Production of Fiber-Rich Powder by the Acid Treatment of Unripe Banana Flour

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ABSTRACT: The acid treatment of unripe banana flour (UBF) was carried out to obtain a fiber-rich product, and some functional and physicochemical characteristics were tested. An experimental design with temperature, time, and acid concentration as independent variables produced 20 experiments that were studied with a response surface methodology to discover the effect of these variables on the total dietary fiber (TDF) content. UBF showed a TDF content of 17% and a total starch content of 73%. The response surface regression model fitted to experimental results of TDF showed a good determination coefficient (94%). The maximum TDF content that predicted the model was 61.0% with conditions of 38°C, 11 days, and an acid concentration of 1.6*M*. During model validation for TDF, the model explained the experimental results to 99.5%. The thermal characterization of the fiber-rich products after the acid treatment [acid-treated unripe banana flour (ATUBF)] showed higher thermal stability than its parental sample. The water absorption index of ATUBF was lower but the water solubility of ATUBF was higher than its native counterpart. The preparation of a fiber-rich product with UBF may be important for the development of food and medical products. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 109: 382–387, 2008

Key words: biological applications of polymers; biomaterials; biopolymers; differential scanning calorimetry (DSC); thermal properties

INTRODUCTION

Bananas are grown extensively in tropical and subtropical regions and are an important food crop. Banana is a climacteric fruit, and in México, it is consumed when the fruit is ripe. For this reason, many fruits are lost during commercialization due to deficient postharvest handle. New economical strategies are now being considered for banana use, such as the production of banana flour (BF) when the fruit is unripe. Starch is the principal component of green bananas and is very resistant to digestion in rats and man. Faisant and coworkers[1,2] studied the digestibility of banana starch granules in the human small intestine and reported the starch breakdown and also the structural features of resistant starch (RS). Recently, the preparation of unripe banana flour (UBF) was described; the flour had a 73.4% total starch (TS) content, a 17.5% RS content, and a dietary fiber level of 14.5%.[3] Also, a fiber-rich powder prepared by the enzymatic starch liquefaction of UBF presented a dietary fiber content of 31.8%, and it was pointed out that this flour might be an important source of polyphenols, compounds that are regarded as natural antioxidants.[4]

Nowadays, the development and use of functional ingredients is widely exploited by the food industry, principally those containing high dietary fiber levels. Recently, it was reported that dietary fiber is an interesting group of nutrients, and it is still a lively topic for further scientific research, discussions, and consumer education.[5] Although bananas represent an alternative source of indigestible carbohydrates, mainly RS and dietary fiber, it is important to keep in mind that when the unripe fruit is cooked, its native RS is rendered digestible.[6] It is also important to stress that the dietary fiber content of this fruit is relatively low compared with other dietary fiber source fruits.[7–12] The technology of starch lintnerization has been applied to starch isolated from unripe bananas for producing RS powder.[13] In this way, it is possible to increase the crystalline structure of

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TABLE I
Experimental Design for the Chemical Modification of Banana Flour (BF)

	Independent variable (real value)		
Treatment	X_1 [temperature (°C)]	X_2 [time (days)]	X_3 [concentration (M)]
1	33	5	1
2	42	5	1
3	33	16	1
4	42	16	1
5	33	5	2.2
6	42	5	2.2
7	33	16	2.2
8	42	16	2.2
9	30	10.5	1.6
10	45	10.5	1.6
11	37.5	1	1.6
12	37.5	20	1.6
13	37.5	10.5	0.6
14	37.5	10.5	1.6
15	37.5	10.5	1.6
16	37.5	10.5	1.6
17	37.5	10.5	1.6
18	37.5	10.5	1.6
19	37.5	10.5	1.6
20	37.5	10.5	1.6

starch and, consequently, the resistance to enzymatic hydrolysis by digestive enzymes. However, the starch isolation procedure increases the labor and, consequently, the cost of the process. It is possible to develop a simple procedure to modify the starch present in the UBF with the concomitant increase in its enzymatic resistance and in the dietary fiber content.

The objective of this study was to obtain a fiber-rich powder prepared by the acid treatment of UBF and to evaluate some of its physicochemical and functional characteristics with surface response methodology.

EXPERIMENTAL

BF preparation

Commercial hard green (unripe) preclimateric banana (*Musa paradisiaca L.*) fruits were purchased from the local market in Cuautla, Morelos State, México. Fruits were cut into 1-cm slices and were immediately rinsed in citric acid solution (0.3% w/v). The slices were dried at 50°C, ground with a commercial grinder (Mapisa Internacional Sociedad Anónima de Capital Variable, México, Distrito Federal) to pass a US 50 sieve, and stored at 25°C in sealed plastic containers until further analyses could be carried out.

Chemical composition of UBF and acid-treated unripe banana flour (ATUBF)

Moisture content was determined by gravimetry; the sample (2–3 g) was heated (130 ± 2°C for 2 h). The ash, protein, fat, and dietary fiber contents were analyzed according to AACC methods 08-01, 46-13, 30-25, and 32.05, respectively.[14] TS was determined by the method of Goñi et al.[15] In brief, 50 mg of sample was dispersed in 2*M* KOH (30 min) and was then incubated with amyloglucosidase (Boehringer, no. 102857, 60°C, 45 min, pH = 4.75), and the glucose content was determined with the glucose oxidase assay the glucose oxidase-peroxidase (GOD-POD). TS was calculated as Glucose (mg) × 0.9; potato starch was used as a control.

Acid treatment of BF

BF (100 g) was added to 400 mL of HCl at different concentrations and allowed to react for diverse times and at diverse temperatures with a stirrer operating at 200 rpm (Table I). The experimental design consisted of 20 runs with six replicates in the central point. The experimental design was chosen to reduce the number of treatments required to obtain relationships for the range of independent variables studies. After the reaction, the blend was neutralized with NaOH at the same concentration of HCl used; the pH was adjusted to 7.0. Thereafter, the wet powder was washed with distilled water. The residue was dried in an oven at 50°C for 24 h, ground with a commercial grinder (Mapisa Internacional SA de CV) to pass in a US no. 50 sieve, and stored at room temperature (25°C) in a sealed glass container.

Thermal analysis

The thermal properties of the BF and fiber-rich powder (ATUBF) were studied with a differential

scanning calorimeter (TA Instruments, model 2010, New Castle, DE) previously calibrated with indium. The transition temperature was evaluated by the method proposed by Paredes-Lopez et al.[16] The sample (2 mg) was weighed (dry basis, sample number (n) = 3) on an aluminum pan, and 7 μL of deionized water was added. The pan was sealed tightly, and then, it was allowed to stand for 1 h before the analysis was carried out. An empty aluminum pan was used as a reference. The sample was subjected to a heating program over a range of temperatures from 20 to 120°C at a heating rate of 10°C/min in air. The peak temperature (T_p) and the transition enthalpy were obtained directly from the analysis of the software TA Instruments OS/2 version 2.1.

Water absorption index (WAI) and water solubility index (WSI)

WAI and WSI were measured according to a modified method of Anderson et al.[17] The sample (2 g, dry basis) was mixed with 25 mL of water in a centrifuge tube. After it was heated for 30 min in a water bath at 30°C, the solution was centrifuged at 3000 × g for 10 min. The supernatant was placed in a Petri dish and dried at 90°C for 4 h to obtain the dry solid weight, and the wet sediment was weighed. The WAI and WSI were determined as follows:

$$\text{WAI} = (\text{Weight of the wet sediment} / \text{Weight of the dry sample}) \times 100$$

$$\text{WSI} = (\text{Weight of the dry solids in the supernatant} / \text{Weight of the dry sample}) \times 100$$

X-ray diffraction analysis

X-ray diffraction allows the determination of crystallinity and composition of crystalline phases in starch samples.[18–20] The samples were stored at room temperature before analysis. They were scanned in the angular range 3–37° (2θ) with an Advance D8 Diffractometer from Bruker (Coventry, UK) at 35 kV with Cu Kα radiation (1.542 Å). The crystallinity percentage (%C) was determined form the diffractogram by calculation of the area corresponding to the crystalline peaks (A_p; from the difference between the area under the curve and the area of the amorphous halo), the total area under the curve (A_t), and the instrumental noise (N) according to the following equation:[20]

$$\%C = A_p/(A_t - N) \quad (1)$$

The amorphous halo was determined with the amorphous component of starch obtained with an extraction procedure reported elsewhere.[21]

Experimental design and statistical analysis

Response surface methodology was chosen to build some mathematical models with a central composite rotational design, which made it possible to quantitatively interpret and describe the relationship between the selected independent variables [temperature, time, and acid concentration (Table I)] and the dependent variable [total dietary fiber (TDF)]. The data were analyzed with the JMP 4.0.4 for Windows program (SAS, Inc., Raleigh, NC, 1989) to investigate the trends of TDF. Surface plots were drawn with SigmaPlot for Windows 5.0 (SPSS, Cary, NC, 1986) computer software to show the effect of two independent variables. Validation of the mathematical model was carried out by the production of fiber-rich powder with the operational conditions predicted by the model for the highest dietary fiber production. Those powders were assessed for thermal characteristics, WAI, and WSI.

RESULTS AND DISCUSSION

Chemical composition of UBF

UBF had a moisture content of 12.64% (Table II), higher than those determined in BF obtained from the pulp (7.1%[3]) and for the pulp and peel (6.0%[4]). The difference might have been related to the time used in the drying process. However, the moisture content of UBF was similar to that obtained for commercial wheat flour (11.4%[22]).

The protein level of UBF (Table II; 4.03%) resembled that reported previously for BF (3.8%[1]) but was slightly higher than that of BF prepared with pulp (3.27%[3]), that of BF prepared with pulp and peel (3.4%[4]), and those measured in eight different varieties of banana, whose values ranged between 2.5 and 3.3%.[23] The differences shown were related to the variety, cultivar, soil, altitude, agronomic trials, and procedure used for flour preparation.

UBF exhibited a 4.64% ash content, which was similar to that reported for BF prepared with the

TABLE II
Chemical Composition of the Banana Flour (BF) (*Musa paradisiaca L.*) Prepared from Unripe Fruit

Component	Content (%)
Moisture	12.64 ± 0.02
Fat	3.24 ± 0.03
Protein[a]	4.03 ± 0.06
Ash	4.64 ± 0.04
TDF	17.14 ± 0.19
TS	73.01 ± 0.06

The data are presented as the mean of three replicates plus or minus the standard deviation (dry basis).
[a] Nitrogen × 6.25.

TABLE III
Effect of the Acid Treatment of Unripe Banana Flour (UBF) on the Total Dietary Fiber (TDF) Content

Treatment	TDF
1	30.80 ± 0.02[d]
2	27.65 ±0.34[e]
3	33.42 ± 0.01[d]
4	27.65 ± 0.04[e]
5	33.13 ± 0.02[d]
6	23.00 ± 0.26[f]
7	44.52 ± 0.13[b]
8	35.64 ± 0.34[c]
9	42.89 ± 0.32[b]
10	37.64 ± 0.22[c]
11	19.81 ± 0.07[g]
12	37.26 ± 0.04[c]
13	30.33 ± 0.11[d]
14	22.36 ± 0.05[f]
15	60.03 ± 0.012[a]
16	60.02 ± 0.02[a]
17	60.16 ± 0.23[a]
18	60.02 ± 0.48[a]
19	60.03 ± 0.02[a]
20	60.04 ± 0.04[a]

The data are presented as the mean of three replicates plus or minus the standard deviation (dry basis). Values followed by the same letter are not significantly different ($\alpha = 0.05$).

pulp (4.70%[3]) and BF prepared with pulp and peel (4.4%[4]). Lower ash contents (2.6–3.5%) were determined in UBFs.[23]

The UBF we analyzed had a lipid content of 3.24%, similar to the value (2.69%[3]) reported for BF but higher than the values obtained for BF elaborated from diverse unripe bananas (0.33–0.82%[23]). The high lipid content of the UBF could have been due to the fact that in our study, a complete banana was used (pulp and peel) and compounds present in the peel (e.g., carotenoids, chlorophylls) were recovered during the extraction, as was observed in the color of the extract obtained after extraction with hexane.

TDF in the UBF was 17.14% (Table II). A lower TDF level (14.52%[3]) was previously determined in BF and BF obtained with a complete banana (10.4%[4]); such a discrepancy may have been due to possible different fruit ripening states and variable characteristics of the cultivars used in these three studies. However, the TDF content of UBF should have been higher because this flour was prepared with a complete banana. TDF contents ranged between 6.28 and 15.5% in flours prepared from eight different banana cultivars.[23] A lower TDF value (9.2%) was reported for another BF preparation.[1]

The pulp of unripe bananas features a high starch content,[2,3] and this was confirmed by our results (73.01%, Table II). In previous studies characterizing unripe BFs, TS contents were reported as 61.3 and 76.5%,[23] 73.36%[3] for BF prepared with pulp, and 76.8%[4] for BF prepared with a complete banana.

Acid treatment of UBF

The TDF content was compared to those of the UBF and ATUBF samples to evaluate the effect of acid treatment on the TDF content. The acid treatment increased the TDF content from 17.14% in the raw UBF to a maximum value of 60.0% (Table III). This might have been due to the fact that acid treatment selectively removed amorphous regions of starch granules and, thus, yielded materials enriched in amylopectin crystallites, as was demonstrated in the study of lintnerized banana starch.[13,24] These crystallites were resistant to enzymatic hydrolysis, and consequently, this residue was quantified in the TDF by an increase in its level.

The response surface regression model fitted to the TDF experimental results showed a good adjusted determination coefficient (94%):

$$\mathrm{TDF} = -486.37 + 22.68T + 7.51t + 112.97C - 0.31T^2 - 0.33t^2 - 36.09C^2 \quad (2)$$

where T is the temperature, t is the time, and C is the acid concentration.

During the acid treatment of UBF, the temperature, time, and acid concentration had a direct effect on the TDF content in the ranges between 33 and 42.5°C [Fig. 1(a)], 5 and 17 days [Fig. 1(b)], and 1.0 and 2.2*M* [Fig. 1(a)]. Also, no interactions among the independent variables studied were found. The empirical model obtained in this study predicted a maximum value of TDF amount of 61.0% at a temperature of 38°C, a time of 11 days, and an acid concentration of 1.6*M*. When validation of the model was carried out under these optimal conditions, five

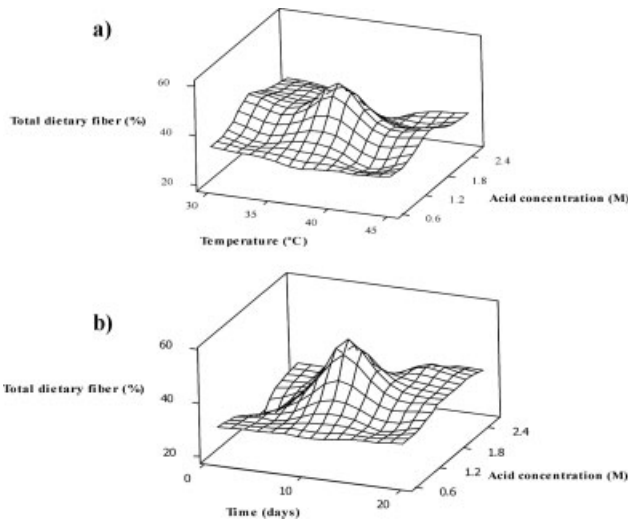

Figure 1 Effect of chemical modification of banana flour (BF) on the total dietary fiber content (TDF): (a) temperature versus acid concentration, and (b) time versus acid concentration.

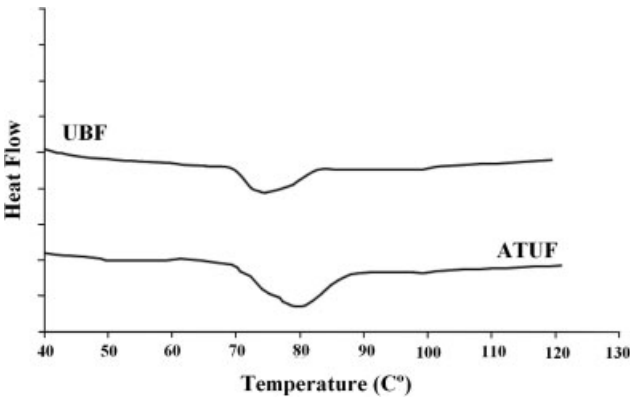

Figure 2 Differential Scanning Calorimetric (DSC) thermograms of lintnerized banana flour. Untreated banana flour (UBF) and acid treated banana flour (ATUBF).

products were obtained with a TDF content of 60.71 ± 0.25%. This result was only 0.5% below the maximum value predicted by the model.

Thermal analysis

The thermograms for UBF and ATUBF are show in Figure 2. Both samples presented an endotherm with a definite peak of the phase transition. The T_p of UBF (72.5 ± 0.4°C) was lower than that of ATUBF (80.5 ± 0.24°C). The endotherm obtained in the UBF was related principally to the starch gelatinization because Millan-Testa et al.[25] reported a T_p for starch isolated from unripe bananas of 77.6°C. The higher temperature of UBF after the acid treatment was due to crystallite formation, which presented perfection, and these were disorganized at higher temperatures. This pattern was corroborated by the value of the enthalpy of the transition because the ATUBF sample presented higher enthalpy values (30.31 ± 0.35 J/g) than UBF (6.49 ± 0.42 J/g). It was reported that the differential scanning calorimetry (DSC) endotherm gives a measure of crystallite quality from T_p and overall crystallinity from gelatinization enthalpy.[26] Their results showed that acid-treated starches had higher crystallinities, as tested by X-ray diffraction patterns, and higher T_p and enthalpy values. However, the authors mentioned that crystallite perfection must be the principal mechanism controlling this phase transition in the acid treatment of starches.

WAI and WSI

The results of WAI and WSI are presented in Figure 3. ATUBF showed lower WAI values than UBF in the range of temperatures tested [Fig. 3(a)]. This pattern was due to the formation of higher crystallinity during the acid treatment, where chain–chain interactions by OH groups were carried out, which decreased the hydrogen bonds between the water molecules and OH groups of glucose residues. Because of the aforementioned crystallinity as tested, the crystallinity of UBF was 19.36% and that of ATUBF was 22.21% because the acid treatment degraded the amorphous zones of the starch present in the UBF, which increased the crystallinity. Aparicio-Saguilán et al.[13] reported that the swelling (g of water/g of dry sample) of lintnerized banana starch did not change with the temperature, and those values were lower than those of its native counterpart. When the temperature increased between 50 and 75°C, the WAI values increased, but at 90°C, the values decreased for both samples. For UBF, this behavior may be explained by the following: at higher temperatures, starch gelatinization was carried out, the granular structure was lost, and only partial water absorption was, therefore, obtained. For ATUBF, this pattern may have been associated with a partial disorganization of the crystallites of amylopectin produced during the acid treatment, which produced solubilization of the starch chains.

Both UBF and ATUBF showed increased WSI values with temperature, and statistical differences were found between both samples at the same temperature and among the diverse temperatures tested [Fig. 3(b)]. ATUBF had a higher WSI than UBF; this pattern was due to the lower thermal stability of crystallites formed during the acid treatment than when they were solubilized in higher amounts, and the effect was more notorious at higher temperatures.

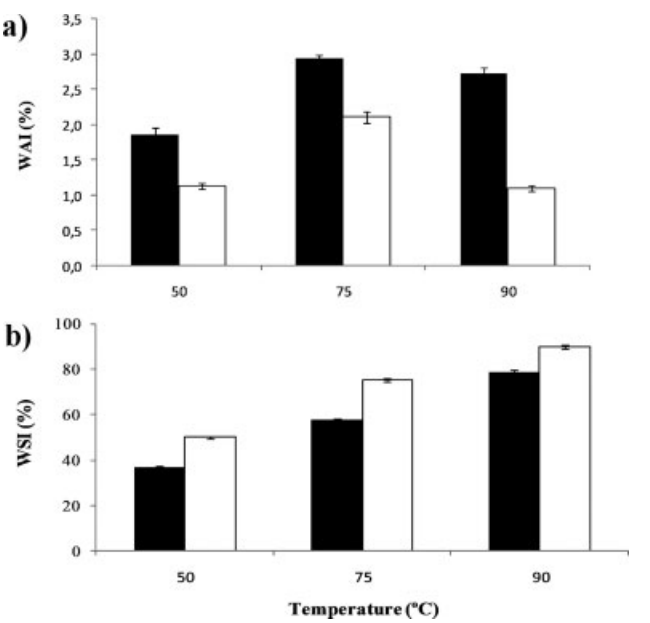

Figure 3 (a) Water absorption index (WAI) and (b) water solubility index (WSI) of lintnerized banana flour (BF): (■) untreated banana flour (UBF) and (□) acid treated banana flour (ATUBF). The data are present as the mean of three replicates plus or minus the standard error.

CONCLUSIONS

Temperature, time, and acid concentration affected TDF formation during the acid treatment. The maximum TDF value in ATUBF was 61%; the model predicted a TDF content with 99.5% exactitude, and this can be considered adequate for the study of response tendencies. The ATUBF had a higher temperature and enthalpy of the phase transition, as assessed by DSC, than its native counterpart, which showed a higher thermal stability. The ATUBF had a lower WAI but a higher WSI than its parental sample. This pattern was attributed to the higher crystallinity produced during the acid treatment, as tested in the X-ray diffraction study. ATUBF could be used in food and medical applications because of the increase in the consumption of fiber-rich products.

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