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Pyrolysis of mangaba seed: Production and characterization of bio-oil

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HIGHLIGHTS

- Use mangaba seed to transformation in bio-oil by pyrolysis process.
- Study of the variables process of pyrolysis for the mangaba seed: temperature, sample mass and prior heating.
- Characterization of the mangaba seed used as biomass in pyrolysis process.
- The bio-oil of mangaba seed showed the presence of hydrocarbons, acids and phenols.

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ABSTRACT

The aim of this study was to evaluate the potential of *Hancornia speciosa* GOMES (mangaba) seeds as a novel matrix for the production of bio-oil. The study was divided into three steps: (i) characterization of the biomass (through elemental analysis (CHN), infrared spectroscopy (FTIR-ATR), thermogravimetry (TG), and determination of biomass composition; (ii) pyrolysis of mangaba seed to obtain the bio-oil; and (iii) characterization of the bio-oil (thermogravimetry and gas chromatography/mass spectrometry-GC/qMS). The TG of the sample showed a mass loss of around 90% in 450 °C. In the pyrolysis experiments the variables included temperature (450 and 600 °C), sample mass (5 and 11 g) and prior heating (with or without), with the best conditions of 600 °C, 11 g of seeds and prior heating of the furnace. The GC/qMS analysis identified carboxylic acids and hydrocarbons as the major components, besides the presence of other compounds such as furanes, phenols, nitriles, aldehydes, ketones, and amides.

1. Introduction

The agro-industry generates a large quantity the residues, which may be employed in the energy generation, mainly as fuels of second generation, and as raw material in chemical industry. In general, the biomass is based on lignocelluloses or triglycerides. Lignocellulosic is mainly comprised of cellulose (40–80% w/w), hemicelluloses (15–30 wt%) and lignin (10–25 wt%) and a small quantity of extractives and oil (Huber et al., 2006) while triglyceride biomass has a high content of oil.

According to the biomass used, a mixture of different compounds will be obtained in the thermochemical conversion process, namely pyrolysis, which is applied to chemical transformation (Ucar and Ozkan, 2008). According to Zilnik and Jazbinnsek (2012), this process occurs in the absence of oxygen and the presence of an inert gas (helium or nitrogen), and it generated gaseous (carbon monoxide, carbon dioxide and light hydrocarbons), solid (biochar) and liquid (bio-oil). Pyrolysis reduces the environmental impact due to the low emission of gases and the reuse of agricultural and industry residues (Kim et al., 2013).

Seed cake (obtained from the extraction of vegetal oil), seeds, sewage sludge and algae have been used as oil-rich biomass material for the pyrolysis process. Seeds are a suitable raw material for bio-oil production due to the good liquid yield and optimum pyrolysis temperatures between 400 and 600 °C. The advances in pyrolysis of oil-rich seed are described in works to optimize the pyrolysis process, to produce high energy density liquid fuel and, which can be further upgraded into alternative fuels for use of

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catalyst to up-grading of the bio oil or recycle of the bio oil to broken compounds acids and hydrocarbons in light compounds (Katagi et al., 2011; Biradar et al., 2014). The high oil content promotes the presence of carboxylic acids, alkanes and alkenes in addition to compounds resulting from lignin, cellulose and hemicellulose degradation. In this case highlight the use of cherry seed (Duman et al., 2011), pomegranate seed (Uçar and Karagoz, 2009), tamarind seed (Kader et al., 2013), sal seed (Singh et al., 2014). However, the literature did not report the use of mangaba seed in thermochemical process to obtain bio-oil.

Although Brazil is the country with the third largest production of fresh and processed fruits and the largest production of tropical fruits worldwide, studies on the reuse of these residues are scarce. Mangaba (*Hancornia speciosa* Gomes) seed is a residue of the food industry, which is generally disposed of in the soil, as urban waste or incorporated into animal feed. The mangaba seed correspond the 12% of the fruit and it cannot be used as a food product.

For this reason, the aim of this work was to characterize the mangaba seed through elemental analysis (CHN), infrared spectroscopy (FTIR-ATR), thermogravimetry (TG), and determination of ash, protein, oil, fiber, cellulose, hemicellulose and lignin contents. In addition, the bio-oil produced was characterized by thermogravimetry analysis, and gas chromatography with quadrupole mass spectrometry (GC/qMS).

2. Methods

2.1. Materials and sample preparation

The mangaba seed used in this study is a residue obtained from a pulp production plant. This sample was provided by the company Pomar, Aracaju-Sergipe, Brazil. The seeds were manually separated from other components, which could interfere in the sample analysis. After drying for 17 h at 60 °C, the residue was crushed and stored under nitrogen in a glass bottle covered with aluminum.

2.2. Biomass analysis

The moisture, ash and total fiber content of the mangaba seed were determined according to the methods ASTM D 3173-87, ASTM D 3174-89, AOAC (1995), respectively. The oil content was determined by Soxhlet extraction using *n*-hexane at the normal boiling point for 8 h, followed by solvent removal under vacuum at 40 °C. The cellulose, hemicelluloses and lignin were determined according to Van Soest's method (1967) and the elemental analysis (carbon, hydrogen and nitrogen) of the mangaba seed was conducted using a fully automatized elemental analyzer (Thermo Finnigan, model Flash 1112 Serie EA). The oxygen was calculated by difference, as described by Sheng and Azevedo (2005).

2.2.1. Thermogravimetric analysis (TGA)

The thermal decomposition analysis was carried out using DTA-TG apparatus (Shimadzu, model DTG – 60H). Nitrogen was used as the carrier gas with a flow rate of 100 mL/min. The temperature program used for the TGA was as follows: the samples were heated from ambient temperature to a final temperature of 1000 °C at a rate of 10 °C/min. A sample mass of around 5 mg was used for each test.

2.2.2. Fourier transform infrared (FT-IR) spectrometry

Functional group compositional analysis of the biomass was carried out using Fourier transform infra-red (FT-IR) spectrometry in attenuated total reflectance (ATR) mode on a Varian (model 640-IR) FT-IR spectrophotometer. The infra-red spectrum of the sample was obtained with a range of 400–4000 cm^{-1}, resolution of 4 cm^{-1} and 32 scans. All spectra were baseline-corrected.

2.3. Pyrolysis conditions

Laboratory-scale pyrolysis equipment was used to conduct the experiments. The biomass was pyrolyzed in a fixed-bed quartz reactor (L = 260 mm and Ø 60 mm). The reactor was placed in an electrical furnace with a Therma temperature controller (model TH 90DP), power of 1.7 kW and maximum temperature of 1050 °C. The furnace was heated with a stream of nitrogen (1 mL min^{-1}) at a heating rate of 30 °C min^{-1} from room temperature to the predetermined temperatures of between 450 °C and 600 °C. The volatile compounds were collected in an ice bottle, using a condenser of 30 cm, and refrigerated in a thermostatic bath (Microquímica Equipments LTDA, model MQBTC99-20) at approximately 10 °C. The variables were: pyrolysis temperature (450 °C and 600 °C), sample weight (5 and 11 g), reactor with prior heating or without prior heating, and pyrolysis times of 10, 30 and 50 min after of the reactor to be in temperature of pyrolysis. The heating rate is constant (30 °C min^{-1}) for every experiments.

The bio-oil was separated from the aqueous fraction for the chromatography analysis as described in detail by Onorevoli et al. (2014). The pyrolysis process resulted in solid, liquid (bio-oil + water) and gas products. Mass balance calculations were performed to estimate the yield: solid (wt%) + liquid (wt%) + gas (wt%) = 100.

2.4. Bio-oil analysis

2.4.1. Thermogravimetric analysis (TG)

Thermogravimetric analysis of the bio-oil was performed using a TGA analyzer unit (Shimadzu, model DTG – 60H) under a nitrogen atmosphere (flow rate of 100 mL/min) at atmospheric pressure. The temperature program used for the TGA was as follows: the samples were heated from ambient temperature to 600 °C at a heating rate of 10°C min^{-1}. Approximately 5 mg of sample was used for each analysis.

2.4.2. Gas chromatography/quadrupolar mass spectrometer (GC/qMS)

The bio-oil samples were derivatized with bis(trimethylsilyl)tri fluoroacetamide (BSTFA) and trimethylchlorosilane (TMCS) to volatile trimethylsilylester derivatives. Around 10 mg of the bio-oil sample was dissolved in dichloromethane and derivatized with 40 μL of BSTFA and 40 μL of pyridine. The solution was mixed in a vortex (IKA® VORTEX 1) and left to stand for 30 min at 60 °C, after completing the volume to 1 mL with dichloromethane. The samples were then analyzed on a GC/qMS instrument (QP2010 plus, Shimadzu, Tokyo, Japan) equipped with an AOC20i auto-injector (split/splitless mode). The chromatographic separation was performed using a DB-5 column (methyl silicone with 5% phenyl groups – 30 m × 0.25 mm id × 0.25 μm film thickness). The oven temperature was programmed as follows: the column was held at 50 °C for 2 min, heated to 200 °C at a rate of 5°C min^{-1} and then to 230 °C at 10 °C min^{-1}, held at 230°C for 5 min, heated to 245 °C at a rate of 2°C min^{-1} and then to 300 °C at 10°C min^{-1} and finally held at this final temperature for 10 min. The injector and detector temperatures used were 280 °C and 300 °C, respectively. The injection as carried out in the split mode (1:20) and the carrier gas (He, ultra pure, White Martins S.A.) flow was 1.4 mL min^{-1}.

All data were treated by the GCMS solution software 2.6 (Shimadzu, Japan) and the compounds were tentatively identified using the NIST-05 spectral library database. The identification was based on the comparison of spectra with those in the NIST and WILEY libraries and also detailed analysis of MS spectra and