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Thermochimica Acta

journal homepage: www.elsevier.com/locate/tca

A lumped kinetic model for banana peel combustion

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ARTICLE INFO

ABSTRACT

Article history: Received 22 April 2015 Received in revised form 11 June 2015 Accepted 12 June 2015 Available online 17 June 2015

Keywords: Banana peels Devolatilization Combustion Kinetics Thermogravimetric analysis in air of banana peel and related chars, produced at temperatures of 700– 950 K, is carried out. Compared with wood, the two consecutive processes of devolatilization and combustion take place over wider temperature intervals. Two peaks are evident for both the first zone (instead of a shoulder and a peak) and the second zone (instead of a single peak). The analysis of integral and differential data, obtained for a heating rate range of 5–20 K/min, leads to a kinetic model consisting of four reaction steps. The two devolatization steps require low activation energies (82 and 86 kJ/mol), consequent to the presence of a large number of chemical components (starch, sugars, pectin, lipids and proteins, in addition to cellulose, hemicelluloses and lignin). The first and chief combustion step is also described by a low activation energy (112 kJ/mol) whereas the second one requires an activation energy (180 kJ/mol) coincident with that typically estimated for lignocellulosic chars. SEM and EDX analyses reveal a scarcely porous microstructure with a few large channels immersed into a honeycomb-type tissue scattered with deposits rich in potassium and chlorine.

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1. Introduction

The cultures of banana and plantain rank fourth in the most significant world foodstuffs after corn, rice and wheat [1,2]. Banana trees grow in large quantities in tropical and subtropical areas. World production of the Musa variety in 2003 was estimated at 102 million tons, of which about 68% was classified as bananas and 32% as plantains [3]. Plantain and cooking bananas are very similar to unripe dessert bananas in outward appearance, although often larger. The major differences are that they are starchy rather than sweet, used unripe, and require cooking.

As the development of the processing industries of bananas and plantains (dried chips, flours and pulps, jam, spirits distilled from wine or beer) is growing, significant quantities of banana or plantain peels, equivalent to 40% of the total weight of fresh product, are generated. It is thus significant and even essential to find applications for these wastes, also because they cause a real environmental problem [4]. The texture of banana peel is porous and formed by cellulose, hemicellulose, pectins, lignin, starch and proteins, peculiarities that have motivated several applications [5,6]. It is an economic and selective sorbent for the absorption of phenolic compounds and metal ions from aqueous solutions, not only due to the pore structure but also to carboxyl and hydroxyl groups on the pore surfaces. Banana peel extract is used for the synthesis of palladium, silver and gold nanoparticles and for the synthesis of hierarchical porous carbon foams (banana peel zinc complexes). In some cases it has been used for the production of alcohol, methane, food for livestock or compost. Also attempts are under way [7] to utilize highadded value compounds of this waste, including the dietary fibre fraction that has a great potential in the preparation of functional foods.

Banana peel is a waste with a high initial moisture content (about 80% on a total basis), which is most likely the main reason for its scarce consideration in thermal and chemical conversion processes apart from a recent analysis as a biochar precursor [8]. However, for a preliminary evaluation of its actual potential, the knowledge of its main properties in pyrolysis and combustion is needed. This study represents the first step in this direction. Thermogravimetric curves, in air, are measured of pre-dried dessert banana peels and pyrolysis chars aimed at the formulation of a lumped kinetic model. Also Scanning Electron Microscope (SEM) and Energy Dispersive X-ray (EDX) analyses are applied to investigate the morphological structure of the material.

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2.1. Chemical composition

The specific chemical composition of the dessert banana peel. originated from Ecuador and at an average ripeness level, used in this study has not been determined but the chief information on this aspect, which is useful to explain the presence of various reaction zones in the thermogravimetric curves, can be found in the literature. In fact the chemical composition of this waste, which highly deviates from those usually reported for lignocellulosic biomass, requires the application of specific methods and has been the topic of several papers. In particular, as the composition of banana and plantain pulp changes dramatically during ripening, the chemical composition has been examined [5,9] at three stages of maturation. Considering the dessert banana varieties, which are of interest for the present study, the reported inorganic matter content range from about 9 to 13% of the total dry mass, figures that include that found for the sample under study (11%, determined according to the procedure described in Ref. [10]). It appears [5] that the major components are potassium, phosphorus, magnesium and calcium, while iron, zinc, manganese and copper are present in low amounts. More precisely, potassium (values approximately around $55000-63500 \text{ mg kg}^{-1}$ is the most abundant, followed by phosphorus, calcium, and magnesium. On the whole [5,9], the content of total dietary fibers is around 40-50% but the contents of cellulose (7.5%), hemicellulose (6-8%) and lignin (12–7%) are much lower than those typically observed for lignocellulosic biomass. The significant part of the water soluble part of the dietary fibers is most likely constituted by pectin (10-13%). The total content of sugars increases with the ripeness degree (glucose 1-14%, fructose 1-18% and sucrose 1.5-0.5%) essentially at the expenses of the starch percentage which decreases (11-3%). The amount of crude vitamins and fats also increases with the ripeness stage (6-10% and 4-11%, respectively). From these figures, it can be reasonably assumed that the main component of the banana peels examined in this study approximately consists of sugars (30%), comparable values of cellulose, hemicellulose, lignin and pectin (around 10% each), on one hand, and comparable values of proteins, fats and starch on the other (around 5%).

2.2. Experimental details

Two different sets of tests are carried out with the scope of investigating 1) the thermogravimetric behavior of banana peel and banana peel char combustion, aimed at producing data for kinetic analysis, and 2) the morphological structure of char produced from banana peel pyrolysis, studied by means of SEM and EDX analyses (this set of experiments also provides the char samples to be used for the thermogravimetric tests).

The first set of experiments is made in air using banana peel and banana peel char (this produced at various temperatures), previously milled to powder (particle sizes below 80 µm) and pre-dried for 8 h under a forced air flow at 323 K and for 24 h in a static oven at 338 K. The thermogravimetric tests are made using a non-commercial system already extensively applied to study solid conversion under conditions of kinetic control [11-21], which allow for an optimal control of the sample temperature. Experiments are made with a sample mass of 4 mg and heating rates of 5,10 and 20 K/min up to a final temperature of 950 K. These conditions, aside from allowing for a rigorous control of the sample temperature, also guarantee that mass transfer limitations are absent. Indeed, no variation is observed in the measured thermogravimetric curves as long as the mass sample is maintained below 7.5 mg (the investigation is made for the most critical thermal condition i. e. 20 K/min). Each thermogravimetric test is

The second set of experiments is made in nitrogen using single banana peel particles (slabs $30 \text{ mm} \times 5 \text{ mm}$ corresponding to a mass around 134 mg) with no pretreatment apart from pre-drving as above. The particles are instantaneously suspended in a preheated (isothermal) cylindrical stainless reactor [22] the temperatures of 700, 800, 900 and 950 K. Each pyrolysis test is made in triplicate, showing an excellent reproducibility in relation to the char yield (standard deviation of 0.1%). The char yields are 35 (700 K), 33 (800 K), 31.5 (900 K) and 29.7% (950 K) on a dry mass basis. These samples are used to investigate the influence of the pyrolysis conditions on the combustion reactivity of the chars (thermogravimetric measurements at 5 K/min up to a temperature of 950K using a 4 mg mass sample) and the morphological structure (together with banana peels) using SEM and EDX analyses. The conditions of the thermal analysis, aside from allowing for a rigorous control of the sample temperature, also guarantee that mass transfer limitations are absent. Indeed, no variation is observed in the measured thermogravimetric curves as long as the mass sample is maintained below 5.5 mg (the investigation is made for the most critical thermal condition i. e. the char sample produced at 950 K).

3. Results

3.1. Thermogravimetric characteristics

The thermogravimetric curves for banana peel, measured in air at 5 K/min, are compared with those of beech wood in Fig. 1. Also, for comparison purposes the measurements obtained in nitrogen (a 4 mg sample heated at 5 K/min up to 950 K) using a commercial system (Mettler TGA/1) are included. Using beech wood as a comparison term, it can be immediately seen that banana peel devolatilization and combustion occur over a much wider temperature range, with the beginning anticipated by about 65 K and the burnout delayed by about 100 K. As a consequence, the rates of mass loss are, on the average, lower also because of the significant inorganic matter content. Moreover the position of the peaks/shoulders is different. The devolatilization of banana peels presents two well evident peaks that are anticipated with respect to the shoulder and peak exhibited by beech wood. In fact, the first relevant event at low temperature (about 470 K) is a well defined

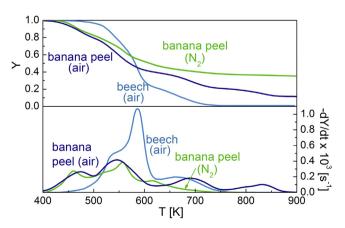


Fig. 1. Mass fraction, Y, and mass loss rate, -dY/dt, for banana peel and beech wood measured in air versus temperature (heating rate 5 K/min). For comparison purposes, the data for banana peel obtained in nitrogen are also included.

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