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Oxidative fast pyrolysis of banana leaves in fluidized bed reactor

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ABSTRACT

Dried banana leaves were previously chopped, characterized by proximate and elemental chemical analyses, thermogravimetric analysis (TGA), differential thermal analysis (DTA) and higher and lower heating value and submitted to oxidative fast pyrolysis in an auto-thermal fluidized bed reactor. The pyrolysis products were gases, bio-char and bio-oil (heavy and light phase). The gases were burnt in a combustion chamber and the energy was used for to heat the fluidization air in the reactor. The light bio-oil was analyzed by gas chromatography-mass spectrometry (GC/MS); the heavy bio-oil by infrared spectroscopy (FTIR/ATR) and higher and lower heating value; and the bio-char by elemental and proximate analysis, TGA, DTA and scanning electron microscopy (SEM). The mass yield and energy efficiency of the process were determined by mass and energy balances. The process produced 49.6% gases, 27.0% bio-oil and 23.3% bio-char. The light and heavy bio-oil presented complex chemical compounds and phenolic and acid nature. The heavy bio-oil showed elevated higher heating value of 25 MJ/kg. The bio-char released high energy under combustion, enabling it to be used as fuel. The results suggest potential for generating fuel products and chemical inputs from fast pyrolysis of dried banana leaves.

1. Introduction

In the last decades, the production of banana expanded in most producing countries; rose from 35 million to 102 million tonnes between crops 1978 and 2012. This was due especially the more intensive use of technology, resulting in higher levels of productivity. Only six countries account for almost 65% of world production. India leads the world production (24.4%), followed by China (10.3%), the Philippines (9.1%), Ecuador (6.9%), Brazil (6.8%) and Indonesia (6.1%) [1]. In Brazil, bananas are cultivated throughout all regions of the federation and the country ranks fifth among the world's largest producers. In 2013, the national harvest of bananas recorded an area of 485,162 ha reaching 7,292,164 tons of produced fruit with average yield of 15,030 kg/ha. Santa Catarina state located in southern of Brazil participated with approximately 9.5% of the Brazilian banana production, being state ranked fourth in domestic production. In the past three years, banana production in Santa Catarina has alternated with apple production in socioeconomic importance. Banana cultivation has been a strong component in the income of a great number of small farmers [1]. According to Fernandes et al. [2], for each ton of harvested banana, 100 kg of fruit is rejected, and approximately four tons of lignocellulosic waste is generated (three tons pseudostem, 160 kg of stalks, 480 kg leaves and 440 kg peels). In 2013, 29,137 million tons of banana wastes (leaves, pseudostem and stalk) were generated [1]. Most of these wastes remain in the cultivation area until their decomposition by microorganisms producing greenhouse gases (methane gas and carbon dioxide). The use of such waste for the production of inputs, in addition to reducing environmental pollution by their removal from the field, provides added value to banana cultivation, which has been facing great challenges over recent years due to the product's fluctuation in the domestic market. Among the possibilities of enhancing the value of these wastes is to use it as biomass in the generation of renewable energy and to produce chemical inputs. The banana wastes can be compacted into briquettes [3–5], be biochemically converted to methane gas with anaerobic digestion [6] and fermented to ethanol [7–9]. Direct combustion of pseudostems and leaves can also generate power [6].

Various studies using different biomasses such as sawdust, banana wastes, rice husks, coffee wastes, sugarcane bagasse and corncobs for the production of energy and chemical inputs have been conducted and have demonstrated the great potential of these [2,10–12]. These studies generally use thermochemical conversion

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processes, such as liquefaction, gasification, pyrolysis and combustion and wastes that are readily available in the region in which they are generated from harvesting and processing [13,14]. Within the biomass thermochemical conversion technologies, pyrolysis has been receiving special attention and has been investigated by various groups. It has become a common method of biomass conversion due to its simple operation and occurs in a continuous process. Pyrolysis is a process which breaks down the original molecular structure of a determined compound through the action of heat. In biomass pyrolysis, the particles are generally heated between 400 and 500 °C, in inert atmosphere or with a low concentration of oxygen, causing the formation of a carbon (bio-char) rich waste and a volatile fraction composed of condensable organic gases and vapors (bio-oil) [11]. The proportions of these compounds depend on the biomass characteristics and the pyrolysis method used (slow pyrolysis or carbonization, rapid and ultra-rapid pyrolysis), that depend on process parameters and the architecture of the reactor, such as temperature, residence time of the biomass particle, heating rate, pressure used, type of atmosphere and use of catalysts [15–17].

Fast pyrolysis is mainly used to maximize liquid product yield such as bio-oil (heavy and light), using moderate temperature of around 500 °C, high heating rate (>100 °C/s) and short vapor residence time (from 0.5 to 10 s). Very high heating and heat transfer rates generally require feeding by finely ground biomass with particle size smaller than 1 mm, carefully controlled reaction temperature and pyrolysis vapors and aerosols must be quickly cooled to generate the bio-oil [13,18]. The commercial operation currently used for bio-oil production based on vegetable biomass pyrolysis is reached in fluidized bed reactor and circulating fluidized bed. Fluidized beds have been extensively studied and plants already exist in Brazil, being manufactured and sold [19].

Various studies related to fast pyrolysis in fluidized bed reactors for the production of energy and inputs from biomasses have been presented. Fast pyrolysis of *Eucalyptus grandis* wood was conducted in a continuous-feed fluidized bed reactor by Heidari et al. [20], under temperatures between 450 and 600 °C and in inert atmosphere. The maximum bio-oil yield (50.8%) with the minimum water content was obtained at 450 °C. The gas yield was increased from 29.4 to 48.4 wt% when the reaction temperature increased from 450 to 600 °C while the amount of bio-char yield decreased from 19.7 to 14.2 wt%. Four types of Canadian waste biomass including wheat straw, saw dust, flax straw and poultry litter were used by Azargohar et al. [11] for fast pyrolysis using a mobile unit. The pyrolysis products showed that mobile pyrolysis unit can operate for wide range of non-food biomass and its products have great potential for fuel or agricultural applications. Mesa-Pérez et al. [19] studied oxidative fast pyrolysis of sugar cane straw in an auto-thermal fluidized bed reactor, between 470 and 600 °C. According authors, due to the pyrolysis plant configuration used, between 10 and 15 wt% of the biomass fed is burned with air to generate the heat necessary to warm the bed of inert material and achieve an adequate temperature for the beginning of the pyrolysis reaction of around 450 and 470 °C. As a result, an auto-thermal regime is obtained, which facilitate energy integration and reduce operating costs, improving process feasibility. The maximum bio-oil yield was achieved at temperature of 470 °C and the product yields of bio-oil and bio-char were up to 35.5 wt% and 48.2 wt%, respectively. In this type of process, the bio-oil yield is lower when compared to pyrolysis in an inert atmosphere, due to the combustion of part of the biomass with the air used for fluidization, however, the charcoal yield is high.

Aimed at exploiting and adding value to the wastes produced by banana cultivation, which are generated in large quantities in Brazil, Fernandes et al. [2] evaluated the use of wet and semi-dried banana leaves as a potential energy source. The chemical characteristics and the thermal behavior demonstrated by the semi-dried banana leaves indicate their potential for use as biomass, with results similar to other agro-industrial wastes currently used. In another study, Fernandes [21] carried out slow pyrolysis of wastes generated in banana cultivation (leaves and pseudostem) in a fixed bed reactor, under inert atmosphere, obtaining high bio-char yield (56.8% for the leaves and 58.4% for the pseudostem) and low yields for the bio-oil (9.4% for the leaves and 11.8% for the pseudostem), characteristic of slow pyrolysis. The pyrolysis products were characterized and the technical viability of the slow pyrolysis of banana leaves and pseudostem has been demonstrated on basis of the results obtained by the authors. In order to expand these studies, in this study, the thermochemical conversion of dried banana leaves in products such as bio-oil (light and heavy phase), charcoal and gases was evaluated. The thermoconversion process used was the oxidative fast pyrolysis in an auto-thermal pilot-scale plant similar to that used by Mesa-Pérez et al. [19] and under similar operating conditions. The characteristics of the biomass and products (bio-oil and bio-char) generated in the process were evaluated by chemical and thermal analysis and mass and energy yields were determined. The non-condensable gas were directly burned without any auxiliary fuel in a combustion chamber and used to heat the air used in fluidization contributing to the auto-thermal process and to reduce the energy consumption. The use of air as fluidizing agent instead of inert gases also causes reduction of operating costs in the pyrolysis plant.

2. Experimental study

2.1. Biomass preparation and characterization

The banana leaves samples were obtained from the *Musa cavendishii* species on a property located in the municipality of Joinville/SC, Brazil. Only the leaves which were found in a dry state were picked directly from the banana tree or gathered from the ground. The banana leaves did not require drying because they presented 7.8% moisture, adequate level for the fast pyrolysis process. Once collected, the samples were chopped in a hammer mill, CID 125 mm model and submitted to granulometric analysis according to ASTM E828-81 (2004) using Tyler series sieves of different meshes, with shaking time of 15 min and 80 Hz frequency. Around 83% of the particles presented diameters of less than 1 mm and the rest between 1 and 2 mm.

To evaluate the potential of the biomass for the fast pyrolysis process, the banana leaves particles were characterized by chemical and physical analyses. Moisture (%M), volatile matter (%VM) and ash were determined by proximate chemical analysis using thermogravimetry (dried in oven and burnt in muffle furnace) according to procedures described, respectively, in the ASTM E871-82, ASTM E872-82 and ASTM E1755-01 standards. All procedures were carried out in triplicate and the crucibles used had been previously cleaned and dried. Fixed carbon (FC) was determinate using the data previously obtained in the proximate analysis using the formula $\% FC = 100 - (\% Ash + \% VM)$.

Ultimate analysis was performed in order to determine the elemental composition of biomass. The carbon (C), hydrogen (H) and nitrogen (N) contents were measured in the Perkin-Elmer CHN 2400 elemental analyzer. The method consists of burning the samples in oxidizing atmosphere, with fully developed combustion. The samples are reduced to a group of gases such as CO_2, H_2O and N_2), which are continually measured and based on this, the C, H and N element percentages are calculated. The sulfur (S) content was determined by Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES) in the Spectro Ciros CCD equipment. The