

Energy potential of yam and plantain peels

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Abstract: Peels are the wastes produced when yam and plantain are processed for human consumption. This study evaluated the potential use of these wastes as energy feedstocks by conducting thermal decomposition studies in a thermogravimetric analyzer coupled to a Fourier Transform infrared spectrometer (FTIR) and in a differential scanning calorimeter. The peels have ash contents of about 8%-9% hence a slightly lower energy contents in comparison to other biomass feedstocks. The pyrolysis process for both yam and plantain peels was found to consist of two main stages - moisture loss at temperatures less than 150°C, and decomposition of the dry matter component that peaked at temperature of 300°C. Both samples reached exothermic reactions that also peaked at 300°C. Based on FTIR analysis, the major gases that evolved during pyrolysis were carbon dioxide, carbon monoxide, acetic acid, methane, methyl isocyanate and ethanol.

Keywords: thermal decomposition, syngas, waste, differential scanning calorimetry, Fourier transform infrared spectroscopy, thermogravimetric analyzer

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1 Introduction

Yams (*Dioscorea* spp.) and plantains (*Musa paradisiaca*) are staple foods in humid and sub-humid tropical countries of the world such as Nigeria. According to the Food and Agriculture Organization (FAO) statistics (faostat.fao.org), Nigeria produced 31 million metric tons of yam tubers and 3 million metric tons of plantain in 2007. Before being consumed, yam tubers and plantain are peeled and prepared for consumption by boiling, roasting, grilling, frying or pounding boiled tubers and plantain into dough. Even though several studies have shown that the waste peels from both yam and plantain can be used as ingredient for animal feeding (Ekenyem et al., 2006; Adeloje, 1992; Falaye and Oloruntuyi, 1998; Omole et al., 2008), the peels are still largely discarded. This study is aimed at investigating the possible use of these peels as feedstocks

for energy.

In 2006, about 94% of the energy consumed in Nigeria (EIA, 2009) was from fossil fuel. From a sustainable view point, fossil fuels are limited and are non renewable energy. In addition, there are environmental problems associated with extracting, transporting and using fossil fuels. An unavoidable solution in reducing dependency on fossil fuel is the use of renewable resources. Waste generated during processing of agricultural materials and food (e.g. peels from yam and plantain) are renewable resource that can potentially be used to produce energy hence reducing the use of and the dependency on fossil fuel.

Pyrolysis is one of the promising thermal approaches that can be used to convert biomass to energy (Bernhart and Fasina, 2009; Yang et al., 2004). Thermogravimetric (TG) analysis and differential scanning calorimetry (DSC) are commonly used to study thermal decomposition and identify thermal events during pyrolysis of biomass feedstock (Garcia-Nunez et al., 2008; Lee and Fasina, 2009). Thermal decomposition and thermal events are required for the design, operation, and

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control of thermochemical conversion units such as gasifiers and pyrolysis reactors (Miranda et al., 2007).

The main objective of this study was to determine and compare the thermal degradation of peels from yam and plantain using TG and DSC measurements, and quantify the composition of gases evolved from thermal decomposition of the peels.

2 Materials and methods

Yam tuber and plantain used in this study were obtained from an international grocery store in Atlanta, USA. Peels from the yam tubers were obtained by using a kitchen knife to carefully remove the peels. In general, the peels were about 5 mm in thickness. The peels from plantain were obtained by manual peeling. The peels were then immediately oven dried at 45°C for 24 hours. The dried peeled were then ground through a 40-mesh screen using a Wiley mill and stored in a desiccator until when they were analyzed for their energy potential.

The heating value, ash, carbon, and hydrogen contents of the samples were determined. Heating value was obtained with an IKA C200 calorimeter (IKA Works, Wilmington, N.C.). Ash determination was carried out according to ASTM Standard D5142 (ASTM, 2004). Carbon and hydrogen were determined by means of an elemental analyzer (Model 2400 Series II, Perkin Elmer, Shelton, CT). The Van Soest analysis was used to determine the hemicelluloses, cellulose and lignin fractions of the sample. In this process, samples were separated progressively into neutral-detergent fibre (NDF), acid-detergent fibre (ADF) and acid-detergent fibre-lignin (ADL). This method of analysis has been used for other biological materials such as hazelnut shells, wood, rice straw and corn stover (Haykiri-Acma, 2006; Lie et al., 2008; Littlefield, 2010). Hemicellulose content was estimated from the difference between NDF and ADF, cellulose content from subtracting ADL from ADF with the ADL values being used as the lignin content for the peels (Bransby et al., 1989). The extractive contents (i.e. lipids, proteins, or non-structured carbohydrates such as starch and sugars) were then obtained by subtracting the estimated cellulose,

hemicellulose and lignin contents from the original sample mass. The values of these properties were reported on dry basis by correcting moisture content according to CEN Standard 15296 (SIS, 2006). Moisture contents of samples were determined with 10 g of sample placed in a convection oven (set at 105°C) for 24 hours.

A Pyris 1 TG analyzer (Perkin Elmer, Shelton, CT) and a Model Q200 DSC (TA Instruments, New Castle, DE) were used to quantify the thermal degradation of the peels. About 5 mg of each sample was used for each test. Samples loaded into the TGA were heated from 30 to 800°C at a heating rate of 10°C/min under nitrogen gas atmosphere. Based on results obtained from TGA and because of limitation of the DSC equipment, DSC samples were heated from 30 to 550°C at heating rate of 10°C/min. Both pieces of equipment were calibrated with standards that were obtained from equipment manufacturer.

A Fourier Transform infrared (FTIR) spectrometer (Model 100, Perkin Elmer, Shelton, CT) was used to quantify the gases evolved during pyrolysis in the TGA. A transfer line was used to connect the FTIR to the TGA. The transfer line was heated and maintained at a temperature of 220°C to prevent the condensation of the volatile gases evolved during the pyrolysis process (Lee and Fasina, 2009). The software provided by the FTIR spectrometer was used to obtain spectra of the gas flowing through the measurement cell every 20 s. Quantitative analysis of the series of spectra was then carried out by (a) matching the spectra against those from the library search of a software (QASOFT, Infrared Analysis Inc., Anaheim, CA) thereby identifying constituents of the gas as each spectra, and (b) using the software to quantify the concentration of the identified gases.

3 Results and discussion

3.1 Characterization of peels

The average initial moisture content of the peels of yam and plantain were 68.2% and 87.8% (wet basis) respectively. After the 45°C drying, the data obtained

on heating value, ash, carbon, hydrogen cellulose, hemicellulose and lignin contents of the yam and plantain peels are summarized in Table 1. Also shown on the table are the corresponding values for switchgrass – a high yielding perennial grass that has been identified to have potential as a bioenergy feedstock by the US Department of Energy (McLaughlin and Kszos, 2005). Statistical analysis using the analysis of variance procedure showed (SAS, 2009) that ash, heating and carbon values of yam peel are significantly different ($P < 0.05$) from those of plantain peel and switchgrass. We attribute the lower heating value of the peels to its significantly higher ash content which reduces the amount of combustible material (primarily carbon and hydrogen) per unit mass. This implies that more of the peels (about 15% more) will be required to provide the same amount of energy as switchgrass when used for bioenergy applications. As expected, the cellulose, hemicellulose and lignin contents of the peels were significantly lower than those of switchgrass. Of significance is the high amount of extractives in the peels which may suggest the possible utilization of the peels in other value-added applications such as pharmaceuticals and food applications. The values of cellulose, hemicellulose, lignin and extractives are similar to those reported by other researchers for switchgrass (Hu et al., 2010).

Table 1 Heating value and composition of yam and plantain peels

Property	Yam peel	Plantain peel	Switchgrass ²
Ash, % d.b.	8.49 ^a ± 0.23 ¹	9.92 ^b ± 0.18	2.96 ^c ± 0.11
Heating value, MJ/kg	16.39 ^a ± 0.09	16.12 ^b ± 0.05	19.20 ^c ± 1.21
Carbon, % d.b.	39.40 ^a ± 0.67	40.32 ^b ± 0.54	48.21 ^c ± 2.21
Hydrogen, % d.b.	6.12 ^a ± 0.02	5.99 ^a ± 0.03	5.58 ^b ± 0.31
Cellulose	9.67 ^a ± 0.51	10.54 ^a ± 0.21	47.4 ^b ± 0.43
Hemicellulose	21.98 ^a ± 1.21	16.88 ^b ± 0.93	23.05 ^c ± 0.85
Lignin	3.19 ^a ± 0.04	4.89 ^a ± 0.03	11.66 ^b ± 0.04
Extractives ⁺	65.17 ^a ± 1.56	67.69 ^a ± 1.13	17.89 ^b ± 0.22

Note: 1. Standard deviation; 2. Fasina (2008), Littlefield (2010).

Values are means of duplicates.

In each row, values with the same letter are not significantly different ($P < 0.05$).

⁺Extractives include lipids, proteins, or non-structured carbohydrates (i.e. starch and sugars).

3.2 Pyrolysis and thermal degradation

Observed thermal behavior (TG curve) of the peels

during pyrolysis is shown in Figure 1. There was an initial decrease in the mass (about 5%) of the samples between 30°C and 150°C due to the release of moisture in the samples. The figure also shows that a significant loss of sample mass (40% of original mass) occurred within the temperature range of 150°C and 350°C and that thermal decomposition was essentially complete at 550°C. Similar to the results obtained for the ash content, the char yield (residual mass after pyrolysis) was higher for plantain peel.

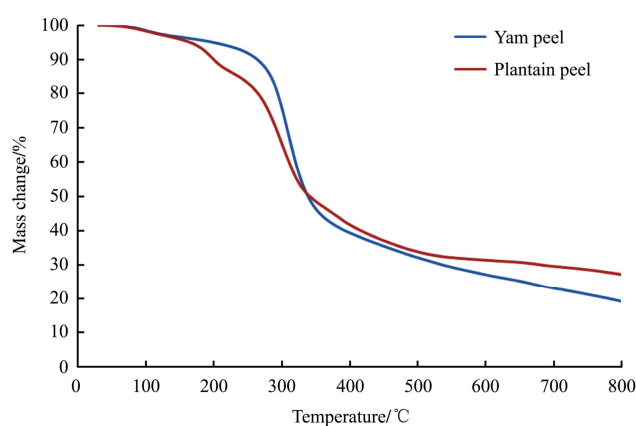


Figure 1 Mass loss from thermal decomposition of yam and plantain peel

Figure 2 shows the mass loss rate (da/dt) curves (derivative thermograms – DTG curves) for the peel samples within the temperature range of 150°C to 800°C. The mass loss fraction (α) was obtained as follows:

$$\alpha = \frac{m - m_o}{m_f - m_o} \quad (1)$$

where, m is the sample mass at any time, t ; m_o is the initial sample mass, and m_f is the final sample mass. There was a clear difference in the thermograms of the samples with the mass loss rate (and hence the amount of reactivity) of plantain peel generally being lower than that of yam peel. We attribute this to the higher energy and carbon contents of the yam peel (i.e. higher percent amount is combusted), hence the increase in mass loss rate. The values of the mass loss rates were about 25% lower than that obtained for switchgrass (Lee and Fasinas, 2009) but 25% higher than the values obtained for poultry litter (Bernhart and Fasina, 2009). Each of the thermograms produced a peak at about 300°C. A small second peak at about 385°C was obtained for plantain

peel. A review of pyrolysis literature indicated that the peak at about 300°C represents hemicellulose decomposition while the higher temperature peak represents the degradation of cellulose (Vamvuka et al., 2003a; Tsamba et al., 2006). This study therefore shows that the hemicelluloses component is responsible for most of the thermal degradation that will occur when peels of yam and plantain are used in pyrolysis applications.

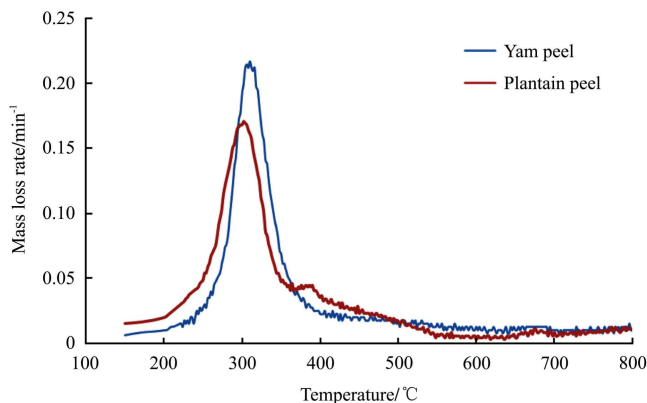


Figure 2 Mass loss rate from thermal decomposition of yam and plantain peels

The heat evolved during pyrolysis reactions for yam and plantain peels are shown in the DSC curves (Figure 3). Both samples reached exothermic reactions within the temperature range of 274–314°C for plantain peel and 290–316°C for yam peel. The peak of the exothermic reaction was about 300°C which corresponded to the peak of the DTG curves (Figure 2). Below the onset temperature for the exothermic reactions, the negative heat values indicate that heat was needed to drive moisture out of the sample and to start the pyrolysis process (Table 2). Exothermic reactions have been reported for coarse fraction of poultry litter (Singh et al., 2008) and for three Mediterranean scrubs (Leroy et al., 2006).

Table 2 Characteristics of DSC thermogram for yam and plantain peel

Parameter	Yam peel	Plantain peel
Endothermic heat above 150°C, J/g	4640.2 ^a ± 95.2 ¹	3649.5 ^b ± 103.2
Exothermic heat, J/g	110.75 ^a ± 2.90	207.55 ^b ± 5.87
Peak exothermic temperature, °C	301.6 ^a ± 0.05	295.7 ^b ± 0.07

Note: 1. standard deviation.

Values are means of duplicates.

In each row, values with the same letter are not significantly different ($P < 0.05$).

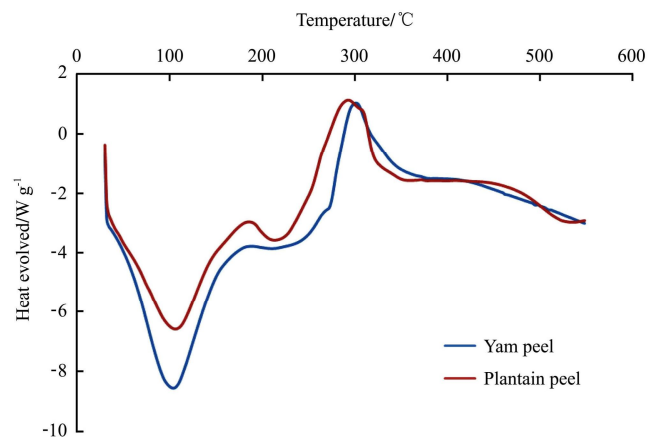


Figure 3 Heat evolved during pyrolysis of yam and plantain peel

3.3 FTIR analysis of gas products

Figure 4 shows a typical three-dimensional plot of the spectral obtained from the gas evolved during the pyrolysis of yam and plantain peels. The main gases identified from the spectra were carbon dioxide, carbon monoxide, methane, acetic acid, methyl isocyanate and ethanol (Figure 5). These gases are typically obtained from pyrolysis of biomass (Zapata et al., 2009; Souza et al., 2009; Biagini et al., 2006) and indicate a possible use of these gases in syngas production. Except for methane that has a peak concentration of 530°C, the peak concentrations for all the other gases occurred at about 300°C. This confirms the mass loss rate and the exothermic reaction peaks obtained from TGA and DSC results. The increases in concentrations of CO₂ and CO at temperatures greater than 600°C has been attributed to oxidation of the carbonized substrate (char) and to high temperature reaction that reacts CO₂ with carbon to produce CO (Baker et al., 2005).

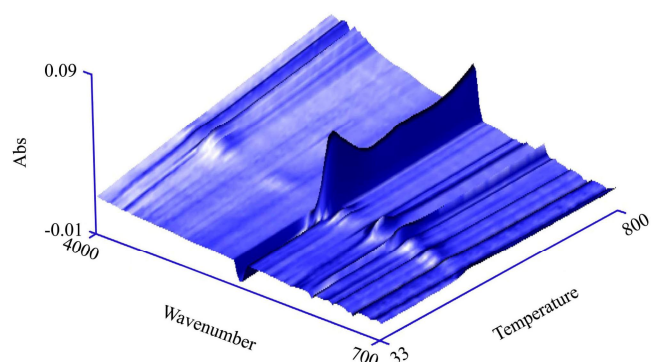


Figure 4 Three-dimensional spectral plot of absorbance of evolved gases as a function of temperature and wavenumber during pyrolysis of yam and plantain peels

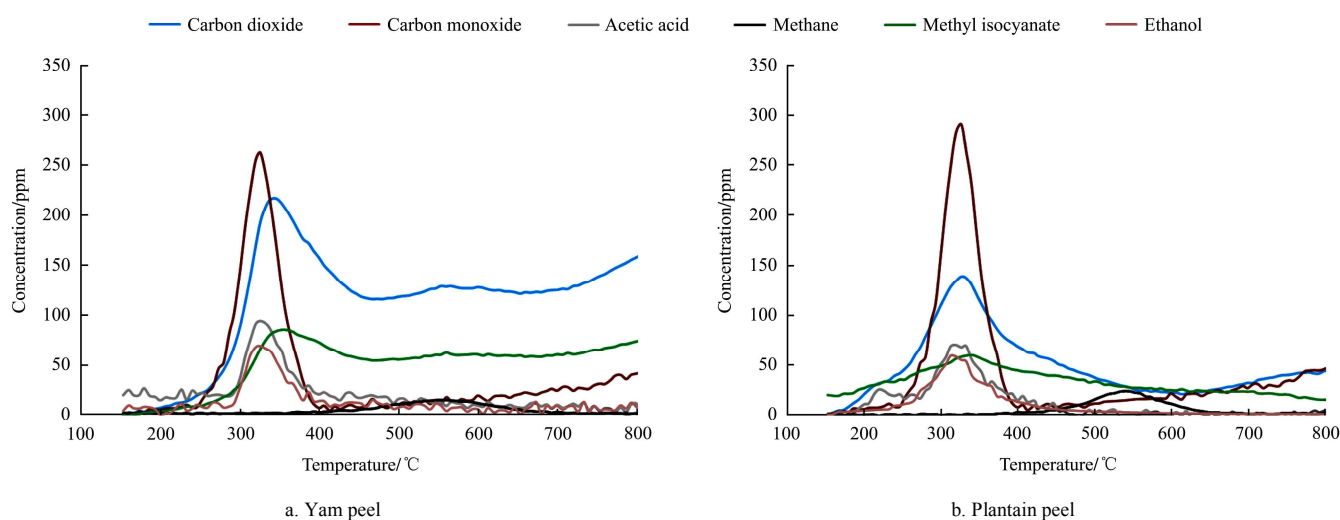


Figure 5 Concentration of gases evolved during pyrolysis of yam and plantain peels in nitrogen atmosphere

4 Conclusions

It can be concluded from this study that:

- 1) Peels from yam and plantain have potential as biomass feedstock because of their relatively high heating value and medium ash content.
- 2) Thermal decomposition of the peels and

exothermic reaction occurred within temperatures of 150°C and 550°C with the maximum mass loss rates and maximum exothermic reaction occurring at 300°C.

- 3) The major gases evolved during the pyrolysis of yam and plantain peels were carbon dioxide, carbon monoxide, ethanol, acetic acid, methane and methylisocyanate.

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