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Evaluation of the Production of Bio-Oil Obtained Through Pyrolysis of Banana Peel Waste

Hernán D. López, Nathaly Ayala, Dionisio Malagón-Romero*

Semillero Energia y Termófluidos, Grupo GEAMEC, Universidad Santo Tomás, Bogotá, Colombia.
dionisiomalagon@usantotomas.edu.co

Banana harvesting only uses 20 to 30 % of its mass, leaving 70 to 80 % as waste, studies have indicated that the wastes of the banana are a potential feedstock for pyrolysis due to the volatile matter and fixed carbon that has been found. Peels were milled for reducing the size and submitted to granulometric analysis using the Tyler series sieve. The experimental design was factorial by duplicate. Pyrolysis was performed at four different temperatures (300, 400, 500, and 600 °C), three heating rates (5, 10 and 15 °C/min) and residence time of three hours. Samples were physically and chemically characterized. The granulometric analysis showed an average diameter of 2 mm. The banana powder had a moisture content of 8.16% ± 0.8. The content of lignin (3.24 %), cellulose (6.15 %) and hemicellulose (10.46 %) was identified, and the ash content was 14.92 %. The obtained bio-oils were characterized using GC. At a heating rate of 10 °C /min, bio-oil present a better yield of 6.43 % at 300 °C. The better gas yield was at 600 °C with 70.30% at 5 °C/min and 67.24 % at 10 °C/min. The percent of Pentadecane ($C_{15}H_{32}$) was the highest with a concentration of 30.018 ppm at 26.4 min of retention time. The bio-oil obtained during pyrolysis experiments had a viscosity of 0.03 ± 0.011 Pa·s determined at 40 °C and density 1118 ± 98 kg/m^3 measured at 16 °C. These results showed that banana peels could be used as raw material for solvents, fuels, or bioenergy production.

1. Introduction

Since some years ago, climate change has been one of the main concerns due to the emission of greenhouse gases caused by the combustion of fossil fuels, causing an increase in the earth's temperature. Burning fossil fuels produce compounds such as particulate material (PM), nitrogen oxides (NO_X), carbon dioxide (CO_2), and sulfur dioxide (SO_2), which have impacted people's health (Ashikin et al., 2014), (Gaffney and Marley, 2009). This problem has generated the search for new sources of energy to replace traditional sources. Biomass is one source for obtaining energy due to the possibility of obtaining renewable energy (McKendry, 2002), and for reducing atmospheric emissions (Shi et al., 2006), making biomass one of the best alternatives to reduce greenhouse emissions and also remove wastes.

Biomass is considered as a natural source of energy that biologically transforms inorganic compounds in organic (Bonechi et al., 2017) and can be extracted from forestry, agricultural, or industrial residues (Wright et al., 2011). However, agricultural wastes are not being properly treated as most of these wastes are being left on the ground, becoming a risk for transmission of diseases and production of greenhouse gases as they decompose (Cohen and Yom Din, 2010). One of the industries that generate a huge amount of wastes is the banana crop industry, which has been increasing over the years. In 2017, banana production dedicated about 5.6 million hectares of land globally, generating 114 million tons around the world (FAO, 2019). Nevertheless, banana harvesting only uses 20 to 30 % of its mass, leaving 70 to 80 % of waste (Mazzeo M. et al., 2010) and most of these wastes are being burned at an open field, polluting soils and degrading ecosystems that increase carbon footprint (Kumar and Joshi, 2013). One possibility for reusing banana wastes is their transformation in solvents and fuels though pyrolysis (Sellin et al., 2016).

Pyrolysis is a thermochemical technology that transforms biomass in different products with superior properties that could be used as fuels or solvents, so obtained products could be harnessed as an energy source or for chemical supplies (Mohan, Pittman Jr, and Steele, 2006). Heating rate and residence time are parameters that

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classified pyrolysis in slow, fast and flash (Kan, Strezov, and Evans, 2016). Pyrolysis has been extensively studied because of its advantages as having a higher conversion rate to produce different bio-product and reduce the environmental risk of the contaminants (Gong et al., 2019). In fact, several of the processes for obtaining chemical compounds such as benzaldehydes, cyclopentane, and pyridine (Bridgwater and Peacocke, 2000) use agricultural wastes as feedstock with pyrolysis due to the simplicity of performance, high warming speed, easy control (Heidari et al., 2014).

Studies have indicated that banana wastes are a potential feedstock for pyrolysis since it was found volatile matter of 88.02 % and fixed carbon of 2.7 % in them (Kabenge et al., 2018). Additionally, other studies have found different yields of products obtained from banana peels pyrolysis, at a heating rate of 10 °C/min, temperatures from 350 to 550 °C and residence time between 45 and 90 minutes 35.64 % of char was obtained (Omulo et al., 2019). Other authors obtained with a heating rate of and 7 °C/min, temperature between 400 °C and 700 °C and residence time of 20 minutes, yields of 28.03 % of bio-oil and more than 30 % of gas at 700 °C (Ozbay et al., 2019). Besides, in the literature, it is reported the potential of production of char with a yield of 47.7 % (Shiung et al., 2018)

The aim of this paper is to expand the studies that already exist and give an additional value to wastes, specifically peels, from banana crops and determinate if this process could be an energy opportunity for banana producers as Colombia.

2. Materials and methods

2.1 Biomass preparation and characterization

Banana peel samples (*Musa cavendish*) were obtained from an urban zone of Garagoa- Boyacá, Colombia. There, 25 kg of mature peels were collected. The initial moisture content of banana peels was determined by drying according to ASTM E1757-19. Then, samples were dried for reducing the moisture content in an oven (Memmert, Germany) for 24 hours at 110 °C. Once dried, peels were milled in domestic equipment and sieved using Tyler series sieves according to ASTM C136. 2400 g of banana peel powder were isolated in sealed plastic bags, at room temperature (19 °C), to avoid biological contamination. The banana powder was characterized by proximate and ultimate analyses. Moisture and ash content were determined following methods ASTM (ASTM E1358-97) and ASTM E1755-01, respectively. Elemental composition of banana powder carbon (C), hydrogen (H), nitrogen (N), oxygen (O), and sulfur (S), were characterized according to ASTM D3178. The lignocellulose analysis was developed according to Van Soest Method for determining cellulose, hemicellulose and lignin fraction. Thermogravimetric Analysis (TGA) of banana powder was carried out in Mettler Toledo equipment. Samples were heated up from room temperature to 900 °C at three heating rates of 5, 10, and 15 °C/min.

2.2 Pyrolysis equipment

The experiments were developed in the pyrolysis equipment designed by Universidad Santo Tomás (Bogotá, Colombia). Figure 1 shows a diagram of the equipment. The equipment consists of three elements: reactor, condenser and control system. The reactor was built in stainless steel AISI 316, equipped with an electrical resistance for heating (1.6 kW). The reactor volume has a capacity of 1 L. The reactor has an insulating material in the ceramic fiber blanket. The reactor is connected with a pipe schedule 40 to a condenser. The condenser has a capacity of 4.5 L and has two valves to regulate the amount of water. The equipment has an activated carbon filter responsible for the adsorption of volatiles substances (Demirbas, 2004). The equipment is controlled by Maxthermo MC 5438 trade controller, which allows programming the time and heating speed of the reactor.

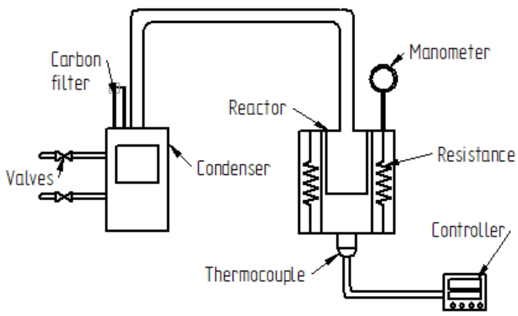

Figure 1. Schematic diagram of the pyrolysis apparatus

2.3 Experimental design

The pyrolysis assays were carried out under a factorial design by duplicated. Two factors were evaluated: temperature (300, 400, 500, and 600 °C) and heating rates (5, 10 and 15 °C /min); these conditions were selected according to the literature reviewed (Taylor et al., 2014). For each assay, samples of 200 g of banana powder were put inside the reactor and hermetically sealed, after the reactor reached the run temperature, samples were kept at a residence time of three hours. The heating rate was programmed with the control system. During residence time, condensable gaseous products were collected in the condenser for its quantification and analysis. Mass yield of the products was determined according to the quantity of product generated: char, bio-oil and gas.

2.4 Bio-oil characterization

Density analysis was evaluated to the liquid product of pyrolysis in a pycnometer, according to ASTM D 6822-12. The kinematic viscosity was developed at a temperature of 40 °C in a viscometer according to ASTM D-445-06. The chemical composition of the bio-oil collected from the condenser was characterized according to ASTM D2887- 16a using a standard mixture of n-alkanes (ASTM D2887 – 12). The liquid was injected directly into Shimadzu GC 2010 chromatograph, equipped with a quadrupole mass spectrometer Shimadzu QP 2020 and a SH-Rxi-5 sil column MS, 30m L x 0.25 mm I.D. x 0.25 µm. Helium was used as a gas carrier at a flow rate of 1 mL/min and injector temperature of 250 °C. The column conditions were at an initial temperature of 40 °C for 10 minutes at 8 °C/min until 250 °C, then at 10 °C/min until 300 °C for 10 minutes. The percentages compositions were determinate by an alkane standard Resket brand catalog number 560295, which contained the series listed for 27 hydrocarbons.

3. Results and discussions

3.1 Characterization of biomass

The content of Moisture in banana peels samples was 44 % ± 31 due to dry process, this content was reduced to 8.16 % ± 0.8, which is similar to other studies that present moisture ranged between 6.7 % to 11.6 % (Kabenge et al., 2018). This water content indicated that the feedstock is acceptable for pyrolysis experiments since biomass with higher moisture content requires more thermal energy to vaporize the contained water (Kabenge et al., 2018), and water could change the product obtained due to heating value decreases with moisture content (García et al., 2012). The granulometric analysis of powder showed an average diameter of 2 mm ± 0.5. This size was selected because a large size represents decomposition delay in pyrolysis, known as the thermal resistance effect (Seebauer, Petek, and Staudinger, 1997), that causes temperature gradients inside the particle. Meanwhile, a size particles from 0.4 mm to 2 mm do not influence in products obtained, presenting only small differences due to experimental errors (Taylor et al., 2014). The banana powder had hemicellulose, cellulose and lignin contents of 10.46 %, 6.15 % and 3.24 %, respectively. The content of hemicellulose and cellulose are lower than the presented in other studies which have contents of hemicellulose and cellulose of 41.38 % and 9.9 % (Kabenge et al., 2018), (Fernandes et al., 2013) respectively and can be attributed to the microbial action in the degradation of peels due to the exposed time to the environment (Fernandes et al., 2013). Moreover, the lignin content (3.24 %) is also lower than other papers with contents of 17 % in banana leaves and 8.9 % in banana peels (Kabenge et al., 2018). The ash content of 14.92 % is high compared to content of 9.28 % presented by (Omulo et al., 2019), but it is not a problem as long as it remains below 20 % (Fernandes et al., 2013). Even this content can be an advantage for pyrolysis and for gasification (García et al., 2012). The low content of sulfur (0.16%) and nitrogen (1.12 %) are like the presented in literature, with content of 0.49 % of sulfur and 0.98 % of nitrogen (Sellin et al., 2013) and are the expected since these compounds during combustion generate toxic gases for the environment (García et al., 2012) and are undesirable for a thermochemical conversion design (Fernandes et al., 2013). The high content of carbon (38.54 %) and oxygen (40.13 %), were as expected and desire since they are the main compounds of fuels and influence the higher heating value (Fernandes et al., 2013) and are similar to the presented in literature with contents of 47.5 % of carbon and 45.5 % of oxygen (Shiung et al., 2018).

3.1.1 Thermogravimetric analysis

Thermogravimetric analysis, presented in figure 2, showed the degradation of banana powder with three different heating rates, 5 °C/min, 10 °C/min and 15 °C/min. From room temperature to 100 °C the sample presents a loss of weight of 12 % due to evaporation of moisture. Also, the sample could lose formic acid and acetic acid from inside the particle (Fernandes et al., 2013). The most important weight loss occurs between 200 °C and 400 °C with a mass loss from 85 % to 45 % that can be attributed to thermal degradation of volatile matter, including hemicelluloses, small lignin and cellulose fraction (Fernandes et al., 2013). Therefore, from

400 to 500 °C, occurs the complete loss of cellulose being similar at the three heating rates. Above 550°C, the degradation of lignin is complete (Sellin et al., 2016). The samples at the three heating rates present up to 500 °C a similar performance. However, above 500 °C at 10 K/min, the degradation rate of biomass becomes relatively constant with the complete degradation of lignin. At the end of the degradation of the mass at heating rate of 5 K/min, there was 25 % solid waste, at the end of 10 K/min by 30 % and the largest mass loss was at the 15 K/min rate leaving 15 % solid waste (Yang et al., 2007), which is a similar result compared to other studies that present that after 550 °C the weight loss occurs essentially in a range of 50 % and 40 % (Ozbay et al., 2019). Experiment at 15 K/min is the best condition for generating lower content of solid waste, and the quantity of solids is similar to ash content.

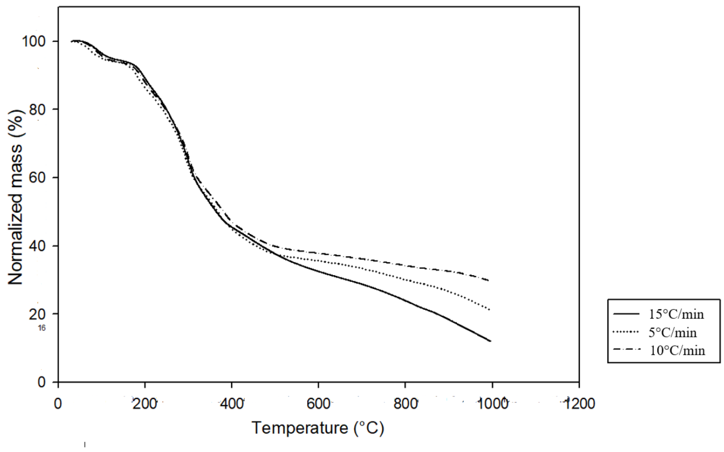

Figure 2. Thermal behavior of banana peels by TGA

3.2 Mass yield of pyrolysis products

Table 1 show the yield of each product, char, bio-oil and gas, obtained at four different temperatures (300, 400, 500 and 600 °C) and three heating rates at 5 °C /min, 10 °C /min and 15 °C /min in pyrolysis equipment. Most products corresponding to gas, and the bio-oil content is the lowest for all experiments. When the temperature increased, at the same heating rate, the gas percentage increased too. The best gas yield was obtained at 600 °C (70.30 %) at 5 °C /min, which is different to other studies with a gas yield of 35 % at 700 °C and heating rate of 7 °C/min (Ozbay et al., 2019). The best yield of bio-oil (6.43 %) was at 300 °C and 10 °C/min of heating rate. However, the amount of bio-oil is low compared to other studies where bio-oil yield was 28.03 % at 550 °C and heating rate of 7 °C/min (Ozbay et al., 2019). The amount of char, for all experiments, was higher than the ash content reported, indicating that increasing the temperature up to 700 °C would reduce this content. Differences between this paper and other reports consulted are due to the amount of feedstock and the design of the pyrolysis equipment (Omulo et al., 2019), so the scale-up of the pyrolysis process it is difficult for the variability of the results.

Table 1. Mass yield of pyrolysis

Heating rate	Temperature (°C)	Yield of char (%)	Yield of bio-oil (%)	Yield of gas (%)
5 °C/min	300	33.11 ± 5.34	6.13 ± 9.83	60.76 ± 15.17
	400	33.37 ± 0.63	4.89 ± 3.67	61.72 ± 3.03
	500	33.08 ± 5.03	4.75 ± 1.69	62.17 ± 6.73
	600	26.38 ± 13.90	3.31 ± 0.03	70.30 ± 13.87
10 °C/min	300	31.48 ± 11.77	6.43 ± 5.69	60.07 ± 17.47
	400	36.00 ± 0.56	4.53 ± 4.89	59.47 ± 4.32
	500	31.33 ± 7.01	4.15 ± 8.52	64.55 ± 15.54
	600	28.17 ± 19.29	4.57 ± 3.32	67.24 ± 22.62
15 °C/min	300	32.77 ± 1.48	6.02 ± 1.53	61.00 ± 0.10
	400	35.25 ± 7.37	3.02 ± 1.49	61.70 ± 8.90
	500	40.55 ± 22.77	3.76 ± 1.02	55.70 ± 23.80
	600	34.15 ± 0.54	4.03 ± 2.45	61.80 ± 3.00

3.3 Products characteristics and properties

Bio-oil obtained during pyrolysis experiments had a viscosity of 0.03 ± 0.011 Pa·s determined at 40 °C, according to ASTM D-445-06. Samples present a density of 1118 ± 98 kg/m^3 measured at 16 °C. Other studies about products obtained from biomass pyrolysis, as sawdust and wheat straw, present similar results even though they are different feedstock; density is within the same range with variation from 918 to 1239 kg/m^3 (Azargohar et al., 2013).

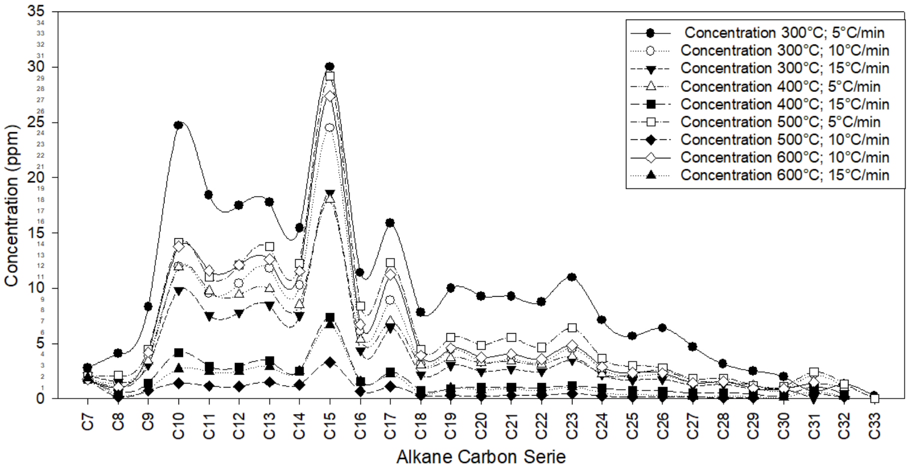

Figure 3. Chromatogram of bio-oil

The chemical composition of bio-oil was determined by GC-MS analysis, and this analysis showed a mixture of linear alkanes (C7 - C33), as shown in Figure 3. The compounds were grouped in low molecular weight (LMW; C7 - C11), medium molecular weight (MMW; C12 - C22), and high molecular weight (HMW; C23 - C33). The best conditions corresponding to 5°C/min and 300 °C, in which the percent of pentadecane (C15H32) and decane ($C_{10}H_{22}$) were important with a concentration of 30.018 ppm and 24.699 ppm, respectively. The experiments that present the less concentration of alkanes were at a heating rate of 10°C/min at 500 °C, where the only significant concentration was of pentadecane ($C_{15}H_{32}$) with 3.322 ppm. The heating rate is an important factor for concentration since concentrations at 5 °C/min are better than the presented at a heating rate of 10 and 15 °C/min, the highest peaks occur equally in the LMW and MMW sectors. Lower temperature ranges have a higher concentration. These results have shown that banana peels could be as raw material for solvents, fuels or bioenergy production (Hussain et al., 2019).

4. Conclusions

Banana peels presented a high content of oxygen, carbon and low content of sulfur and nitrogen, indicating the potential as a feedstock for conversion to fuel by pyrolysis. Results showed that temperature and heating rate influenced gas, liquid, and char products. The best gas yield was at 600 °C and 5 °C/min, while the best bio-oil yield was at 300 °C and 10 °C/min. The chemical compounds found in bio-oil with the highest concentration were Pentadecane ($C_{15}H_{32}$) and Decane ($C_{10}H_{22}$), which are components for industrial purposes. This result confirms that banana peels could be used as solvents and fuel production. Therefore, for future investigations, it is expected to identify more compounds of the bio-oil obtained.

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