MODIFICATION OF CEREAL FLOURS WITH HYDROCHLORIC ACID[1]

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ABSTRACT

A soft white winter flour predried to less than 3% moisture was modified with 1.3 to 1.6% hydrochloric acid applied as a $4N$ solution at 90°, 100°, and 110°F. Each 10°F. increase in temperature doubled the rate at which viscosity decreased, as measured by a rapid-cooking viscometer. The difference in acid content had little effect. When flour was modified with 0.5% acid, the reaction was relatively slow, even at 160°F. When flour at normal moisture was modified with $12N$ solution, the rate was retarded.

Data are presented on starches and other cereal flours that illustrate the influence of protein content and type on the reaction rate and on product characteristics. The cost of producing these acid-modified flours is estimated at 1.9 cents per lb. above the price of the raw material.

Although acid modification of starches has been practiced for many years, there is little in the literature describing the kinetics of the reaction. Acid modification of cereal flours is further complicated by the presence of various extraneous materials, chiefly proteins, which have a decided effect on the over-all reaction rate as well as on the quality of the end product (1). Despite these difficulties, flours were modified into economical materials for evaluation as binders, adhesives, and sizes.

Although starches may be acid-modified either as slurries or in the dry state, flours are usually modified dry because wetted protein interferes with recovery of the product. The conventional method of modifying starches by adding a small amount of acid and then heating has been successfully used with flours when color formation and moisture losses are not serious disadvantages. For more exacting requirements such as production of a tub size for paper, Rankin *et al.* (2) found that more acid and relatively low temperatures were preferable and that, under these condition, flours could be modified in a few hours. A small-scale reactor was built to produce materials for large-scale testing and to investigate modification by hydrogen chloride gas (3).

The acid-modification reaction ceases when acid is removed by depletion, evaporation, or neutralization. In the process considered here, it is stopped by neutralization. The primary object of acid modi-

fication is to reduce the viscosity of high-solid pastes made from the product so that they are more easily applied to a substrate. An important problem was to devise a means of quickly predicting the pasting properties of the material during the reaction. The problem was solved by measuring the viscosity of a neutralized paste with a rapid-cooking viscometer equipped with a recording milliammeter (4). With this device, flour could be modified approximately to the point where it would produce a paste of desired viscosity, regardless of the type of flour or the operating conditions. For a tub-sizing agent, the acceptable range was taken to be between 70 and 110 B.U. for a 20% paste at 55°C. on the cooling cycle after cooking in the amylograph at 90°C. for 17 min. (see "Methods" section). In Fig. 1 a relation is shown be-
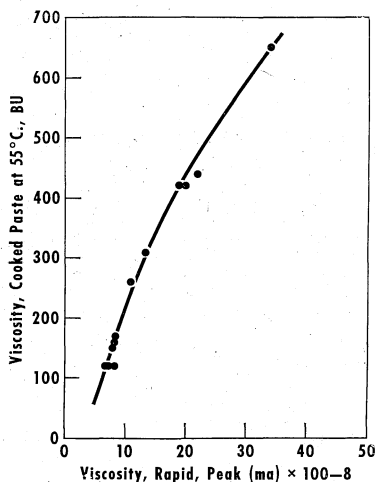

Fig. 1. Cold-paste viscosity can be predicted from measurements of hot-paste peak obtained with a rapid-cooking viscometer.

tween Brabender cold-paste viscosity and the hot-paste peak by the rapid method.

The reaction of aqueous hydrochloric acid with a single wheat flour was explored and the product evaluated. Other flours were examined more cursorily. Starches were also studied for comparative purposes. This paper reports the results of these investigations and presents a cost estimate for modifying flours with dilute aqueous hydrochloric acid.

Materials and Methods

The principal flour investigated was a straight flour commercially milled from Genesee soft white winter wheat grown in Michigan.

Other flours were: (a) milo flour, straight commercial; (b) second clears, commercial hard red winter wheat; (c) corn flour from yellow dent corn, commercial, coarse. The yellow dent and high-amylose (55%) corn starch and the wheat starch investigated were commercial samples, pearl grade.

The equipment and methods used were those described previously (3,4). With the dilute (4N) acid, from 1.2 to 1.6 liters was sprayed onto the surface of 14.5 kg. of flour in about 40 min. while it was being agitated in a ribbon mixer. A Spraying Systems Co. 1/4 JP (hard rubber) pneumatic atomizing nozzle gave satisfactory dispersion. The 12N acid (400 ml.) was added at the same spraying rate, which is near the minimum for this nozzle. In addition, the flours and starches were examined for soluble protein, dispersibility, and Blue Value by the methods of Rankin *et al.* (1). Viscosities were obtained with a type VAVI Visco-Amylo-Graph, C. W. Brabender Instruments, Inc. (700 cm.g. cartridge).

Results and Discussion

Soft White Winter Flour, Predried. An acid-modification method was investigated in which the flour was dried to about 2% moisture and sprayed with 4N hydrochloric acid. The rates of modification (Fig. 2) represent smoothed curves fitted to data taken at 5- to 15-min. intervals after the acid was added. Although spray rate, drying conditions, and amount of acid were varied, these had a negligible effect on
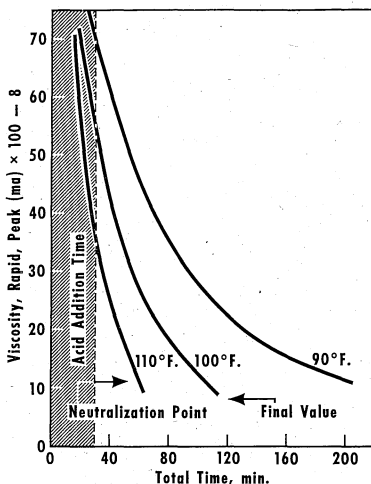

Fig. 2. The rate of viscosity reduction is a complex measure of reaction rate and depends primarily on temperature applied within a range of 1.3 to 1.6% HCl in the flour.

rate over the range examined. The viscosity values in Fig. 2 are arbitrary units with the rapid method, and are related to Brabender viscosities, as discussed later. When these units are converted to torque (4), the rate data follow a first-order law quite well. The data of Fig. 2 diverge during the acid addition period after 15 min. and can be expressed by the equation:

$$\log y = 2.41 - K\,(t - 15)$$

where y is viscosity as g. cm., t is time in min., and K is a proportionality constant, equal to 0.0046 at 90°F. and doubling for each 10° increase over the data range.

Viscosity and protein dispersibility of the product depend on the amount of alkali used in neutralization. An alkaline paste is somewhat difficult to achieve with precision, because pH changes rapidly between 6 and 8 and more slowly between 2 and 5. Since the reaction is so slow that it appears to cease above pH 3.5, a product with a slurry pH of 4.5 to 6 is now standard.

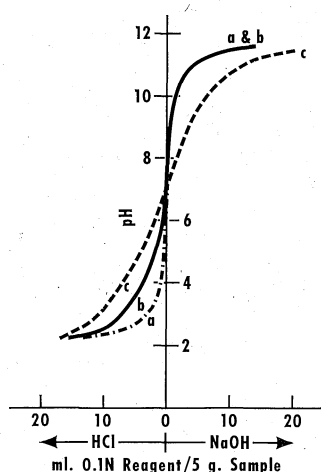Figure 3 will serve as a guide to control of pH. Data for these curves

Fig. 3. The protein in wheat flour buffers the starch so that more acid is required for modification: a, wheat starch; b, flour from soft wheat; c, second clears from hard wheat.

were obtained by titrating slurries of flours and starch with acid and alkali. The starch curve is much sharper in its vertical rise between pH 2 and 10, since the protein buffers the flours.

The values for the relation in Fig. 1 were obtained on alkaline products with a pH close to 8. Higher alkalinity tends to increase

Brabender viscosities but does not appreciably influence the rapid viscometric values. The Brabender cold-paste viscosity in Fig. 1 reflects, therefore, the unadjusted discrepancies that are due to pH effects. Also, the relation will change with change of material.

Data in Fig. 2 were obtained on acidic reacting material that had been mixed with dilute alkali soution to give a slurry pH about 9. The final product was also measured and was 3 to 6 units lower than its unneutralized counterpart, depending on the rate of reaction.

Protein dispersibility tends to increase as pH increases because of the well-known solubilizing effect of alkali on proteins. Rankin *et al.* (1) show that protein is almost entirely dispersible at pH 10; our results indicate an increase of about 10% over the range from pH 5 to pH 8. In any case, protein dispersibility is not increased appreciably by acid modification; the protein in the parent flour is about 40% dispersible in a 2%-cooked paste. Firm conclusions about the protein-pH relation are not possible, primarily because discrepancies occur in measuring pH. Although reproducible with certain samples, pH varies widely, depending on whether a slurry, a dilute paste, a freshly cooked paste, or an aged paste is tested and, perhaps, on other factors as well.

Consequently, it can be seen from the data in Table I that differ-

TABLE I

ANALYTICAL RESULTS ON TWO LOTS OF ACID-MODIFIED FLOUR, MEAN VALUES,
AND STANDARD DEVIATION OF MEAN

	FIRST SHIPMENT (Eight Runs)	SECOND SHIPMENT (Four Runs)
Temperatures, °F.	90 and 100	90 and 110
Amount of HCl (cc. of $4N$ per 100 g.)	9 and 11	9 and 11
Protein dispersibility, %	63 ± 1.8	46 ± 2.5
Dispersibility, %	92 ± 0.6	92 ± 0.8
Blue Value,% of original	95 ± 2.5	90 ± 3.6
Reducing sugars, % as maltose	....	2.9 ± 0.1
pH of a 20% slurry	7.8 ± 0.2	5.6 ± 0.2
Viscosity cooked paste at 55°C., B.U.	131 ± 10	91 ± 14

ences between products prepared under a fairly wide range of conditions are small when they are modified to approximately the same degree.

Because the differences in treatment produced no significant effects except those illustrated in Fig. 2, only averages are given.

Two different shipments of the same type of flour were tested; the tests were separated by 9 months. At that time, one of the flours was 12 months old and had been stored in an outside bin. The other was tested within 2 weeks of receipt.

Other Methods. Two other methods of aqueous acid modification of the soft flour were investigated. To discover whether higher temperatures could be substituted for acid as a reaction accelerator, a modification was attempted at 130°F. and higher in a closed tumble blender. When 3.5 cc. of 4N HCl per 100 g. was used, the reaction was retarded, so that after 7 hr. the viscosity of a cold paste of the product was 260 B.U. In another run at 160°F., after 10 hr. the viscosity was 1,000 B.U. when 2 cc. per 100 g. was added. The modification reaction is very slow and sensitive to the amount of acid in this region.

Another promising method is to spray concentrated acid on a mildly dried flour. Two extremes were investigated using 12N HCl. When the flour was predried to 3% moisture, the acid was not absorbed well by the flour, and the reaction was very slow. When concentrated HCl was sprayed into flour of 10% moisture, the time required for modification was about twice that required when the flour was predried. Also, Blue Value decreased to 36% of its original value, and an appreciably larger amount of reducing sugars was formed. Where these quality factors are not important, use of strong acid may be a useful and economical process.

Other Materials. Starches reacted much more rapidly than did the protein-containing flours (Table II) and were modified at a lower

TABLE II
ACID MODIFICATION OF VARIOUS CEREAL PRODUCTS[a]

MATERIAL	TIME	VISCOSITY	PROTEIN DISPERSIBILITY	DISPERSIBILITY	BLUE VALUE O.D.
	min.	B.U.[b]	%	%	
Starches, 90°F.					
Corn	120	70	..	100	0.174
Wheat	98	70	..	95	.188
High-amylose					
corn	78	..	..	66	.288
Flours, 100°F.					
SWW, straight	105	120	67	94	.151
Coarse residue	103	370	90	92	.131
Milo	78	90	8	87	.135
Second clears	192	190	31	81	.106
Corn	110	140	9.5	89	0.139

[a] Predried to less than 3% moisture; 9 cc. of 4N HCl per 100 g. dry product.
[b] On a 20% paste at 55°C. after cooking 17 min. at 90°C.

temperature in order to gain control of the final viscosity. For the flours, the rate depended on the type of flour and its protein content. When corn starch was reacted at 100°F., the reaction was completed before all the acid had been introduced, and by the time the product was neutralized it had degraded to a point where its paste had no

significant viscosity in a 20% solution. For starches, as Rankin *et al.* (1) imply, less acid would probably be desirable.

In general, protein dispersibility increases but slightly on acid modification, but total dispersibility increases to the point where the starch portion is about 95% or more soluble; the nondispersibles are then mostly proteins. Because wheat proteins are proportionately more dispersible than those of corn or milo, the total dispersibility is lower for products from corn and milo flours. Because second clears are high in initial protein they were high in the amount of insoluble protein, which reduced their dispersibility.

The Blue Value of a parent material depends on its amylose content, which, in turn, depends on the source and protein content. The reduction in Blue Value during modification may be as much as 10%, though the reduction for high-amylose starch was 15%. This starch is unique in its dispersion properties: from 19% original dispersibility, there was threefold increase during modification. Final viscosity was controlled by the rapid-cooking viscometer, which cooks at 100°C. with high shear. In the Brabender at 90°C. with low shear, the starch would not even swell appreciably, so a paste would not form. Control by the rapid method was very good for the other products.

Cost. The data show that with proper control of temperature, most materials can be modified in less than 3 hr. For a conservative cost analysis a total time per batch of 3 hr. was selected. This period should provide ample time for neutralizing, blending, discharging, and clean-up operations. The capacity needed to dry the flour to 1.5% moisture was also included in cost estimates. With well-designed dryers, this process step can be done in about 6 hr. without overheating the flour and causing browning and protein denaturation. Of course, pumps for hydrochloric acid and the reactors would be of corrosion-resistant materials.

It is estimated that a plant for producing 20 tons per day, 300 days a year, would require a fixed capital investment of $375,000, and that the cost of making a pound of product, exclusive of raw material cost, would be about 1.9 cents. If flour can be purchased at $5.50 per cwt., the "cost to make" then becomes 7.4 cents per lb. of product (Table III). For such a low-cost product the chemical costs become appreciable, and for some products, savings could be made by using less acid and alkali. A large saving could be made if drying requirements were not so great. Modification of the process through the use of anhydrous acid, with its possibility of adaptation to rapid continuous methods, should permit significant cost reductions.

TABLE III
SUMMARY OF PROCESSING COSTS FOR PRODUCING ACID-MODIFIED FLOUR
(Preliminary cost estimate based on hypothetical plant,
20 tons/day product, 300 days/year)

ITEM	DOLLARS PER DAY	CENTS PER POUND
Raw materials[a]	2,265	5.66
Utilities	68	0.17
Labor and supervision	240	0.60
Maintenance	56	0.14
Fixed charges	147	0.37
General plant overhead	148	0.37
Miscellaneous charges	38	0.09
Estimated "cost to make"	2,962	7.40

[a] Flour available at $5.50/cwt.

Acknowledgment

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