastes with a heterogeneous composition (Amutio et al., 2013b). Furthermore, it is noteworthy that short volatile residence times are suitable for minimizing the catalytic activity of the ashes (Carpenter et al., 2014), which allows obtaining high bio-oil yields (70 wt.%) for rice husk pyrolysis, even though this material has a high ash content (Alvarez et al., 2014a). In addition, this technology has been scaled up to a 25 kg/h pilot plant, in collaboration with IK4-Ikerlan Research Centre, with its performance being excellent for pine and poplar wood pyrolysis (Fernandez-Akarregi et al., 2013; Makibar et al., 2015).

2. Methods

2.1. Raw material

Eucalyptus globulus waste from the paper industry sector has been used as feedstock for the pyrolysis process. This material is composed of the wastes (wood, bark and leaves) remaining from the cutting down of the eucalyptus trees. The biomass has been collected, dried and ground to a particle size in the 1–2 mm range. The proximate analysis of the raw material (TGA Q500IR thermogravimetric analyzer) reveals that it is made up of 9.5 wt.% of moisture, 87.4 wt.% of volatile matter, 11.4 wt.% of fixed carbon and 1.2 wt.% of ash. Furthermore, the carbon, hydrogen, nitrogen and oxygen contents are 46.5, 5.1, 0.6 and 46.6 wt.%, respectively (LECO CHNS-932 elemental analyzer). Finally, the higher heating value (HHV) has been set at 17.4 MJ kg^{-1} (Parr 1356 isoperibol bomb calorimeter).

2.2. Conical spouted bed pyrolysis plant

The continuous conical spouted bed bench scale plant used in this study is outlined in Fig. 1. This plant has been fine tuned on the basis of previous studies involving the pyrolysis of other biomass residues, such as pinewood (Amutio et al., 2012), forest shrubs (Amutio et al., 2013b) and rice husk (Alvarez et al., 2014a).

Biomass is fed by means of a vessel provided with a vertical shaft connected to a piston, which allows the continuous feeding of up to 200 g h^{-1} of biomass. Nitrogen, whose flow rate is controlled by a mass flow meter, is used as fluidizing agent and it is heated to the reaction temperature by means of a preheater.

The reactor is a conical spouted bed with an upper cylindrical section, with a total height of 34 cm and a cylindrical section diameter of 12.3 cm. The height of the conical section is 20.5 cm, with an angle of 28° and a bottom diameter of 2 cm. The gas inlet diameter is 1 cm. Furthermore, the reactor is equipped with a lateral outlet for the continuous and selective removal of the char from the bed throughout the process, which is possible due to the cyclic movement of the particles in the bed (Amutio et al., 2011).

The volatile products formed in the pyrolysis process together with the nitrogen used for fluidization pass through the gas cleaning system, which consists of a high efficiency cyclone and a sintered steel filter that are maintained at 280 °C in order to avoid the condensation of the heaviest compounds. The vapor residence time within the fine-particle retention system is less than 1 s, thus avoiding the partial cracking of the organic products before their condensation. The condensation of the bio-oil is carried out by means of a double-shell tube condenser cooled by tap water and two coalescence filters, which ensure the recovery of the heavy compounds.

2.3. Product analysis

The pyrolysis volatiles have been analyzed online by means of chromatographic techniques. The reactor outlet stream has been monitored prior to condensation using a gas chromatograph (GC) (Varian 3900) equipped with a flame ionization detector (FID). The line from the reactor outlet to the chromatograph is heated to a temperature of 280 °C in order to avoid the condensation of heavy oxygenated compounds and to ensure that all the volatile products formed during pyrolysis enter the gas chromatograph and are analyzed online. Unlike hydrocarbons, the FID response to oxygenated compounds is not proportional to their mass, and therefore a calibration has been performed. Furthermore, the non-condensable gases leaving the condensation system have been analyzed using a micro-chromatograph (Varian 4900). This micro-GC has also been used to measure the water yield, following a similar procedure to that described for the standard gas chromatograph.

The volatile products have been identified by analyzing the bio-oil recovered in the condenser and filters by means of a GC/MS (Shimadzu UP-2010S) and the gaseous products by means of a micro-GC connected to a mass spectrometer (Agilent 5975B). Furthermore, the char fraction has also been characterized by carrying out its ultimate (LECO CHNS-932) and proximate (TGA Q500IR) analyses, as well as measuring its higher heating value (Par 1356).

2.4. Experimental procedure

The runs in the bench scale plant have been carried out at 500 °C, which has been set as the optimum temperature for maximizing the bio-oil yield in woody biomass pyrolysis (Amutio et al., 2012). 100 g of biomass have been continuously fed in each run with a feeding rate of 2 g min^{-1}. The reactor bed was made up of 100 g of sand with a particle size in the 0.3–0.63 mm range and the nitrogen flow rate has been set up in 10 Nl min^{-1} in order to ensure stable spouting and guarantee high heat transfer rates and bed isothermicity.