Effect of Tempering Parameters on Extraction and Ash of Proso Millet Flours, and Partial Characterization of Proso Starch[1]

G. A. YANEZ and C. E. WALKER[2]

ABSTRACT

White proso millet (*Panicum miliaceum*) samples were tempered at three moisture levels and five different times before milling in a Brabender Quadrumat Jr. mill and sifting to obtain bran, coarse, and fine flours. The ash content and percent extraction decreased with increasing temper time, although flour extraction reductions were less pronounced. Ash content seemed to increase with increasing moisture, especially at higher levels. Starch characteristics were measured using a "microbowl" Brabender amylograph, differential scanning calorimetry, and Kofler hot stage. Results showed that the method used to isolate the starch influenced its characteristics. Under microscopic observation, proso starch granules were found to resemble those of rice but were similar to corn (maize) in gel and pasting characteristics.

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The millets are small-seeded, annual cereal grasses of the family Graminae, many of which are adapted to hot dry climates. Along with sorghum, millets constitute a major source of energy and protein for millions of people in Asia and Africa (Hulse et al 1980).

Proso millet (*Panicum miliaceum*) is the only grain millet of economic importance in the United States, where it is used in a rotation crop system for animal feed and birdseed. Only a very small portion of this crop is used directly as human food, mainly because of its poor palatability principally caused by the high ash and fiber content of the hulls (Desikachar 1976, Luis et al 1982). An additional reason for its infrequent use in human food is that very little research has been conducted on this grain, and it is unfamiliar to most U.S. food scientists and consumers. Until now, good food applications have not been found.

Lorenz and Dilsaver (1980) showed that good quality flour can be obtained by comilling proso with wheat and using the flour in bread, cookies, and noodles. Few investigations have been made, however, on individual proso millet constituents.

The objectives of this study were to determine the effect of moisture levels and tempering time before milling on the ash content and yield of the flour, and to isolate and partially characterize proso millet starch.

MATERIALS AND METHODS

Milling

A bulk sample of white proso millet (variety Dawn) was obtained locally. The test weight of the grain was measured using a sample container of known volume, filling it and leveling off the grain, and averaging the weight of 10 determinations. The 1,000-kernel test weight was determined by choosing 100 seeds at random, 10 times, and recording their weights. A cyclone sample mill (Udy Corp., Boulder, CO 80301) with a 1-mm screen was used to prepare a whole grain flour. No tempering or sifting was used in preparing this comparison flour.

The samples, initially at 11% moisture, were tempered to three moisture levels (15, 16.5, and 18%) before milling, five different times for each moisture level (0.5, 1.0, 1.5, 2.0, and 3.0 hr). These starting points were chosen based on the work of Perten (1977), who tempered pearl millet for 30 min. A response surface methodology (RSM) program (Walker and Parkhurst 1984) was used to analyze the data and predict a general equation describing the results.

Tempered samples of 100 g each were milled in a Brabender Quadrumat Jr. laboratory mill (C. W. Brabender Instrument Inc., South Hackensack, NJ 07606). The milled sample was then sifted through 60 and 100 mesh, U.S. standard 8-in. sieves for 160 sec. A gyratory shaker (Strand Manufacturing Co., Minneapolis, MN 55426) was used to separate the samples into bran (+60 mesh), coarse (−60, +100 mesh), and fine (−100 mesh) flours.

The proximate composition of the whole grain flour, and the ash and moisture for each of the tempered flours, were determined according to AACC (44-19, 46-12; 1983) and AOAC (7.010, 7.045, and 7.054; 1975) standard methods. Average flour particle size was measured with a Fisher sub-sieve sizer model 95 (Fisher Scientific and Allied Co., Pittsburg, PA 15219).

Starch

A laboratory wet-milling technique developed for corn (Nerying and Reilly 1984) was used as one of the two methods for the isolation of proso millet starch. Extra steps were added, including centrifuging and scraping the gluten from the starch-gluten slurry several times, and lactic acid was used (instead of sulfuric) to adjust the pH to 4–5. The second laboratory method used was described by Juliano (1984) for the preparation of rice starch using alkaline solutions and shorter steeping times. This method was selected because of the microscopic resemblance in size and shape between rice and proso starch granules. Flow charts for the procedures are shown in Table I.

Whole grain starch content was determined using the techniques of Gaines and Mitchell (1979) and Yoshida et al (1976). Amylose content was determined according to Juliano et al (1981), using known amylose/amylopectin mixtures (Sigma Chemical Co., St. Louis, MO) to obtain the standard curve.

A "microbowl" Brabender amylograph, as modified by Sandstedt and Abbot (1961), without cooling, was used to analyze proso millet starch for pasting properties. The starch suspensions to be analyzed were prepared with 6.4 g of starch at 14% mb and 70 ml of diluted buffer (prepared and added as described in method 22-10; AACC 1983) with enough water to adjust the starch moisture to 14%. Wet-milled Argo corn starch (CPC International Inc., Englewood Cliffs, NJ 07632) was used as a reference.

Gelatinization temperature was measured with the Kofler microscope hot stage (Arthur H. Thomas Co., Philadelphia, PA 19105), using the technique of Schoch and Maywald (1956). Data for the initial and final gelatinization points were recorded.

The particle size distribution of proso starch granules was measured with a binocular microscope at 400×, using a stage micrometer to calibrate the eye piece reticule.

Thermal analysis of proso starch was performed using a Perkin-Elmer differential scanning calorimeter (Model DSC-2) with a Perkin-Elmer thermal analysis data station. Samples were prepared by weighing approximately 3 mg of starch and adding 10 μl of water. The amount of water was varied to give various volume fractions. The samples were allowed to equilibrate for at least 1 hr, then analyzed at 10° C/min heating rate beginning at 290 K and ending at 380 K. The DSC was calibrated using tristearin. A sample DSC thermogram is illustrated in Figure 1.

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[2]Department of Food Science and Technology, University of Nebraska, Lincoln 68583-0919.

RESULTS AND DISCUSSION

Milling

Test weight of the kernels was 6.8 g/1,000 kernels and 74.35 kg/hl or 57.83 lb/bu, falling within the range 48–60 lb/bu given by Matz (1959). Table II contains proximate analyses, which show that the fine flour had lower ash and fat contents than the coarse flour. This observation may be important, as not all millet species follow the same pattern as wheat, in which the fine flour normally has the lower ash. Perten (1977) showed that pearl millet (*Pennisetum thyphoides*) and sorghum had an opposite pattern during hammer milling.

Figure 2 shows the values for percent extraction (coarse + fine flour yields) and percent ash for different moisture values and tempering times. The extractions predicted from two-way RSM equation as a function of moisture and temper time gave $r = 0.86$ and SE = 1.01. The percent ash, calculated from three-way RSM as a function of moisture, temper time, and total yield, gave $r = 0.94$ and SE = 0.02.

With increasing temper time, the percent ash decreased, but at the same time the flour yield also decreased, although the yield reductions were less pronounced. A possible explanation is that water wets the hulls and aleurone layer, making them tough and less friable during milling. With increasing moisture, however, the percent ash seems to increase, which may happen because the proportion of coarse flour (with the highest ash content) is being increased. This decreased extraction of fine flour then may be explained because, as more total water becomes available, the endosperm becomes softer and finer and tends to blind the sieves.

Once the water has migrated further into the grain (longer tempering time), the aleurone layer and some of the hull, which have higher contents of silica and other mineral matter, may again start being fragmented in small pieces, becoming part of the fine flour. This is a possible explanation for why, after 3 hr of tempering, the ash percentage comes close to the values for 2 hr at higher moisture contents.

The effect of moisture content and tempering time on flour average particle size is shown in Table III. At higher temper moistures, the average particle size of both the coarse and fine flours decreased. At higher temper times the fine flour particle size decreased, but the coarse flour seemed to remain unaffected. More work needs to be done in order to confirm these changes and to determine their cause(s).

A report by De Francisco et al (1982) showed that the particle size distribution of pearl millet flours did not show significant changes when the grain was tempered to three different levels of moisture and milled with a Hobart mill, further indicating that

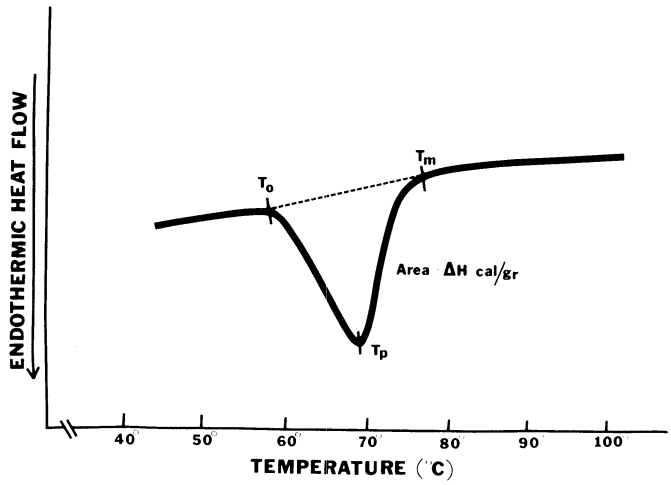

Fig. 1. Typical differential scanning calorimetry thermogram. To = onset temperature, Tp = peak temperature, and Tm = melting temperature.

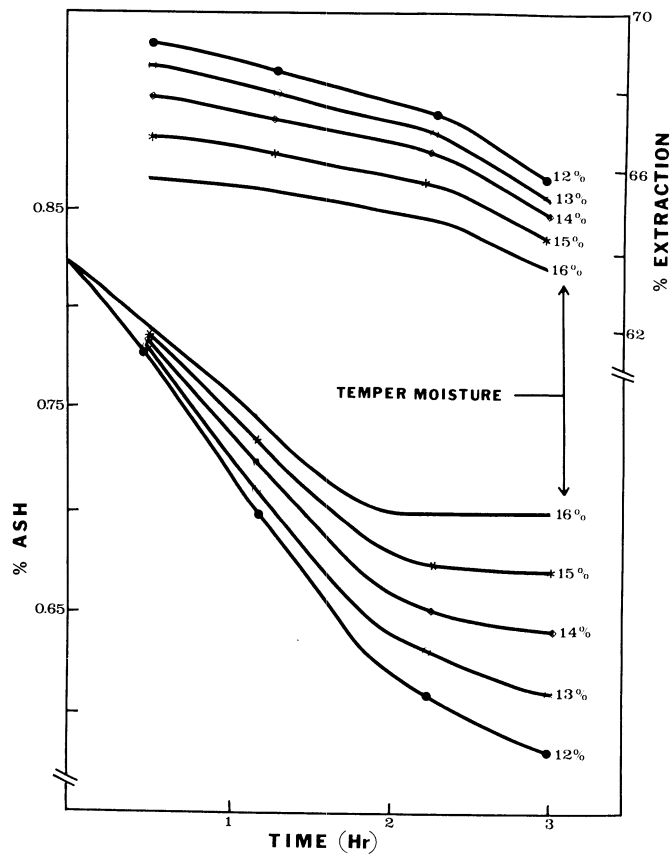

Fig. 2. Values of percent of extraction and ash content of proso millet at different levels of moisture and tempering times.

TABLE I
Methods Used in the Isolation of Proso Millet Starch

Step	Acidic Method	Alkaline Method
1	Steep 50 g of grain with 250 ml of 0.15% SO_2 soln at 52° C for 48 hr.	Steep 70 g of grain with 400 ml of 0.25% NaOH soln at room temp. for 24 hr.
2	Mill with Osterizer blender	Mill with mortar and pestle.
3	Filter through 40-mesh sieve and wash with water.	Add 400 ml of 0.25% NaOH, stir, then settle overnight.
4	Mill by mortar and pestle and repeat step 3.	Drain off and repeat steps 2 and 3
5	Filter through 200-mesh sieve and wash with water.	Drain off and mill with Osterizer blender using small amounts of 0.25% NaOH.
6	Filter through 270-mesh sieve and wash with water.	Continue as in acidic method from step 3.
7	Centrifuge and scrape the gluten from the starch several times, as necessary, with small amounts of water.	
8	Filter using Whatman No. 2 and Buchner filter.	
9	Dry in a convection oven at 45° C overnight.	

TABLE II
Proximate Analysis of the Fractions Obtained from the Quadrumat Jr. Mill and Whole Grain from the Udy Mill[a]

Sample	% Extraction	Protein[b]	Ash	Fat	Fiber
Whole grain (Udy)	100.00	12.60	3.06	4.36	7.38
Bran (+60)	30.22	12.59	8.09	9.00	21.21
Coarse flour (−60, +100)	33.18	17.56	1.06	3.14	1.08
Fine flour (−100)	36.60	8.02	0.66	2.13	0.53

[a]Average of two determinations (% moisture free basis).
[b]Nitrogen × 6.25.

millet species, as well as the type of mill used, can influence the performance of the grain during milling.

Starch

The starch content of the whole grain was found to be 64.02%. The proximate analysis and amylose content of the isolated starches are given in Table IV. Isolating starch by the corn wet-milling technique (acidic method) resulted in higher protein and lower amylose contents than the alkaline method. When the amylose content results were adjusted for contaminant protein or other components, the difference was only about 1%, but the alkaline method still resulted in a slightly higher amylose content, contrary to expectations.

The pasting properties illustrated in Figure 3 show that the method used to isolate the starch influences its pasting properties. Starch isolated by the alkaline method presented a double peak, generally rare in starch pasting curves. This may have been an artifact of the close tolerance of the pins in the microbowl, combined with the formation of small gelatinized globules observed at the peak temperature. However, this double peak has

TABLE III
Effect of Tempering Time and Moisture on Average Particle Size of Proso Millet Flours (μm)[a]

Conditions	Flour	
	Coarse	Fine
Tempering time (15% moisture)		
1 hr	30.90	26.28
2 hr	30.90	25.80
3 hr	30.04	24.36
Tempering moisture (2 hr)		
15%	30.90	25.80
16.5%	29.94	24.30
18%	28.00	23.32

[a]Average of two determinations by Fisher sub-sieve sizer.

TABLE IV
Proximate Analysis and Amylose Content of Proso Millet and Corn Starches[a]

Starch	Protein[b]	Ash	Crude Fat	Crude Fiber	Amylose	Amylose Amylopectin[c]
Alkaline method	0.69	0.63	0.59	0.05	29.14	0.424
Acidic method	4.31	0.51	0.60	0.11	27.16	0.404
Corn starch	0.43	0.05	0.12	···	26.3	0.357

[a]Average of two determinations, percent moisture free basis.
[b]Nitrogen × 6.25.
[c]Corrected for residual protein and other components.

TABLE V
Gelatinization Temperature (°C) by Kofler Hot Stage of Corn and Proso Starch Samples[a]

Gelatinization Temperature	Starch		
	Corn Starch	Alkaline Method	Acidic Method
Initial	59.4	69.2	69.6
Final	70.2	77.0	76.0

[a]Average of three determinations.

TABLE VI
Differential Scanning Calorimetry Characteristics of Proso Millet Starch from Two Isolation Methods

Isolation Method	Volume Fraction	Water/ Starch Ratio	Temperature (°C)			$-\Delta H$ (cal/g)
			Onset	Peak	Melting Point	
Alkaline	0.85	3.72	72.81	76.11	83.34	3.11
	0.82	2.95	72.65	75.83	84.41	3.15
	0.70	1.60	72.30	75.95	91.27	3.84
	0.69	1.58	71.80	75.55	94.48	4.24
	0.51	0.69	71.77	75.18	102.16	3.30
	0.50	0.70	69.21	75.08	102.03	3.32
Acidic	0.83	3.23	73.94	77.77	89.59	3.61
	0.81	2.93	73.59	77.62	89.51	3.54
	0.68	1.48	73.57	78.37	90.86	4.08
	0.63	1.15	71.75	78.88	94.98	4.24
	0.46	0.59	73.27	78.50	97.23	1.19
	0.45	0.57	73.08	79.91	100.62	1.34

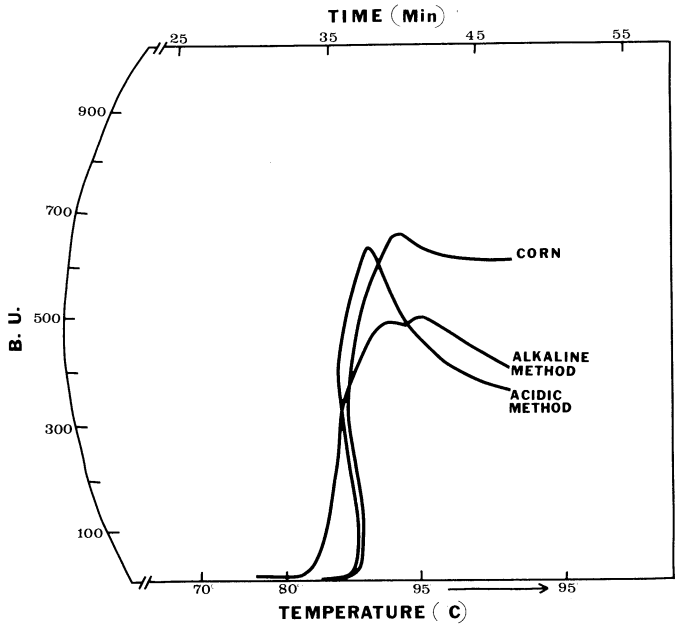

Fig. 3. Pasting characteristics of proso millet and corn starches (average of three determinations).

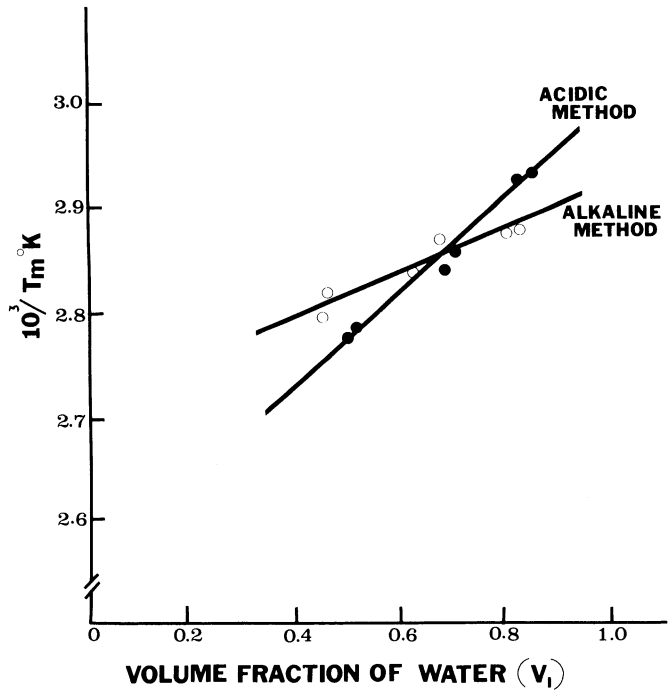

Fig. 4. The differential scanning calorimetry reciprocal melting point 1/Tm (K), plotted against the volume fraction of water (V_1), for proso millet starch isolated by the two methods.

also been observed when studying reconstituted flours in the large amylograph bowl, so there may be another explanation. The corn starch had almost the same pasting temperature and peak viscosity as proso starch isolated by the acidic method, the only difference being that the peak viscosity in corn did not decrease as much during the 95° C holding period. These pasting characteristics were similar to those observed by Lorenz and Hinze (1976), where the proso variety used influenced amylograph performance.

Proso starch analyzed by the Kofler hot stage was found to have higher gelatinization temperatures than corn starch, but the ranges were slightly smaller (Table V).

The particle size, by microscope, of proso starch granules varied from 5 to 11 μm, with a mean granule size of 7 μm, with an appearance and shape very similar to rice. Rice starch has been reported at 3–10 μm in the mature grain, with a mean granule size ranging from 4 to 6 μm (Juliano 1984). Corn starch granules are reported to be spherical to polyhedral, with a diameter of 2–30 μm (Matz 1959).

Biliaderis et al (1980) studied legume starch using DSC, and found a significant linear correlation between volume fraction of water (calculated as the ratio of the volume of water to the total volume of starch plus water) and the reciprocal of the melting point (1/mp). Significant correlations were also found for the proso starch samples studied (alkaline method $r = 0.95$, and acidic method $r = 0.99$) (Fig. 4). Observing the slopes, a difference can be seen in the behavior of the starches isolated by the two methods. The temperatures and chemicals involved in the isolation methods might have affected the starch granules in different ways, changing their properties (Krueger et al 1986), although another reason for the difference could be interference by the relatively high protein content of the starch isolated by the acidic method.

Wootton and Bamunuarachchi (1979) found that there is a linear relationship between certain ranges of water/starch ratios and $-\Delta H$ of gelatinization. The present study is not in complete disagreement with the findings of these authors. Although the heating rates were not equal, some similarities can be shown. In Table VI it can be observed that as the water/starch ratio increases, there is evidence that $-\Delta H$ also increases until a point where, at ratios above 2.0, the $-\Delta H$ starts to decrease. These ratios were not tested in Wootton and Bamunuarachchi's study, but they concluded that different ratios would probably not follow the same relation.

CONCLUSION

Results from this study show that both moisture and tempering time parameters exert influence on the extraction rate and ash content of proso millet flours. The ash content and percent extraction decreased with increasing tempering time, and the ash content seemed to increase with increasing tempering moisture.

Both DSC and the amylograph were found to be more sensitive in detecting differences between proso starch samples isolated by the two methods than was the Kofler hot stage.

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