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Fast pyrolysis of trunk wood and stump wood from a Brazilian eucalyptus clone

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ABSTRACT

The objective of this study was to compare yields and chemical composition of volatile fraction of bio-oil produced from fast pyrolysis of trunk wood and stump wood of *Eucalyptus urograndis*. Ground material was processed in a fluidized bed pilot plant equipped with a continuous reactor at temperatures of 500–600 °C. Light biooil fraction from each material was collected and vacuum distilled. The oily volatile fraction was characterized by GC/MS. Yield of charcoal was higher for stump wood than for trunk wood and the opposite behavior was observed for the yield of light and heavy bio-oil fractions and of gases. Yields of volatile compounds were statistically equal for trunk and stump wood, both representing about 6% of the initial dry biomass. The results demonstrate the technical viability of having stump wood as a source of volatile oils with chemical composition similar to commercial liquid smoke products.

1. Introduction

After Eucalyptus forests are harvested, the remainingstumps can be serious hindrance by preventing mechanized operations for soil preparation for the next planting, or to grow other crops. The solution to this problem is to remove stumps by using tubular saws or other machines able to rip them out along large roots. These operations are often be expensive and time consuming [\(Casseli, 2013;](#page--1-0) [Foekel, 2014](#page--1-1); [Gomez et al., 2014](#page--1-2)). In order to amortize the cost of stump removal, some kind of end use must be given to them. Thus, uses of that waste as fuel, for extraction of active compounds and for pulping have become economically and technically feasible ([Casseli, 2013;](#page--1-0) [Frazão and Frazão, 2014;](#page--1-3) [Gominho et al., 2015\)](#page--1-4). Despite being laborious, stump removal is attractive because it can increase the yields wood per area by up to 19–20% ([Gomez et al., 2014](#page--1-2)). However, the stumps typically come with roots that retain soil, sand and small rocks.

The presence of these contaminants combined with the irregular shape of stumps and remaining roots make their used as fuel for direct burning or charcoal production difficult. Stumps first have to be converted into chips before being burned in furnaces.

Fast pyrolysis is a technology able to maximize the production of pyrolytic oils from trunk wood and other lignocellulosic raw materials typically yielding up to 75% bio-oil based on initial dry mass of raw material [\(Gómez et al., 2008](#page--1-5)). However, it is true only under certain circumstances (very high heating rates, very short residence time, etc.), that are only achieved with some types of reactors: fluidized, circulating, spouted beds, auger or rotating cone. One of the most advantageous characteristics of fast pyrolysis is the ability to process different raw materials such as agricultural, forestry and even urban wastes. Due to their irregular granulometry, these materials are not appropriate for use in conventional equipment, so they require particle

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standardization [\(Dinesh et al., 2006;](#page--1-6) [Bhaskar et al., 2011](#page--1-7)). Thus, after being reduced to fine particles, large amounts of woody wastes can be suitably converted into bio-oil, which can be used as substitute for liquid fossil fuels or a source of chemicals ([Mullen and Boateng, 2008](#page--1-8); [Zhang et al., 2013\)](#page--1-9). More comprehensive knowledge of what chemical compounds can be recovered from each type of biomass is important to indicate the most appropriate uses. Besides this, as pointed out by [Mullen and Boateng \(2008\)](#page--1-8) and [Kato et al. \(2014\),](#page--1-10) the assessment of chemical composition of bio-oils is of great relevance since it can provide information about their quality, stability and suitability for chemical upgrading. However, despite the production of many chemicals from bio-oils and identification of hundreds of organic molecules in their composition, much is still not known about their complex mixtures ([Alsbou, 2014\)](#page--1-11).

The main hindrance to the exploitation of chemicals from bio-oil is the large distribution of molecular weight associated with a wide variation of polarity, which prevents efficient separation. Since bio-oil still has a relatively high cost with current technologies, efforts must be carried out to improve its quality and increase the range of products ([Ali et al., 2016](#page--1-12)). Catalytic pyrolysis processes are a promising route to convert lignocellulosic raw material into fuels and chemicals. Such strategies, whose major objective is to obtain byproducts of low oxygen content, are compatible with the petrochemical structure, especially in larger facilities ([Xiu and Shahbahzi, 2013;](#page--1-13) [Dickerson and Soria, 2013](#page--1-14); [Lëhto et al., 2013](#page--1-15); [Radlein and Quignard, 2013\)](#page--1-16). Another interesting approach, demonstrated by [Zhang et al. \(2013\)](#page--1-9), is atmospheric pressure distillation of bio-oil coupled with co-pyrolysis with the goal of maximizing the recovery of chemicals such as acetic acid, propanoic acid and furfural in yields higher than 80%.

The use as bio-oil as energy source is also promising ([Choi et al., 2014](#page--1-17); [Sukumar et al., 2015;](#page--1-18) [Hou et al., 2016\)](#page--1-19), but if more value could be added to derivative chemical compounds, a new option would be available to increase the economic profitability of fast pyrolysis by opening new markets for its byproducts. Thus, the simpler the fractionation processes is, the lower the cost of obtaining the chemical products derived from bio-oil will be. Bearing that in mind, we describe a simple fractionation method to obtain volatile chemicals from bio-oil. The main goal of the process developed was to separate chemicals from bio-oil and leave behind a liquid fraction than can be used as fuel. Our more specific goals were: (1) to assess and compare the yields and chemical composition of byproducts from fast pyrolysis of trunk wood and stump wood of a hybrid eucalyptus clone (*Eucalyptus urophylla* x *Eucalyptus grandis*); (2) to obtain high volatile fraction yields by submitting trunk and stump wood bio-oils to vacuum distillation; and (3) to evaluate the efficiency of a method using three kinds of solvent extraction to isolate the volatile fraction of bio-oil prior to GC/MS analysis for identification.

2. Materials and methods

2.1. Biomass collection and preparation

The trunk and stump wood was collected during forest harvesting in a stand of Eucalyptus composed of hybrids of *Eucalyptus urophylla* x *Eucalyptus grandis* collected in forest areas (7-years age) belonging to Duratex. Logs and stumps were collected at random in sufficient amounts to compose two samples having wet weight of 1.5 metric tons of each sample. The stumps were pulled from soil using a tractor equipped with a steel fork adapted for the operation. After collection, logs were promptly debarked in a ring debarker and stumps with their roots were washed to remove remaining soil and sand. Next, both materials were separately ground in an industrial mill (Nogueira model

DPM-4, São João da Boa Vista, SP, Brazil) with capacity to process from 90 to 100 kg/h, using a 1.5 mm classification sieve. After this, the pulverized biomass samples were respectively dried until reach 0% moisture content in a continuous tumbler dryer (Lippel, Agrolândia, SC, Brazil) with evaporation capacity of 35 tons of water/h.

For stump wood and trunk wood characterization, total carbohydrates (holocellulose) and lignin were determined by following the standard procedures preconized by [NREL \(National Renewable Energy](#page--1-20) [Laboratory\)](#page--1-20). Extractives and ash contents were determined following the procedures preconized by [TAPPI \(Technical Association of the Pulp](#page--1-21) [and Paper Industry – Standards T204 and T211\).](#page--1-21) Biomasses densities (prior grinding) were determined by following the procedures described by the [ASTM Standard D2395-17.](#page--1-22)

2.2. Fast pyrolysis

Both biomasses were processed in a fast pyrolysis pilot plant system (Bioware model SDB200, Campinas, SP, Brazil). Bioware system consists in a fluidized be plant equipped with a continuous reactor. The system can process 0.5–3 tons of biomass per hour. Further details and technical information on the fast pyrolysis system as well, the properties and quality of byproducts obtained with several types of biomass are available in the works of [Alonso-Pippo et al. \(2004\)](#page--1-23) and [Gómez](#page--1-5) [et al. \(2008\)](#page--1-5). [Fig. 1](#page--1-24) shows the diagram of the pyrolysis system, consisting of the following components: (1) lung bin, (2) feeder screw, (2a) biomass intake valve, (3) fluidized bed reactor, (4) centrifugal fan, (5) collector cyclone, (5a) charcoal sampler valve, (6) expander, (6a) water cooled heat exchanger, (7) centrifuge, (8) combustion chamber, and (8a) chimney.

The fast pyrolysis was performed using 0.5 ton of each dried biomass in triplicate, to obtain yields of charcoal, light and heavy bio-oils. The pyrolysis reactor consists of a fluidized bed (3) with its internal walls protected with refractory concrete and ceramic fiber plates to prevent heat losses. Before pyrolysis, the reactor ignition is achieved by hot air blown by the centrifugal fan for heating the sand. The air is heated with the burning of charcoal fines, a process that continues until the bed reaches 550–600 °C. In these conditions and as soon as the mass flow of air reaches the ideal value, the biomass feed is started by the screw (2) and the intake valve (2a) in amounts able to keep internal temperature stabilized in the range of 450–480 °C. Hot air admission is kept until the reactor can achieve an autothermal regime. After leaving the reaction bed, charcoal and vapors were separated in the collector cyclone (5). Vapor and gases were driven off through an expander (6) and then cooled in the water-cooled heat exchanger (6a). The cooling water was circulated to the cooling tower to maintain the proper temperature. Vapor not separated inside the heat exchanger was aspirated by the centrifuge and recirculated until complete liquefaction. Non-condensable gases are burned inside the combustion chamber (8) and the chimney (8a) releases hot gaseous products. The pyrolysis system as designed to permit the recovery of liquid products in sequential fractions. This way, the bio-oil was separated into two fractions, here called light and heavy bio-oils. The light bio-oil was recovered when temperature of the cyclone was in the range of 50–70 °C (collected at the top of condenser) and the heavy bio-oil in the range of 70–90 °C (collected at the bottom of the condenser).

[Table 1](#page--1-25) reports operating parameters of the fast pyrolysis system using eucalyptus trunk and stump wood as raw materials.

The following properties of light and heavy bio-oils were determined: density (digital density meter model DDM 2910, Rudolph Research, according [ASTM D 4052/1988\)](#page--1-26), viscosity (Automatic viscometer model MiniQV-X, Cannon Instruments, according [ASTM D 445/](#page--1-27) Download English Version:

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