Air Classification of Corn Grits. II. Fine Grinding and Air Classification of Protease-Treated Grits

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ABSTRACT

Tempering grits 24 hr. at 120°F. and 30% moisture with bromelain at 2 mg. enzyme per g. grits (dry solids), flaking to 0.012-in. thickness, and freeze-drying, increased grinding capacity in a pin mill approximately fourfold and reduced energy consumption by about 75%. Concomitantly, the proportion of total grit dry substance reduced to $<$ 32 μ in size was increased from 31 to 94%. Despite the near total disintegration of the grit, air classification gave no fraction with less than 5.5 nor more than 31.4% protein, starting with grits analyzing 8.5% protein. Scanning electron photomicrographs showed that flour from finely ground enzyme-treated grits contained starch granules with attached pieces of protein.

Air classifiers utilize the principles of centrifugal force and aerodynamics in separating components of a mixture. Size, shape, and density of particles are important. Of these factors, size offers the greatest possibilities for controlled manipulation to achieve separation of starch and protein from corn grits.

In a preceding publication (1), proteolytic enzymes were shown to solubilize as much as 40% of the protein in corn grits at 30% moisture, by acting primarily on the matrix protein, glutelin. This greatly weakened the grit structure, as judged by a slurry-milling and sizing test. Utility of the proteolytic treatment in facilitating dry grinding and air classification of corn grits is the subject of this report.

MATERIALS AND METHODS

Sample Preparation

Based on laboratory screening tests previously reported (1), the enzymes bromelain, fungal protease, and papain were used in this work. Papain and fungal protease were applied in water solutions; bromelain was applied in water alone and with sulfur dioxide (SO_2). In all cases moisture level was 30%, incubation time was 20 hr., and incubation temperature was 120°F.

A major objective of this phase of the program was to devise a method for preventing protein from hardening during drying of treated grits. Two general approaches were employed. One consisted of removing soluble constituents prior to drying; the second involved the use of mild drying techniques. Solubles were removed by steeping in the presence of proteolytic enzymes or by leaching grits after enzyme treatment at 30% moisture but prior to drying. Drying techniques included air-drying (evaporative drying) at various temperatures, and freeze-drying (sublimative drying). For more rapid moisture removal, some samples were coarsely flaked prior to freeze-drying.

Fine-Grinding Tests

An Alpine 250 CW pin mill (counter-rotating pin disks) was used to grind grit samples. Initially, the maximum combined tip speed of the two disks was about

30,000 ft. per min., but this was later increased to 38,000 ft. per min., or about 90% of the maximum operational speed recommended by the manufacturer. Test samples were either 50 or 60 lb.

Particle-Size Distribution Measurements

Particle-size distributions of milled grits were estimated with an Alpine Air Jet sieve. Products were sized successively on screens with apertures of 74, 44, 32, 20, 15, and 10 μ.

Air Classification

Milled products were air-classified with the Alpine Model 132MP classifier, designed to make cut points in the range of 5 to 20 μ. Cut points were started on the small end of the size range. Fine fractions were removed, and a coarser cut made on the residue. This progression was continued to the coarse end of the distribution. Machine capacity was sacrificed to attain best possible separation performance.

RESULTS AND DISCUSSION

Preliminary Fine-Grinding Tests

Samples evaluated in the first series of tests are described in Table I. Adding enough SO_2 to reduce pH of grits to 4.0 (based on previous laboratory calculations) and holding 20 hr. at 120°F. softened grits only slightly, as indicated by a minimal increase in machine capacity and minimal reduction in energy requirements. Fungal protease, at the level used (2 mg. enzyme preparation per g. grits), was only slightly more effective. Both bromelain and papain treatments produced grits that were much easier to grind than were untreated grits. These results are in line with those obtained by the laboratory slurry-milling technique (1).

Grinding grits at higher moisture levels (low drying temperature) reduced capacity and increased energy consumption (Table I). Microscopic examination of

TABLE I. EFFECTS OF SO_2, PROTEASES, COMBINATIONS OF PROTEASES AND SO_2, AND DRYING CONDITIONS ON GRINDING CAPACITY AND ENERGY REQUIREMENTS OF CORN GRITS IN AN ALPINE 250 CW PIN MILL

Enzymes and Chemicals Used[a]	Drying Temperature °F.	Approximate Final Moisture Content %	Grinding Capacity lb. dry solids/hr.	Grinding-Energy[b] Requirements (approximate) kw. hr./ton
None	120	10	994	30.0
SO_2 (pH 4.0)	120	10	1,062	28.1
Fungal protease	120	10	1,138	26.2
Papain	120	10	1,659	18.1
Bromelain	120	10	1,783	16.7
SO_2-bromelain	120	10	1,677	17.8
SO_2-bromelain	90–100	15	1,382	21.5
SO_2-bromelain	70–80	19	1,243	24.0

[a] All samples were incubated at 120°F. and 30% moisture for 24 hr. Enzymes were added at a level of 2 mg. per g. grits, d.b.

[b] The pin mill was operated at approximately 30,000 ft. per min. over-all tip speed.

the milled products showed no advantage for low-temperature drying, as judged by extent of starch and protein association. Therefore, low-temperature air-drying at atmospheric pressure was eliminated from further consideration.

Other grit treatments were evaluated preliminarily on a smaller scale that did not allow accumulation of quantitative grinding data of the type reported in Table I. The first of these treatments, drying to low moisture levels (<5%) in a vacuum oven at low temperature (50°C.), gave no improvement in grit susceptibility to grinding. This technique was employed in an attempt to remove all free or liquid water, leaving only bound water in the product. Similarly, steeping 24 hr. in SO_2-bromelain, or tempering with SO_2-bromelain at 30% moisture and leaching for 1 hr. in water prior to drying, did not affect grinding properties. None of these products was air-classified, since advantages were not expected.

Freeze-drying proved to be the most effective treatment. Grits tempered with bromelain were freeze-dried in the laboratory to a moisture level of less than 5%. These grits were very soft and could be easily crumbled between the fingers. Though initial sample size was too small to permit measurement of machine capacity or energy consumption, it was obvious that these grits ground easier than any material previously processed and resulted in the greatest particle-size reduction. Both enzyme treatment and freeze-drying were evaluated singly, but neither compared favorably with the combination of the two.

Fine-Grinding for Air Classification

Two different techniques were used to prepare 60-lb. samples of freeze-dried grits. In each case grits were adjusted to 30% moisture with a solution containing 2 mg. bromelain per g. grits. Samples were held 24 hr. at 120°F. The first lot was frozen at the end of the incubation period and freeze-dried; the second was coarsely flaked by passing through a roller mill with a 0.012-in. gap prior to freeze-drying. Several different batches were prepared to accumulate the required 60 lb. of each lot. A similar quantity of enzyme-treated, air-dried grits was included for comparison.

Both the intact and coarsely flaked freeze-dried grits were quite fragile. The lot flaked prior to freeze-drying was especially fragile and could be largely disintegrated merely by shaking. To illustrate this, both freeze-dried samples were sized before milling and compared with the air-dried grits. The air-dried product consisted almost entirely of grits larger than 1,200 μ in size, whereas almost one-tenth of the freeze-dried grits by weight were smaller than 74 μ and about a third of the flaked, freeze-dried grits were smaller than 74 μ.

All three enzyme-treated grit samples and an untreated control sample were ground in the Alpine pin mill operating at an over-all tip speed of 38,000 ft. per min. Grinding capacity of air-dried, enzyme-treated grits was more than 2.5 times that of untreated grits, while energy consumption was less than 40% of the untreated control (Table II). At the same time, the proportion of grits reduced to a size of 32 μ or smaller was more than 80% greater for enzyme-treated, air-dried grits.

Enzyme-treated, freeze-dried grits showed even greater improvement over the control. Grits flaked prior to freeze-drying were softest, but poor flow properties of this product in the vibratory feeder did not allow accurate measurements of grinding capacity or energy consumption. Almost all (94%) of these grits were

TABLE II. EFFECTS OF BROMELAIN TEMPERING AND METHOD OF DRYING (AIR- OR FREEZE-DRYING) CORN GRITS ON GRINDING PROPERTIES IN AN ALPINE 250 CW PIN MILL

Bromelain-Tempered	Drying Conditions	Grinding[a] Capacity lb./hr.	Grinding[a] Energy kw. hr./ton	Weight % of Milled Product <32 μ in size
No	Air, 120°F.	635	47	31
Yes	Air, 120°F.	1,642	18.2	57
Yes	Freeze-dried	2,438	12.3	82
Yes	Flaked ≃ 0.012 in., Freeze-dried	...	...	94

[a] Pin mill operated at 38,000 ft. per min. over-all tip speed.

reduced to a particle size of 32 μ or smaller, whereas only 31% of the untreated grits were reduced to 32 μ or smaller by similar grinding. Grits which were freeze-dried without flaking had better flow properties and permitted capacity and energy-consumption measurements. Grinding capacity was about 3.8 times that of the control, whereas energy consumption was only slightly more than one-fourth as great. The proportion of this product reduced to 32 μ or smaller in size was slightly less than that with flaked, freeze-dried grits.

Based on all observed relationships between particle-size reduction, grinding capacity, and energy consumption, flaked grits would be expected to require less energy for grinding and result in higher machine capacities than any of the other products if a positive feed method were used. To produce equivalent quantities of material within the approximate size range of free starch granules (maximum size, 32 μ), untreated corn grits would require about 12 times as much grinding capacity (or time), consume about 7 times as much energy, and require 3 times as much raw material (no recycling) as would enzyme-treated, freeze-dried grits.

Complete particle-size distributions of the three enzyme-treated products are presented in Table III. Though a high percentage of the freeze-dried enzyme-treated

TABLE III. PARTICLE-SIZE DISTRIBUTION AND RELATIONSHIP BETWEEN PARTICLE SIZE AND PROTEIN CONTENT OF FINELY GROUND, ENZYME-TREATED CORN GRITS EITHER AIR-DRIED OR FREEZE-DRIED PRIOR TO GRINDING

	Air-Dried, 120°F.			Freeze-Dried			Flaked, 0.012-in., and Freeze-Dried		
Particle Size[a] μ	Weight % retained on sieve	Protein, % d.b.	% of total protein	Weight % retained on sieve	Protein, % d.b.	% of total protein	Weight % retained on sieve	Protein, % d.b.	% of total protein
74	19	12.2	25.9	...	...	...	...	...	...
44	14.5	9.5	16.0	12.7	13.0	19.0	...	...	...
32	10.0	10.0	11.2	5.0	12.3	7.6	6.0	16.1	11.0
20	10.0	9.6	11.2	6.0	10.8	7.6	10.0	12.0	15.1
15	28.0	7.2	23.5	48.0	6.7	38.0	45.0	6.3	35.6
10	16.0	6.5	12.3	28.0	8.6	27.8	40.0	7.7	38.4
<10	Trace	...	...	Trace	...	...	Trace	...	...

[a] Particle size determined with Alpine Air Jet sieve.

products, in particular, was well within the size range of corn starch granules, protein also was distributed throughout all size ranges in fairly high concentration. Whether this protein was adhering to starch granules or was present as unattached particles could not be determined from these data. Therefore, samples were microscopically examined, using a scanning electron microscope. Grits tempered in water alone, air-dried, and pin-milled, were compared with grits tempered with bromelain (2 mg. per g. grits), flaked, freeze-dried, and pin-milled. Also, for reference, unmodified corn starch from wet-milling was included.

Examination of relatively large fields at low (200X) magnification (Fig. 1, upper) clearly shows the difference between enzyme-treated and untreated grits. At this magnification, the enzyme-treated grits appear to have been totally disintegrated, whereas the untreated grits contain chunks of unfragmented endosperm. At higher (1,000X) magnification (Fig. 1, lower), appearance of starch granules from both treated and untreated grits is similar. In both cases many small pieces of material, presumably protein, can be seen adhering to the starch granules. This contrasts sharply with the very clean starch granules from wet-milling as illustrated in Fig. 2.

No broken starch granules are obvious in the enzyme-treated grits, but one granule in the untreated grits is clearly split in two (left half of Fig. 1, lower left). Some starch-granule damage could be expected from milling the vitreous, untreated endosperm so finely. The surface of the unfragmented endosperm chunk shown in the right half of Fig. 1, lower left, is typical of several viewed, and indicates that this chunk is from the dense peripheral-endosperm layer which is high in protein and low in starch. Though starch granules are small and relatively sparse in this region, it is a bit surprising that the cleavage apparently occurred through the matrix protein without exposing any starch granules.

The nature of the association between starch granules and adhering proteinaceous particles was not determined, but appeared as if it might be rather tenuous and possibly not strong enough to withstand the rigorous treatment to which the material would be subjected in an air classifier.

Air Classification

Both enzyme-treated, freeze-dried grit samples and the enzyme-treated, air-dried grit sample were air-classified. Bromelain-treated grits that were freeze-dried intact gave slightly greater protein shifts than air-dried grits (Table IV). A significantly higher yield of very fine material was obtained at a slightly higher protein content. Bromelain-treated grits that were flaked prior to freeze-drying gave best protein shifts. More than 45% of the protein was recovered in fractions with particles smaller than 10 μ and representing only 17.8% of the total weight. The fraction with minimum (<7 μ) particle size analyzed 31.4% protein and contained more than a third of the total protein. The quantity of this material was much greater than expected from sizing (Table III). Apparently, factors other than size, such as shape and density, contributed to better air-separation efficiency. Also, the tendency for the very fine material to agglomerate on the Air Jet sieve probably accounts, in part, for this discrepancy. Accuracy of these fractionation results on screens with apertures smaller than 15 μ is questionable.

Though significant protein shifts were achieved, no fraction contained a low enough protein content to be considered as "starch". Probably, much of the

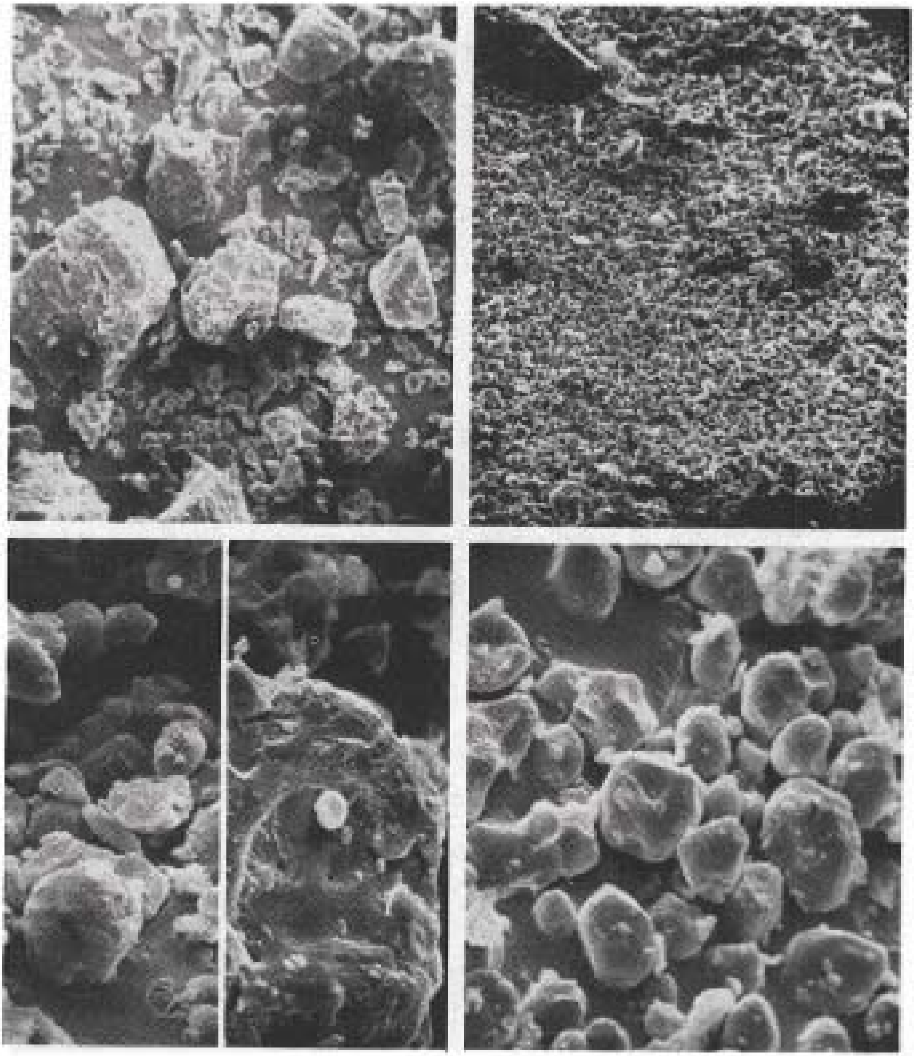

Fig. 1. Scanning electron photomicrographs. Left, corn grits after pin-milling; right, bromelain-tempered corn grits after pin-milling. Original magnifications: Upper, 200X; lower, 1,000X.

protein remaining in the various fractions is not adhering to starch granules. If this is true, reprocessing might purify the starch to a greater extent, as is possible with wheat flour, but probably would not produce starch and protein fractions in yield and purity approaching those attained by the conventional wet-milling process.

CONCLUSIONS

Air-classification results obtained in this study apparently were the best ever

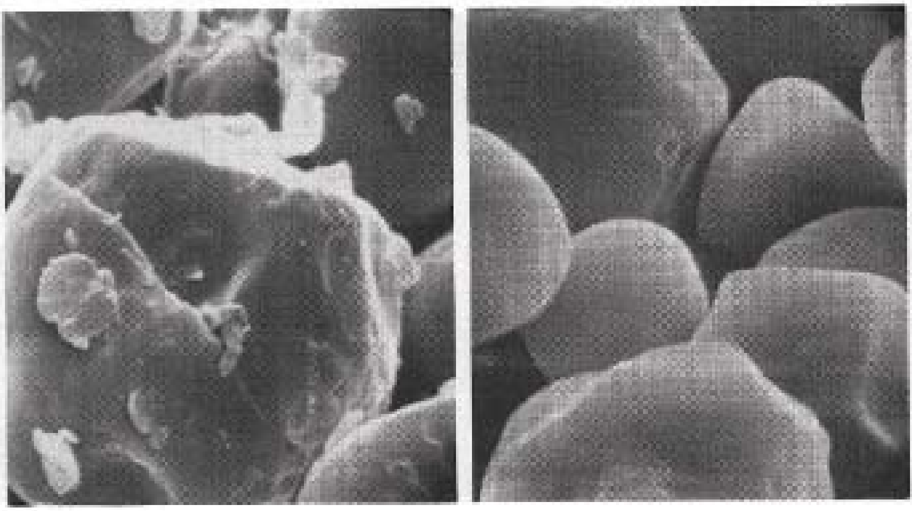

Fig. 2. Scanning electron photomicrographs. Left, starch granules from bromelain-tempered corn grits after pin-milling; right, corn starch granules from wet-milling. Original magnification, 4,000X.

TABLE IV. EFFECTIVENESS OF AIR CLASSIFICATION IN SEPARATING STARCH AND PROTEIN FROM FINELY GROUND CORN GRITS FOLLOWING TREATMENT WITH BROMELAIN AND AIR-DRYING AT 120°F. OR FREEZE-DRYING

Cut Point Size Range[a] μ	% (by wt.) of Total Dry Substance	Protein, % d.b.	% of Total Protein
	Air-Dried (120°F.) Grits		
0–10	3.3	14.5	5.2
10–13	3.1	13.1	4.4
13–17	6.8	10.0	7.5
17–20	11.5	7.2	9.1
20–32	40.8	8.0	35.9
>32	34.5	10.2	37.9
	Freeze-Dried Grits		
0–10	13.0	15.2	21.5
10–13	4.4	11.6	5.5
13–17	19.4	7.7	16.2
17–20	23.7	9.3	23.8
>20	39.5	7.7	33.0
	Flaked, 0.012-in. Freeze-Dried Grits		
0–7	11.8	31.4	34.3
7–10	6.0	20.0	11.3
10–12	6.2	10.4	6.0
12–13	5.0	8.9	4.1
13–15	10.3	6.6	6.2
15–17	21.2	5.9	11.8
17–20	12.9	5.5	6.4
>20	26.6	8.1	19.9

[a] Size range estimated microscopically.

achieved with corn grits. The protein-shift index, δ, (2) for bromelain-tempered, pressed, freeze-dried, pin-milled *grits* was 27.7. This compared with δ = 10.5 for corn *flour* reground once (3), and δ = 9.2 for corn *grits* reground three times (4), and δ ≃ 24 for corn *break flour* soaked in a large excess of an isotonic buffer at 4°C. for 24 hr., freeze-dried, pin-milled, air-classified, and selected fractions reground twice and reclassified (5).

Though the improvement achieved by techniques we devised was significant, we did not obtain starch and protein fractions of sufficient purity to justify further development research. The techniques we used were selected for maximum effectiveness, with no regard for cost at this point.

Literature Cited

1. SPANHEIMER, J., FREEMAN, J. E., HEADY, R. E., and HEADLEY, V. E. Air classification of corn grits. I. Softening grits with enzymes and chemicals. Cereal Chem. 49: 131 (1972).
2. GRACZA, R. The subsieve-size fractions of a soft wheat flour produced by air classification. Cereal Chem. 36: 465 (1959).
3. PFEIFER, V. F., STRINGFELLOW, A. C., and GRIFFIN, E. L., Jr. Fractionating corn, sorghum and soy flours by fine grinding and air classification. Amer. Miller Process. 88: 11 (1960).
4. STRINGFELLOW, A. C. Fractionation of corn and other cereal flours. Report of Sixth Annual Corn Dry Milling Conference, Peoria, Ill., p. 24 (June 7, 1965).
5. CHRISTIANSON, D. D., STRINGFELLOW, A. C., BURDICK, D., and INGLETT, G. E. Endosperm fragmentation of ordinary and high-lysine corn. Cereal Chem. 48: 558 (1971).

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