



Evaluation of Brazilian biomasses as feedstocks for fuel production via fast pyrolysis[☆]



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ABSTRACT

Two Brazilian biomass samples, namely sugarcane trash and *Eucalyptus benthamii* were evaluated as feedstocks for liquid and solid fuels production by fast pyrolysis, using a fluidized bed reactor and two different sets of process conditions. In the first, an inert gas (N₂) was used as a fluidizing agent while in the second, a mixture of N₂ and recycled pyrolysis effluent gas, mainly CO, CO₂, H₂ and light hydrocarbons, was used as the fluidizing agent and to also create a reducing reaction atmosphere for the process. Comparing both processes, the reducing atmosphere had a significant deoxygenation effect on the pyrolysis oil from the two feedstocks, improving the quality and stability of the oils by reducing water, total acid number (TAN), viscosity, and increasing the higher heating value (HHV). For both feedstocks, reduced amounts of acetic acid, acetol and levoglucosan, and increased amounts of aromatic hydrocarbons not initially present in the traditional bio-oil were observed for the organic fraction of the bio-oil. However, there was a reduction of 13.5 wt% (db) in the bio-oil yield from *E. benthamii* when a reactive atmosphere was used. Comparing both feedstocks, the eucalyptus yielded on the average, 50% more bio-oil than the sugarcane trash while the trash yielded 50% more permanent gas. Apart from the high ash content associated with biochar from sugarcane trash, biochar produced from both feedstock samples had similarities with bituminous coal in terms of moisture content, fixed carbon content, and heating values.

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Introduction

The production of renewable-based energy has increased around the world. Both developed and developing countries have demonstrated concerns for the environmental and economic impacts of petroleum-based fuels. In Brazil, renewable fuels are responsible for about 44.1% of the total energy resource (BRASIL, 2012). In addition to the familiar ethanol and biodiesel products, newer fuels are being developed by advanced thermochemical conversion technologies. Processes such as pyrolysis and gasification are well known for producing fuels and valuable coproducts from a wide variety of feedstocks, including wastes, but they have not had the same presence as biochemical technologies. Responding to this call, Embrapa Agroenergy and USDA's Agricultural Research Service (ARS) entered into a collaborative agreement to explore technologies related to fuels production from Brazilian biomass via pyrolysis.

Brazil is not deficient of biomass feedstocks or their supply that can be harvested in quantities that are suitable for medium to large scale fast pyrolysis systems. Depending on the region of the country, feedstocks comprising wood, fruit and seed residues, oilseed press cakes, and many others can be abundant in the supply chain. Eucalyptus and sugarcane residues (bagasse and trash) are considered two of the most important feedstock pools for energy production in the country.

Sugarcane production in Brazil jumped from 50 million metric tons in 1970 (Moreira and Goldemberg, 1999) to 589 million in the 2012/2013 season, covering 8.5 million hectares of land spread in 23 of the 26 states (BRASIL, 2013). Sugarcane trash, as they call it in Brazil, is a mixture of dry leaves, green leaves and tops of the stalks left in the field after mechanical harvesting. For each ton of harvested sugarcane stalk, 14 wt% (dry basis) is considered trash (Hassuani et al., 2005).

There are more than 700 different species of eucalyptus. According to the Brazilian Association of Forest Plantation Producers (ABRAF, 2012) the total area planted with Eucalyptus in Brazil was 4.9 million ha in 2011. The main eucalyptus species cultivated in Brazil are Grandis, Saligna, Urophylla and Urograndis. According to Embrapa Forestry, Benthamii has been explored as the potential species to be used as an energy source in the South region of Brazil, especially in areas with potential for severe frosts.

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Pyrolysis, the thermal decomposition of organic materials in the absence of oxygen, produces three types of fuel streams: liquid (pyrolysis oil, bio-oil), solid (biochar) and producer gas (non-condensable pyrolysis gases). Depending on the characteristics, the liquid fuel can burn directly in boilers or blend with other fuels like ethanol, diesel or biodiesel. It can also be upgraded to the so-called “drop-in” fuels (gasoline, diesel and aviation fuel) or to high-value products like chemicals. Biochar can be used as a solid fuel, for soil amendment and carbon sequestration, manufacture of electrodes for electric arc furnaces and can also be used as activated carbon in industrial process (Meier et al., 2013).

The high oxygen content present in traditional pyrolysis oil is responsible for three main issues: instability during storage, lower heating value when compared to fossil fuels, and high acidity. In order to solve these problems, numerous studies have focused on deoxygenation of pyrolysis oils. Catalytic pyrolysis, a process that employs an oxygen-rejecting catalyst such as zeolites in the fluidized bed medium is a common technique to promote the deoxygenation of bio-oil. Despite their high deoxygenation efficiency, zeolite catalysts deactivate easily due to coke deposition. For this reason, the pyrolysis reactor must have a much more complex system that allows for continuous regeneration of such catalysts. As an alternative to zeolites, our research group has been working on the partial recycling of pyrolysis tail gases to promote the production of bio-oils with a comparable quality and stability to that produced by the aid of catalysts (Mullen et al., 2013a, b).

In this work we compared two feedstocks of Brazilian origin, sugarcane trash and *E. benthamii*, as potential feedstocks for liquid and solid fuels production by fast pyrolysis. *E. benthamii* was selected after a comparative study, that included proximate and elemental analysis, with three other species available i.e., *E. urograndis*, *E. grandis* and *E. urophylla*. Also compared were the deoxygenation effect and quality of the products from the recycled process.

Material and Methods

Biomass

Debarked eucalyptus trunks from *Benthamii*, *Urophylla*, *Grandis*, and *Urograndis* species were provided by Embrapa Forestry. The 5-year-old trees from *E. grandis*, *E. urophylla* and *E. urograndis* were harvested in February, 2012 in the city of Ponta Porã, Mato Grosso do Sul State, of the center-western region of Brazil. The 6-year-old trees from *E. Benthamii* were harvested in July, 2012 in the city of Candoi, Paraná State, southern Brazil. Sugarcane trash samples were from *Saccharum* variety IAC 873396 (4th ratoon) and was provided by the Jalles Machado Company, located in the city of Goianésia, Goiás State, also of the center-western region of Brazil. Sugarcane trash samples were manually collected from the field in October 2012. All biomass samples were ground in a Wiley mill (Macro Star FT-60 Fortinox) and sifted through a 2-mm screen (#10 US Mesh), located at Embrapa Agroenergy laboratory in Brasília, Brazil.

Proximate analysis (moisture, volatile matter and ash content) was carried out according to ASTM Methods E 871, E 872 (ASTM E871, 1998; ASTM E872, 1998) and D 1102 (ASTM, 2011), respectively. Elemental analysis (C, H, N and S content) was performed using a Thermo EA1112 CHNS/O analyzer by complete combustion of the material followed by GC quantification of the combustion products. Oxygen was determined by difference after accounting for the primary combustible elements, water and ash (Mullen and Boateng, 2011). Calorific values were determined using a Leco AC600 bomb calorimeter.

The ashes of each biomass sample were digested in hydrochloric acid to extract the inorganic elements that were quantified using a Thermo iCAP 6000 ICP spectrometer. Four point calibration lines were produced for each element analyzed for using solutions made from serial dilutions of 1000 ppm standards purchased from Inorganic Ventures, Inc. Thermogravimetric analysis (TGA) of biomasses was performed

using a TA Instruments' Q500 Thermogravimetric Analyzer according to Biagini et al. (2006). First, the samples were subjected to an isothermal condition (105 °C) for 10 min to remove the moisture; next a ramp of 20 °C/min was applied until a 900 °C was reached.

For initial thermochemical analysis of the samples with respect to their pyrolysis behavior, py-GC/MS was employed as a first step to advise larger or pilot-scale experimental design. Micro scale pyrolysis was first performed on all samples using a Frontier Lab Double-Shot micro pyrolyzer PY-2020iD equipped with an Auto-Shot Sampler AS-1020E coupled to a gas chromatograph, Shimadzu GC-2010. The column used was a DB-1701, 60 m × 0.25 mm, 0.25 µm film thickness. The oven temperature was programmed to hold at 45 °C for 4 min, ramp at 3 °C/min to 280 °C and hold at 280 °C for 20 min. The injector temperature was 250 °C, and the injector split ratio set to 90:1. The flow rate of the He carrier gas was 1 mL/min. Pyrolysis products were determined by comparison of experimental mass spectrum to NIST database using a Shimadzu GCMS-QP2010S mass spectrometer (MS). The most relevant compounds were quantified using authentic compounds as standards to produce calibration curves (Mihalczik et al., 2011).

Pilot-scale fast pyrolysis experiments

Pilot-scale fast pyrolysis experiments were conducted in duplicate using a fluidized bed pyrolysis process development unit (PDU) located at USDA's Eastern Regional Research Center (ERRC). The system has been well described by Boateng et al. (2007) and Boateng et al. (2010). The unit comprises a fluidized-bed reactor, biomass feeding and injection system, cyclone with biochar collector, four condensers in series, two electrostatic precipitators (ESP) in series, a Micro gas chromatograph (GC), and instrumentation for data acquisition and control. The reactor bed consisted of a 7.6 cm diameter pipe and was filled to a depth of 20 cm with sand, fluidizing medium.

Two sets of experiments were performed. In the first one, pyrolysis was conducted under an inert N₂ atmosphere (traditional process approach). Another set of experiments was conducted using the ARS patent pending technology (Mullen et al., 2013a, b) where a predetermined quantity of the tail gas effluent is recycled for use as a fluidizing gas thereby creating a reactive environment for the pyrolysis of biomass. For the latter, the reactor was modified for operation on what is termed a recycle mode. For this a regenerative blower was connected to the ESP outlet to allow ESP tail gases to return to the fluidized bed upon reheating through an electric heater. A gas outlet valve in the blower inlet line was remotely controlled to maintain a constant system volume by discharging the preheated returned gases. A pressure transmitter in the blower inlet line is integrated with the Siemens PCS7 system to modulate the gas outlet valve. The flow provided for the system guarantee the fluidization in the sand bed. A small amount of nitrogen (<0.5 L/min) is required to flow into the feed drop tube to maintain a positive pressure throughout the system as well as to aid in feedstock flow.

For both sets of experiments, the non-condensable gas (NCG) composition was measured online using an Agilent 3000 MicroGC. Pyrolysis product yield distribution was determined gravimetrically and then corrected to account for unrecovered products using a non-linear optimization protocol (Boateng et al., 2012).

Pyrolysis products characterization

Elemental and proximate analyzes, and calorific values were conducted using the same procedure mentioned above. The water content for all bio-oil fractions (ESPs and condensers) was measured using Karl Fischer titration in methanol with Hydranal Karl Fischer Composite 5 (Fluka) as titrant. Total acid number (TAN) was measured using a Mettler T70 automatic titrator using 0.1 M KOH in isopropanol as a titrant and wet ethanol as the titration solvent. Quantification of pyrolysis

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