Characterization of Lignocellulosic Fruit Waste as an Alternative Feedstock for Bioethanol Production

Raymundo Sánchez Orozco,[a,b]* Patricia Balderas Hernández,[c] Gabriela Roa Morales,[c] Fernando Ureña Núñez,[d] Juan Orozco Villafuerte,[c] Violeta Lugo Lugo,[e] Nelly Flores Ramírez,[f] Carlos Eduardo Barrera Díaz,[c] and Pablo Cajero Vázquez [a]

To use a new potential lignocellulosic bioresource that has several attractive agroenergy features for ethanol production, the chemical characterization and compositional analysis of several fruit wastes were carried out. Orange bagasse and orange, banana, and mango peels were studied to determine their general biomass characteristics and to provide detailed analysis of their chemical structures. Semiquantitative analysis showed that the components for each fruit waste differed with respect to chemical composition. Fourier transform infrared spectrometry (FTIR) of the residual biomass showed the presence of various functional groups – aldehydes or ketones (C=O), alkanes (C-C), and ethers (C-O-C). Even water molecules were detected, indicating the complex nature of the feedstocks. The concentrations of total sugars ranged between 0.487 g·g^{-1} and 0.591 g·g^{-1} of dry weight biomass. The thermal profiles (TG-DSC) of the residual fruits occurred in at least three steps, which are associated with the main components (hemicellulose, cellulose, and lignin). The decomposition by thermal analysis was completed at around 600 °C and was influenced by the nature of the component ratio.

Keywords: Fruit waste; Lignocellulosic biomass; Cellulose; Fruit waste

*Contact information: a: Instituto Tecnológico de Estudios Superiores de Jocotitlán, Jocotitlán, Estado de México C.P. 50700, México; b: Universidad Politécnica de Atlacomulco, Ignacio Zaragoza No. 1, Col. Centro, Atlacomulco, Estado de México C.P. 50450, México; c: Facultad de Química, Universidad Autónoma del Estado de México, Paseo Colón esq. Paseo Tollocan s/n, Col. Residencial Colón, Toluca, Estado de México C.P. 50120, México; d: Instituto Nacional de Investigaciones Nucleares, Apartado Postal 18-1027, Col. Escandón, México D.F. C.P. 11801, México; e: Universidad Tecnológica del Valle de Toluca, Carretera del Departamento del D.F. Km 7.5, Ejido de Santa María Atarasquillo, Lerma, Estado de México C.P. 52050, México; f: Facultad de Ingeniería en Tecnología de la Madera, Universidad Michoacana de San Nicolás de Hidalgo, Edif. D, Cd. Universitaria, Morelia, Michoacán C.P. 58060, México; *Corresponding author: rsanchez_o@yahoo.com.mx*

INTRODUCTION

México is well known for its important production of fruits such as orange (3.7 million tons/2012), mango (1.5 million tons/2012), and banana (2.2 million tons/2012) (SAGARPA 2013; FAO 2013). This agricultural field is of great interest because it satisfies the needs of the country for fresh fruits over an appreciable period of the year. Approximately 42 wt% of the fruit production is used to obtain juice, essential oils, citrus honey, marmalade, pectin, and cattle feed (Miranda *et al*. 2009).

Agroindustrial residue, such as peels, seeds, and pulps, represents about 50% of the raw processed fruit. These fruit residues do not find any commercial importance and are largely disposed of in municipal dumps (Mamma *et al.* 2008; Oberoi *et al.* 2010).

Fruit peels represent an important source of sugars, which makes them an interesting choice for the production of chemicals such as ethanol (Sánchez-Orozco *et al.* 2012). Due to their abundance and renewability, these wastes are being considered as raw materials for the production of competitive bioethanol in the open market (Mtui 2009). Thus, bioethanol production from these fruit residues could be an attractive alternative for disposal of these residues.

Lignocellulosic feedstock such as fruit peels are primarily composed of pectin, cellulose, hemicellulose, and small amounts of lignin (Oberoi *et al.* 2010). Orange peel and bagasse waste are a potential feedstock for bioethanol production due to their high carbohydrate content, which is similar to other studied feedstocks (Boluda-Aguilar *et al.* 2010; Wilkins 2009). However, and despite the importance of orange peel waste volume, no published research work has studied the possibility of its use in ethanol production, although there are studies about other uses: for essential oils recovery (Rezzoug and Louka 2009; Neng-Guo *et al.* 2009), as a fermentation substrate for the production of multienzyme preparations (Wilkins *et el.* 2007), and for pectin extraction (Liu *et al.* 2006). The agroindustry has experienced increasing costs for its waste treatment. While a number of investigations have been conducted concerning the composition and possible utilization of banana pulp (Li *et al.* 2010; Happi Emaga *et al.* 2008), studies on banana by-products are focused on pectin extraction, phenolic compounds, flavonoids, and ethanol production (Velásquez-Arredondo *et al.* 2009; Brooks 2008; García *et al.* 2012). The results of other studies have demonstrated the high cellulose content in banana, a promising potential source of polysaccharides because it is rich in sugars such as sucrose, glucose, and fructose (Manikandan *et al.* 2007). In the same way, the utilization of mango kernels as a source of fat, natural antioxidants, starch, flour, and feed has been investigated (Readdy and Sarathi 2007; Berardini *et al.* 2005). The edible pulp makes up 33 to 85% of the fresh fruit, while the peel and the kernel comprise 7 to 24% and 9 to 40%, respectively. On the other hand, by-products of industrial mango processing may comprise 35 to 60% of the total fruit weight (Kaur *et al.* 2004), although studies on peels are limited.

In the present paper, therefore, four biomasses with potential interest for bioethanol production have been characterized to determine if there are no significant differences between them with respect to their morphological and chemical properties in terms of their composition. The biomasses studied include orange peel (OP), orange bagasse (OB), banana peel (BP), and mango peel (MP).

EXPERIMENTAL

Materials

Oranges, bananas, and mangoes were procured from a local supermarket in bulk; the fresh fruits were brought to the laboratory, washed and separated into pulp and peels. The peel was removed using a sharp knife, and the underlying pulp was removed by gently scraping with its blunt edge. The peels were then washed thoroughly with deionized water to remove physically adsorbed contamination and dried to a constant weight at 65 °C in a hot air oven (Riossa E-33D) for a period of 24 to 30 h. The orange bagasse consisted of peels, pulp material including membrane tissues, and seeds after extraction of the juice. After drying, the bagasse, and peels were ground in a mill and then passed through an 80-mesh sieve (0.177 mm). Thus, the biomass used in our experiments and characterization studies were dry fruit wastes (OP, OB, BP, and MP), with a particle size smaller than 0.2 mm in order to avoid heat and mass restrictions within the particle. The phenol, sulfuric acid, D-glucose, and other reagents used in this study were of analytical grade.

Proximate Analysis

The analyses were performed according to the following procedures. Moisture and ash content was determined using AOAC (1998) methods. Briefly, triplicate 10-g samples were dried at 105 °C for 24 h (moisture content) and then transferred to a muffle furnace at 575 °C for 24 h. Neutral detergent fiber (NDF), acid detergent fiber (ADF), and acid detergent lignin (ADL) were analyzed using an ANKOM 200 fiber analyzer (Ankom Technology, United States). The proportion of hemicellulose was calculated from the difference between NDF and ADF, and that of lignin was calculated from the difference between ADF and cellulose. The protein content of wastes was estimated by determining the total nitrogen content using the Kjeldahl method and multiplying by the conversion factor of 6.25 (AOAC 1998).

Total Sugars Analysis

Initially, each substrate in the form of dry particles was slurried with distilled water using a solid to liquid ratio of 10% (w/w) and stirred at room temperature, 300 rpm for 60 min. Subsequently, the samples were centrifuged for 15 min at 4000 rpm. The supernatant fluid was filtered through Whatman filter paper No. 1, and the filtrate was used for determining total sugar by the respective procedure. Quantitative determinations of total soluble sugars were performed using a phenol-sulfuric acid colorimetric procedure (Dubois *et al.* 1956) based on the absorbance at 490 nm of a colored aromatic complex formed between phenol and the carbohydrate. The amount of sugar present was determined by comparison with a calibration curve using a reference standard of D-glucose on a UV–Vis spectrophotometer (Lambda 25, PerkinElmer Inc., Waltham, MA, USA).

Scanning Electron Microscopy and EDS Analysis

Images of the fruit wastes were acquired by scanning electron microscopy (SEM) using a JEOL-5900-LV at 20 kV in high-vacuum mode (no further coating was required) equipped with an energy-dispersive X-ray (EDS) probe for semiquantitative elemental analysis and to determine the elemental composition of individual points or map out the lateral distribution of elements from select areas. Solid particles were dispersed on a graphite adhesive tab placed on an aluminum stub.

FT-IR Spectroscopy

Dried fruit wastes were characterized on a Vertex 70 FTIR spectrometer equipped with a Smart Orbit accessory, which is a horizontal single-reflection attenuated reflectance (ATR) accessory. Each sample was scanned between the wavelengths of 4000 and 600 cm^{-1}. The generated spectra were compared to published FTIR spectra for cellulose (Yang *et al.* 2006) and lignin (Megiatto and Hoareau 2007) to identify the major functional groups.

Thermal Analysis

Thermal degradation of fruit waste was carried out in a simultaneous TGA-DSC (SDT Q600 from TA Instruments). A specimen was first placed into an aluminum sample pan on the platinum basket in the furnace and then heated from room temperature to 600 °C. The heating rate was 20 °C/min under a nitrogen atmosphere. Approximately 10 mg of sample mass was used in every experiment. To separate possible overlapping reactions during measurements, derivative themogravimetric (DTG) analysis was also conducted to measure the mass change of a specimen with respect to temperature (dm/dT) using the same TGA system (Lv *et al.* 2010).

RESULTS AND DISCUSSION

Proximate Analysis

Proximate analysis revealed that the banana peels had the highest moisture content of 86.30%, while the mango peels had the lowest moisture content of 68.54%. The moisture contents of bagasse and orange peels were 82.25% and 84.62%, respectively. The comparatively high moisture contents of these wastes indicated that they should be dried to achieve a better control of the process variables for purposes of acid or enzymatic hydrolysis at laboratory. The ash contents of the selected fruit wastes were 2.87%, 2.82%, 3.90%, and 11.19% for orange bagasse, orange peels, mango peels, and banana peels, respectively. These results show that banana peels had ash content higher than 10%, while the other three fruit wastes had values lower than 4%. The composition percentage of moisture and ash content were in the ranges of the published data on other common fruits (Ajila *et al.* 2007). It has been reported (Aguiar *et al.* 2008; Kaur *et al*. 2004; Berardini *et al.* 2005; Li *et al.* 2010; Brooks 2008) that the peels of oranges, mangoes, and bananas could be a rich, low cost source of dietary fiber, composed mainly of hemicelluloses and pectin polysaccharides.

The proximate compositions of fruit residues are shown in Table 1. The hemicellulose content was present in a significant quantity, ranging from 14.46% to 26.45%, and was found to be the highest in orange bagasse. The cellulose content ranged from 9.19 to 11.93% and was the highest in orange peel. The total protein content in the raw materials ranged from 5.62% to 7.59%. It is clear that there were relatively low levels of lignin, which makes the substrates amenable to the hydrolysis process.

Other authors (Mamma *et al.* 2008; Li *et al.* 2010) have reported relatively higher values for cellulose and hemicellulose and a lower value for lignin in citrus peel waste. Fractions of neutral detergent fiber and acid detergent fiber are in the ranges of the published data for other common fruits (Happi *et al.* 2008; Ajila *et al.* 2007). The relatively low lignin content has potential implications for the effectiveness of the pretreatment processes for releasing carbohydrates for fermentation, and the high hemicellulose content indicates a significant amount of C5 as well as C6 sugars available for conversion to bioethanol.

Table 1. Compositional Analysis of Fruit Wastes on Dry Matter Basis

Component	Fruit waste, wt%			
	OB	OP	BP	MP
Hemicellulose	26.45	14.46	25.52	14.51
Cellulose	9.93	11.93	11.45	9.19
Lignin	2.81	2.17	9.82	4.25
Protein	7.59	5.97	5.62	7.00
Neutral detergent fiber	39.19	28.56	46.79	27.95
Acid detergent fiber	12.74	14.10	21.27	13.44

Total Sugars Analysis

According to the phenol-sulfuric acid method (Dubois *et al.* 1956), the developed complex absorbs UV-Vis light, and the absorbance is proportional to the sugar concentration. This assay has been used to quantify total sugars in a sample containing more than one type of carbohydrate.

A previous report indicated that at 490 nm most sugars can be measured at or near their maximum absorption and that the absorption spectra of mannose, xylose, fructose, galactose, and glucose have peaks at 491, 486, 482, 491, and 493 nm, respectively (Masuko *et al.* 2005). The results showed that the absorption bands slightly overlap due to different sugars present in the sample (Fig. 1). The maximum absorption wavelengths of substrates were all at 490 nm, and the difference in the slopes compared to the absorption at 480 nm was about 13%. This is because the maximum absorption wavelength varies considerably with the monosaccharide. The total sugars content in biomass was calculated from the equation derived from a standard curve. These results show that OB had the highest carbohydrates content, 0.591 $g{\cdot}g^{-1}$, while BP had the lowest carbohydrate content, 0.487 $g{\cdot}g^{-1}$ of dry weight biomass.

The above results may be attributed to the polysaccharides content present in each fruit residue, formed by a heterogeneous mixture of cellulose, hemicellulose, and pectin, which are the main components of plant cell walls. Therefore, the total sugar content from fruit wastes is an important parameter for bioethanol research.

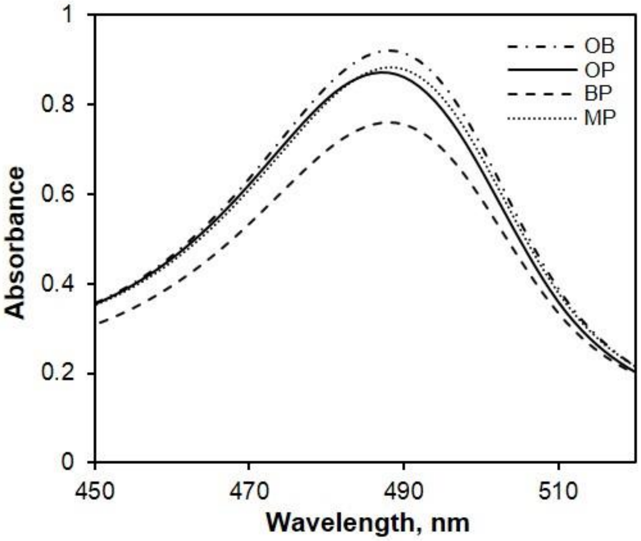

Fig. 1. Phenol-sulfuric acid assay absorbance maximum for total sugars in the fruit wastes

Scanning Electron Microscopy and EDS Analysis

Figure 2 shows the spectra obtained in the SEM using EDS of the particle core and its periphery. As illustrated in these micrographs, irregular particles with heterogeneous morphology were present. The shape of these particles is typical for fractures, and grinding wear. The size reduction of the dry substrates affect its physical properties, that is, the absorption capacity, energy retention, as well as the solubility of the material in solvents. This is very helpful to achieve the increase of the rate of hydrolysis reactions to produce fermentable sugars.

The semiquantitative analysis (Table 2) showed that the relative concentration of the elements in the residue was C > O > K > Ca > Si > Cl. EDS signals from C were predominant in the structure of the waste fruit, whereas K is one of the main components in OB, BP, and MP. In addition to K and Ca, Si and Cl were also detected as minor elements dispersed in the matrix of the residues.

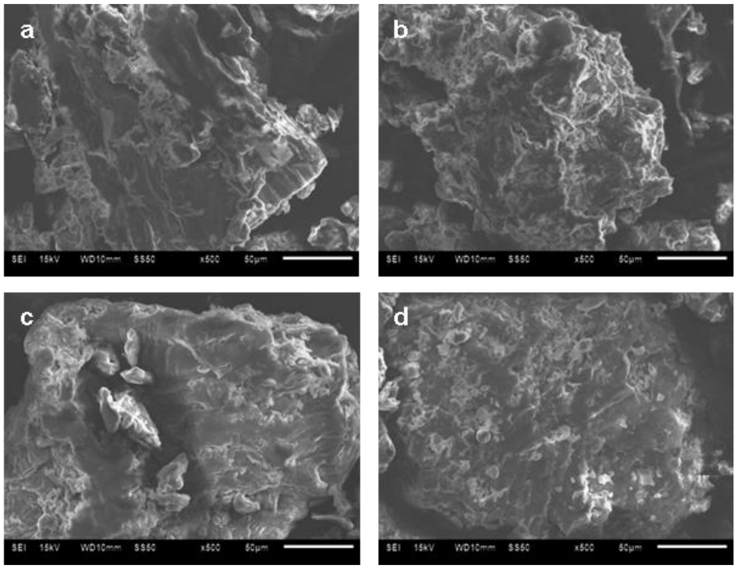

Fig. 2. Scanning electron micrographs of the fruit residues

Table 2. Results of the Semi Quantitative Analysis of the Dried Peels

Sample/Composition, wt%	C	O	K	Ca	Si	Cl
Citrus sinensis (OB)	61.94	37.12	0.24	0.70	-	-
Citrus sinensis (OP)	49.06	50.94	-	-	-	-
Musa paradisiaca (BP)	52.32	39.67	5.93	-	0.49	1.59
Mangifera indica (MP)	57.43	42.25	0.32	-	-	-

FT-IR Spectroscopic Analysis

Fourier transform infrared spectroscopy (FTIR) is widely used to identify functional groups in complex organic mixtures and to compare the similarities between substances. In this study, FTIR spectroscopy was used to demonstrate the physical structure and functional groups of the lignocellulosic materials.

The FTIR spectra of the components of the dried waste fruits are shown on Fig. 3. Most of the bands are common to those observed in cellulose, hemicellulose, and lignin FT-IR spectra (Bodirlau *et al.* 2008, Xu *et al.* 2013). Usually, the band in the high-energy region is due to a large amount of OH groups of carbohydrates and lignin.

The peaks at 3298, 3318, 3275, and 3292 cm^{-1} are due to –OH vibrations from alcohol and pectic acid components of the biomass, as shown in Table 3 and Fig. 3. The peaks at 2924 and 2920 cm^{-1} correspond to the C–H asymmetrical stretching vibration of aliphatic structures, whereas other bands in the fingerprint region (1800 to 900 cm^{-1}) are complex; this is a result of various vibration modes in carbohydrates and lignin (Bodirlau *et al.* 2008). The 1732 and 1717 cm^{-1} region of the absorbance can be assigned to the C=O stretching of carboxylic acids. Note that the C=O stretch vibrations correspond to aldehydes and are typically observed in the range of 1735 cm^{-1} (Mirada *et al.* 2009; Hernández-Montoya *et al.* 2009). The peaks at 1605, 1597, and 1612 cm^{-1} are stretching vibration of the carbon-carbon double bond, C=C. The vibrations of the aliphatic chains -CH$_2$- and -CH$_3$-, which form the basic structure of cellulosic materials, are seen at 1413, 1273, 1368, and 1328 cm^{-1}. The signals at 1045, 1011 and 1026 cm^{-1} can be attributed to C-O-H or C-O-R (alcohols or esters) vibrations (Champagne and Li 2009; Zapata *et al.* 2009). Finally, FTIR spectroscopy was used to investigate the changes in the structure of the proposed wastes, prior to any chemical or biological treatment. Although all biomass spectra were similar (Fig. 3 and Table 3), slight changes were observed from spectrum to spectrum, possibly indicating that equivalent strategies should be employed for releasing fermentable sugars from these lignocellulosics.

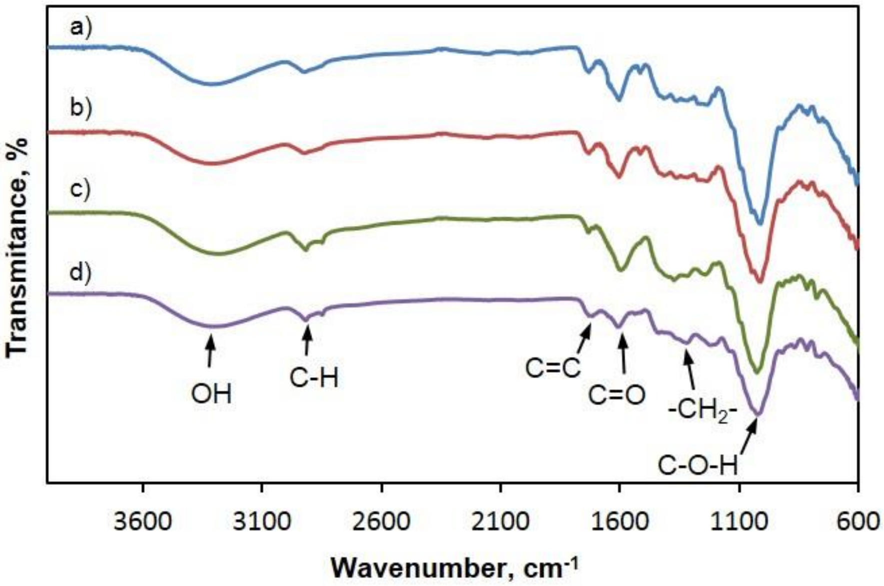

Fig. 3. FTIR spectrum for (a) orange bagasse, (b) orange peel, (c) banana peel, and (d) mango peel.

Table 3. Comparison of Infrared Bands in the 4000 to 600 cm^{-1} Spectral Region

Functional groups	Citrus waste			
	OB	OP	BP	MP
O-H stretching	3298	3318	3275	3292
C-H stretching	2924	2924	2920	2920
C=O stretching	1732	1732	1732	1717
C=C stretching	1605	1605	1597	1612
-CH$_2$- and -CH$_3$- vibration	1413	1273	1368	1328
C-O-H or C-O-R vibration	1045	1011	1026	1026

Thermal Analysis

Thermogravimetric analysis was applied to examine the thermal degradation of single waste components and their blends to determine the composition of the feedstocks. The superposition property is assumed, *i.e.*, a mixture's thermal degradation curve is obtained as the sum of the curves corresponding to its constituents. The results show that if blended, the individual components are more clearly recognized from the differential mass loss curves.

The TG and DTG curves of the waste fruit in a nitrogen atmosphere are shown in Fig. 4. According to the obtained thermal profiles, the feedstock degradation occurred in at least three steps associated with its three main components (hemicellulose, cellulose, and lignin), which can be clearly distinguished up to 600 °C. According to previous studies, the polymeric composition of lignocellulosic materials is complex, and at least two mechanisms coexist during the pyrolysis process. Such as situation can contribute to the overlapping observed in the DTG curves (Amutio *et al.* 2012; Zapata *et al.* 2009). The first one (at lower temperature) corresponds to the pyrolysis and heterogeneous oxidation, whereas the second one is attributed to the combustion of char. The sample mass decreases continuously between room temperature and 590 °C, which is related to the dehydration process and thermal degradation of the fruit wastes. In the TG curves (Fig. 4a), there are three maximal weight losses (T_{max}), and the initial mass loss (~7%) below 100 °C can be attributed to the release of weakly bonded water molecules (physically adsorbed water molecules).

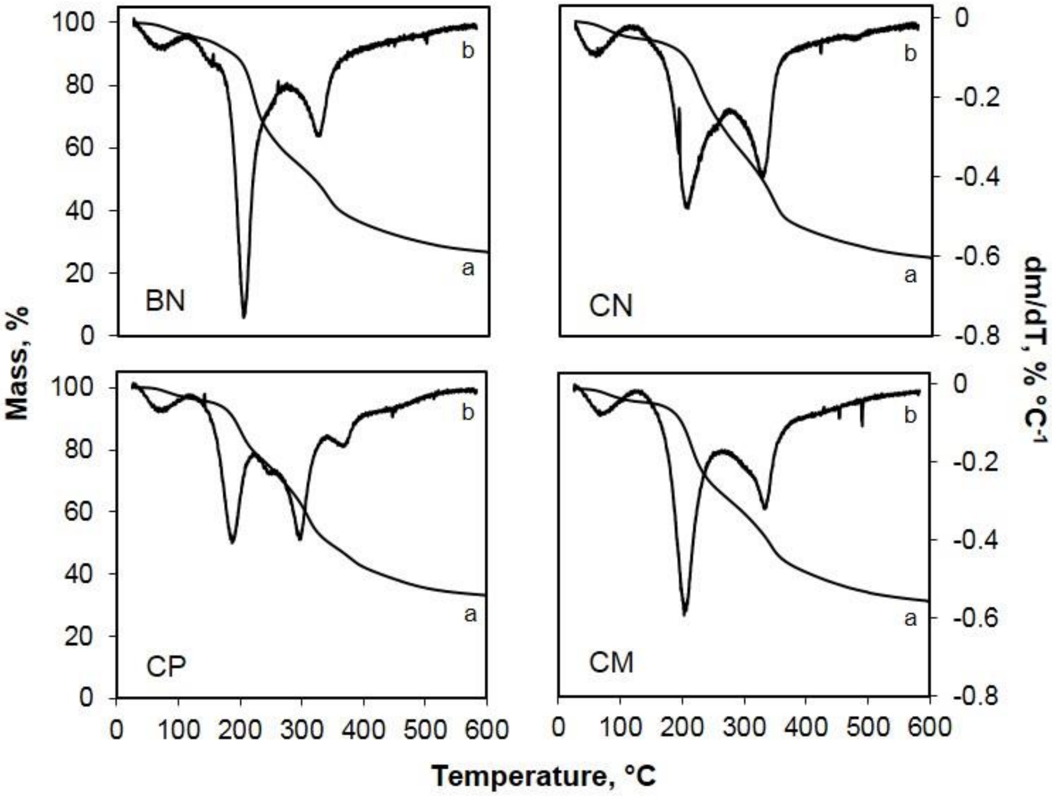

Fig. 4. TG (a) and DTG (b) curves of waste fruits in nitrogen atmosphere

According to the literature (Lv *et al.* 2010; Hernández Montoya *et al.* 2009), it has been established that there is no degradation up to 160 °C. Above this temperature, the thermal stability gradually decreases, and decomposition takes place. The thermogravimetric curves obtained by dynamic scans showed decomposition peaks at the T_{max} of 172 °C (6 wt%), 221 °C (28 wt%), 312 °C (21 wt%), and 381 °C (12 wt%), which are assigned to pectin, hemicellulose, cellulose, and lignin, respectively. Lignocellulosic resources are very susceptible to chemical reactions, and the thermal decomposition of cellulose was complete under around 360 °C. Aguiar *et al.* (2008) reported that hemicellulose decomposes between 200 and 260 ºC, giving rise to more volatiles, less tar, and less char than cellulose. The thermal episode corresponding to the degradation of lignin would be completely overlapped by those two peaks. Lignin is an amorphous cross-linked resin with no exact structure, and its degradation occurs between 280 and 500 °C. The pyrolyzable fraction of this pseudo component starts its devolatilization at the lowest temperature, but it is degraded in a wide temperature range. Lignin degradation is hindered by the decomposition of the hemicelluloses and cellulose, excepting at high temperature. These are clear pieces of evidence for the existence of multi-step processes, which are typical behavior of complex reactions, involving multiple, parallel, and consecutive processes during the degradation of lignocellulosic biomass under inert atmosphere (Amutio *et al.* 2012; Hernández Montoya *et al.* 2009; Zapata *et al.* 2009). The pyrolyzable fraction of hemicellulose was shown to have much lower thermal stability than cellulose's pyrolyzable fraction. Char fractions decompose at higher temperatures, with the hemicellulose non-pyrolyzable fraction being the one that is burnt at lower temperatures, followed by cellulose char. Lignin char was degraded at the highest temperature, and its yield was very high. In this case, the analysis is especially difficult due to the formation of complex phenolic species during lignin decomposition. This behavior has been previously reported by other authors (Amutio *et al.* 2012; Lv *et al.* 2010).

Degradation of citrus pectin also becomes complete below 400 °C (Yang *et al.* 2006; Aguiar *et al.* 2008). Similar weight loss values for the main decomposition process (from TG-DTG) were seen for all obtained biomasses, providing evidence of thermal behavior. In the present work, the thermal degradation of the waste fruit (OB, OP, BP, and MP) was completed at about 600 °C and is considered to be a global process derived from the decomposition of their principal components.

The thermal stability has been established in the following order with respect to the degradation of the main components of residual fruits: hemicellulose > cellulose > lignin (Aguiar *et al.* 2008; Zapata *et al.* 2009). According to Fig. 4a and b, the residual biomasses presented similar thermal behaviors. In general, the DSC curves (Fig. 5) had one endothermic peak and two exothermic peaks. In the spectra, the peaks at around 240 °C were probably due to the onset of the decomposition of hemicellulose. The second broad peaks at around 350 °C can be primarily attributed to exothermic reactions due to depolymerization of cellulose and to the cleavage of carbon-carbon linkages between lignin structural units.

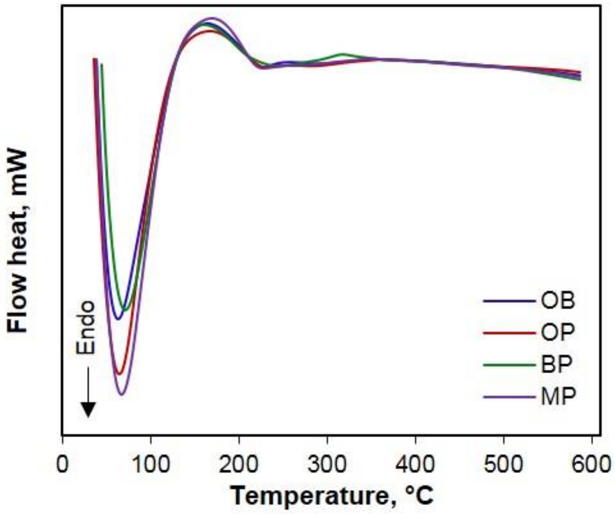

Fig. 5. DSC curves of the fruit wastes

CONCLUSIONS

1. This study evaluated different waste fruits as alternative potential feedstocks for ethanol production because of their low cost and easy availability.
2. The components for each residue studied in this work showed differences in their chemical composition. OB, OP, and MP exhibit analogous total sugars contents, with 0.9194 as the maximum value of absorbance in OB. This further suggests that lignocellulose-derived sugars would be an excellent source of energy.
3. The proposed fruit residues have potential in application as raw material in bioethanol production because of their acceptable content of cellulose and hemicellulose and low lignin content.
4. FTIR of the residual biomass showed the presence of various functional groups; aldehydes or ketones (C=O), alkanes (C-C), ethers (C-O-C), and even water molecules were detected, indicating the complex nature of the feedstocks.
5. Successful correlations between the component contents as determined by chemical and thermogravimetric analyses have been obtained. No significant differences were observed in the thermal behavior of OB, OP, BP, and MP. In the temperature range between 180 and 270 °C, hemicellulose degradation took place, probably due to depolymerization and thermal cracking of functional groups. Subsequently, between 270 and 370 °C, depolymerization and chain breaking of cellulose occur. Then, the degradation of lignin occurs between 385 and 585 °C. The reactivity of the waste components can be tentatively related to the microstructural and chemical properties of each material. The DTG curves exhibit one peak of water-soluble compounds and three main overlapped peaks attributed to hemicellulose, cellulose, and lignin. On the other hand, the thermal properties (TG and DTG curves) of the feedstocks considered in this study were influenced by the nature and component ratio due to their complex structures.

ACKNOWLEDGMENTS

The research reported here was supported by PROMEP under grant PROMEP/103.5/11/6988.

REFERENCES CITED

Aguiar, L., Márquez Montesinos, F., Gonzalo, A., Sánchez, J. L., and Arauzo, J. L. (2008). "Influence of temperature and particle size on the fixed bed pyrolysis of orange peel residues," *J. Anal. Appl. Pyrol.* 83(1), 124-130.

Ajila, C. M., Bhat, S. G., and Prasada, U. J. S. (2007) "Valuable components of raw and ripe peels from two Indian mango varieties," *Food Chem.* 102(4), 1006-1011.

Amutio, M., Lopez, G., Aguado, R., Artetxe, M., Bilbao, J., and Olazar, M. (2012). "Kinetic study of lignocellulosic biomass oxidative pyrolysis," *Fuel* 95(1), 305-311.

AOAC Association of Official Analytical Chemists. (1998). *Official Methods of Analysis of the Association of Analytical Chemists,* 16th ed., Association of Official Analytical Chemists, Washington, DC.

Berardini, N., Knödler, M., Schieber, A., and Carle, R. (2005). "Utilization of mango peels as a source of pectin and polyphenolics," *Innov. Food Sci. and Emerg. Technol.* 6(4), 442-452.

Bodirlau, R., Teaca, C. A., and Spiridon, I. (2008). "Chemical modification of beech wood: Effect on thermal stability," *BioResources* 3(3), 789-800.

Boluda-Aguilar, M., García-Vidal, L., González-Castañeda, F. P., and López-Gómez, A. (2010). "Mandarin peel wastes pretreatment with steam explosion for bioethanol production," *Bioresour. Technol.* 101(10), 3506–3513.

Brooks, A. A. (2008). "Ethanol production potential of local yeast strains isolated from ripe banana peels," *Afric. J. of Biotechnol.* 7(20), 3749-3752.

Champagne, P., and Li, C. (2009). "Enzymatic hydrolysis of cellulosic municipal wastewater treatment process residuals as feedstocks for the recovery of simple sugars," *Bioresour. Technol.* 100(23), 5700-5706.

Dubois, M., Gilles, K. A., Hamilton, J. K., Rebers, P. A., and Smith, F. (1956) "Colorimetric method for determination of sugars and related substances," *Anal. Chem.* 28(3), 350-356.

FAO. Food and Agriculture Organization. Available from: http://www.fao.org [consulted 12.08.13].

García, R., Pizarro, C., Lavín, A. G., and Bueno, J. L. (2012). "Characterization of Spanish biomass wastes for energy use," *Bioresour. Technol.* 103(1), 249-258.

Happi Emaga, L. T., Robert, C., Ronkart, S. N., Wathelet, B., and Paquot, M. (2008). "Dietary fibre components and pectin chemical features of peels during ripening in banana and plantain varieties," *Bioresour. Technol.* 99(10), 4346-4354.

Hernández-Montoya, V., Montes-Morán, M. A., and Elizalde-González, M. P. (2009). "Study of the thermal degradation of citrus seeds," *Biomass and Bioenergy* 33(9), 1295-1299.

Kaur, M., Singh, N., Sandhu, K. S., and Guraya, H. S. (2004). "Physicochemical, morphological, thermal and rheological properties of starches separated from kernels of some Indian mango cultivars (*Mangifera indica* L.)," *Food Chem.* 85(1), 131-140.

Li, K., Fu, S., Zhan, H., Zhan, Y., and Lucia, L. A. (2010). "Analysis of the chemical composition and morphological structure of banana pseudo-stem," *BioResources* 5(2), 576-585.

Liu, Y., Shi, J., and Langrish, T. A. G. (2006). "Water-based extraction of pectin from flavedo and albedo of orange peels," *Chem. Eng. J.* 120(3), 203-209.

Lv, G. J., Wu, S., and Lou, R. (2010). "Kinetic study of the thermal decomposition of hemicellulose isolated from corn stalk," *BioResources* 5(2), 1281-1291.

Mamma, D., Kourtoglou, E., and Christakopoulos, P. (2008). "Fungal multienzyme production on industrial by-products of the citrus-processing industry," *Bioresour. Technol.* 99(7), 2373-2383.

Manikandan, K., Saravanan, V., and Viruthagiri, T. (2007). "Kinetics studies on ethanol production from banana peel waste using mutant strain of *Saccharomyces cerevisiae*," *Ind. J. of Biotechnol.* 7(1), 83-88.

Masuko, T., Minami, A., Iwasakib, N., Majima, T., Nishimura, S. I., and Lee, Y. C. (2005). "Carbohydrate analysis by a phenol–sulfuric acid method in microplate format," *Anal. Biochem*. 339(1), 69-72.

Megiatto, J. D., and Hoareau, W. (2007). "Sisal fibers: Surface chemical modification using reagent obtained from a renewable source; Characterization of hemicellulose and lignin as model study," *J. Agric. Food Chem.* 55(21), 8576-8584.

Miranda, R., Bustos-Martínez, D., Sosa-Blanco, C., Gutérrez-Villareal, M. H., and Rodríguez-Canú, M. E. (2009). "Pyrolysis of sweet orange (*Citrus sinensis*) dry peel," *J. Anal. Appl. Pyrolysis* 86(2), 245-251.

Mtui, Y. S. (2009). "Recent advances in pretreatment of lignocellulosic wastes and production of value added products," *Afr. J. Biotechnol* 8(8), 1398-1415.

Neng-Guo, T., Yue-Jin, L., and Miao-Ling, Z. (2009). "Chemical composition and antimicrobial activities of essential oil from the peel of bingtang sweet orange (*Citrus sinensis* Osbeck)," *Int. J. of Food Sci. and Technol.* 44(7), 1281-1285.

Oberoi, H. S., Vadlani, P. V., Madl, R. L., Saida, L., and Abeykon, J. P. (2010). "Ethanol production from orange peels: Two-stage hydrolysis and fermentation studies using optimized parameters though experimental design," *J. Agric. Food Chem.* 58(6), 3422-3429.

Readdy, L. V., and Sarathi, O. V. (2007). "Production ethanol from mango (*Mangifera indica* L) fruit juice fermentation," *Res. J. Microbiol.* 2(10), 763-769.

Rezzoug, S. A., and Louka, N. (2009). "Thermomechanical process intensification for oil extraction from from orange peels," *Innov. Food Sci. and Emer. Technol.* 10(4), 530-536.

SAGARPA. Ministry of Agriculture, Livestock, Rural Development, Fisheries and Food, http://www.sagarpa.gob. Competitiveness trends report [consulted 12.08.13].

Sánchez-Orozco, R., Balderas-Hernández, P., Flores-Ramírez, N., Roa-Morales, G., Saucedo-Luna, J., and Castro-Montoya, A. J. (2012). "Gamma irradiation induced degradation of orange peels," *Energies* 5(8), 3051-3063.

Velásquez-Arredondo, H. I., Ruiz-Colorado, A. A., and Oliveira-Junior, S. (2009). "Ethanol production from banana fruit and its lignocellulosic residues: Energy and renewability analysis," *Int. J. of Thermodynamics* 12(3), 155-162.

Wilkins, M, R. (2009). "Effect of orange peel oil on ethanol production by *Zymomonas mobilis*," *Biomass and Bioenergy* 33(3), 538-541.

Wilkins, M. R., Widmer, W. W., and Grohmann, K. (2007). “Simultaneous saccharification and fermentation of citrus peel waste by *Saccharomyces cerevisiae* to produce ethanol,” *Process Biochem.* 42(12), 1614-1619.

Xu, F., Yu, J., Tesso, T., Dowell, F., Wang, D. (2013). “Qualitative and quantitative analysis of lignocellulosic biomass using infrared techniques: A mini-review,” *Appl. Energy* 104(1), 801-809.

Yang, H. P., Yan, R., and Chen, H. P. (2006). “In-depth investigation of biomass pyrolysis based on three major components: Hemicellulose, cellulose and lignin,” *Energy and Fuels* 20(1), 388-393.

Zapata, B., Balmaseda, J., Fregoso-Israel, E., and Torres-García, E. (2009). “Thermo-kinetics study of orange peel in air,” *J. Therm. Anal. Calorim.* 98(1), 309-315.

Article submitted: October 2, 2013; Peer review completed: November 2, 2013; Revised version received and accepted: February 2, 2014; Published: February 6, 2014.