

# KINETICS OF ACID MODIFICATION: STARCH AND WHEAT FLOUR<sup>1</sup>

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## ABSTRACT

Wheat flour and corn starch were acid-modified by contacting them with gaseous hydrogen chloride. The kinetics of modification was determined by following the change with time of the viscosity of a paste prepared from the neutralized flour or starch. Isotherms for the specific rates at 90° and 110°F. were determined for acid concentrations from 1.5 to 20 g. of HCl/kg. of solids (m.f.b.). The correlation  $(1/E - 1) = 7.4 P^{0.64}$  corrected the specific rates over a wide range of substrate with both wet and dry HCl modification. In this relationship E is the ratio between the amount of acid required to achieve a given reaction rate with starch to that required to give an equal rate for a flour containing P g. of protein per g. of starch.

The kinetics of starch modification by acids or enzymes has long been of concern to cereal chemists studying the fundamental structure of the starch macromolecule. Although for many years starch has been chemically and enzymatically altered to materials suitable for various industrial uses, little has been done to relate changes obtained to operating variables for prediction of optimum production conditions.

Acid modification is an industrial process involving what is considered to be a mild depolymerization, just sufficient for weakening the starch granule and aiding in its swelling and rupture. The principal object of this modification is to reduce the cooked paste viscosity to a level which facilitates applying it to papers, boards, and the like.

Acid modification of flour (1) differs from that of starch because of the presence of protein. If viscosity of a paste of the product is taken as the outcome variable, the rate data could be analyzed in terms of classic chemical kinetics. Although for any flour substrate, the paste viscosity is related to the degree and kind of starch depolymerization, no simple fundamental relation now exists. This lack of knowledge arises because a starch or flour rheological system is markedly non-Newtonian and changes from one mode of behavior to another during cooking, cooling, and resting. The apparent viscosity of pastes thus depends on the prior history of the sample. Despite these objections, a standardized viscosity measurement is useful for control of product characteristics.

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Application of kinetic principles to the acid-modification reaction by using a method (2) of determining viscosity as a measure of degree of reaction has provided an empirical basis from which extrapolations can be made with a higher degree of confidence than would be possible if arbitrary expressions were employed.

The general acid-modification procedure has been given previously (1-3). About 30-lb. batches were modified by drying the flour to less than 3% moisture and then spraying with 4*N* hydrochloric acid solution.

Although modifications of only two kinds of wheat flour and one corn starch sample have been investigated, the methods that will be described should find general applicability in analyzing the reactivity of other kinds of flour and of starches so that more economical plants can be designed and existing facilities can be operated more efficiently.

### Materials and Methods

The flours used in these experiments were a commercial straight-grade flour milled from Genesee variety soft white winter wheat, grown in Michigan, and a straight-grade flour milled at this Laboratory from a blend of Kansas hard red winter wheat varieties. The starch was commercial pearl-grade corn starch.

Some information is available on the conditions for treating starches with hydrogen chloride gas (4,5). A critical variable in processing flour is moisture content, which should be from 6 to 12%. Below 6% the rate decreases, and above about 12% localized overreaction occurs (6). In the process used in the present study (6), starch or flour was dried to between 8 and 10% moisture and then contacted with gaseous hydrogen chloride. The gas is mixed with air and introduced into the bottom of a ribbon mixer containing the flour. The products from either the present or previous process are similar (Table I). The functional simi-

TABLE I  
COMPARISON OF ACID-MODIFIED WHEAT FLOUR PRODUCTS<sup>a</sup>

PROPERTY	WITH 4 <i>N</i> HCl	WITH ANHYDROUS HCl
Protein dispersibility, %	46	53
Dispersibility, %	92	93
Blue value, % of original	90	86
Reducing sugars, % as maltose	2.9	3.0
pH of a 20% slurry	5.6	6.8
Viscosity, cooked paste at 55°C., B.U.	91	111
Time of reaction, min.	129	162
Particle size, % over 140-mesh	48	19

<sup>a</sup> The same shipment of flour was used in both test series of four runs each at identical temperature (90° and 110°F.) and acid levels. Averages are given.

larity has been confirmed by applying the products to paper in a tub-sizing operation (7). The gas process gives a more finely divided material.

The viscosity method (2) consists of taking a 10-g. sample, adding it to an alkali solution containing enough alkali to neutralize the acid and stop the reaction, and cooking this slurry at 98°C. in a small agitated cooker instrumented to record the motor load required for stirring. Under these conditions, the flour cooks in about 2 min., and the peak motor load is taken as a criterion of degree of conversion.

The method of pasting in this viscosity determination substantially disrupts the starch granules because of the high shear during cooking. The viscosity data may thus be more nearly related to a starch depolymerization than to other viscosity methods in which degree of granule swelling and granule fragility may determine the magnitude of the results.

The original flours and the starch had a viscosity of close to 150, based on the arbitrary units of viscosity obtained by the instrument. By correlation with end-product analyses made in an amylograph, the desirable viscosity for a tub-sizing agent was from 12 to 15. All viscosity measurements reported are in these instrument units.

## Results

Modification reactions were conducted at temperatures of 90° and 110°F. and at acid concentrations of 1.5 to 20 g. of HCl/kg. of dry solids. The data for each run were plotted as the logarithm of viscosity *vs.* time (Fig. 1), as were the previous data (3). These particular data illustrate only part of the present results obtained. In a few runs a slight curvilinearity was indicated, but that usually occurred in a region below the desired end-product viscosity. For convenience in analysis, the relationship was assumed to be rectilinear. In previous work (3) the viscosity units from the viscometer were converted to torque for determining the specific rate (or rate constant) of the first-order reaction. Re-examination of the data showed little advantage in this correction, so that the logarithmic relation previously given has different parameters than the relations used here.

For each concentration-temperature combination, the specific rates were calculated and plotted as functions of acid concentration (Fig. 2). While some variation is evident, the preponderant conclusion is that the dependency of rate on concentration concaves downward at 110°F. At any one concentration, limited data at 80° and 100°F. indicate conformity to the Arrhenius function with an "activation energy" of a high order as previously indicated (3).

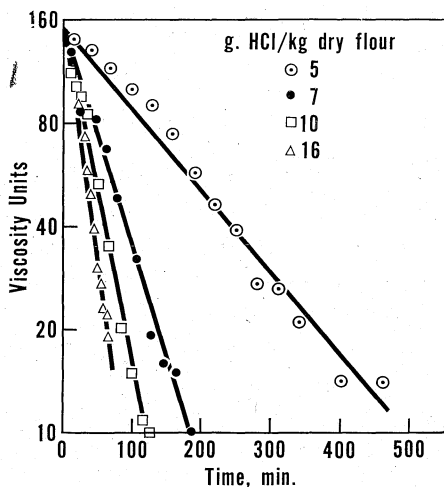


Fig. 1. Plots of logarithm of viscosity are linear with time. SWW flour at 110°F.

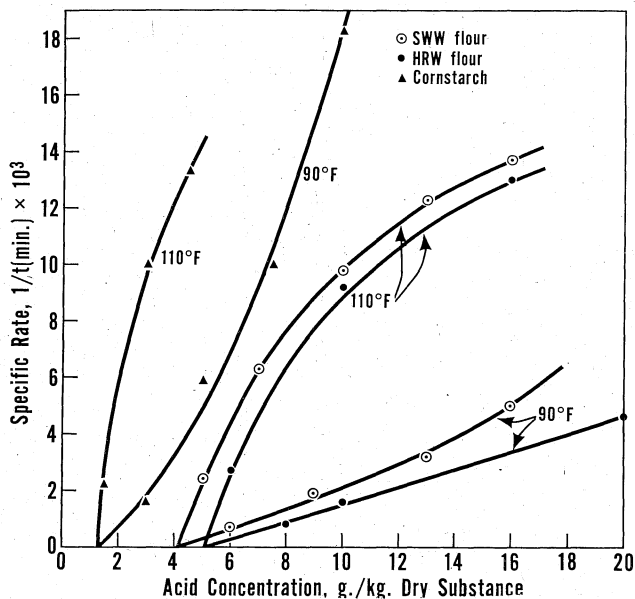


Fig. 2. Rates of modification increase with acid depending on substrate and temperature.

### Discussion

Various means of correlating the effect of protein, temperature, and acid concentration on the specific rate were attempted in order to

arrive at a general expression for the modification kinetics. All indications were that no reaction occurs below a minimum amount of acid, even for the starch. This minimum appears close to the amount required to reduce the pH to about 3.5, as previously indicated (3).

The data in Fig. 2 show that the protein-containing substrates require more acid than does starch to achieve the same specific rate. The protein does not act solely as a diluent, and no simple correction can be made. The protein apparently sorbs much more acid per unit weight than the starch, thus making such acid unavailable for reaction with starch. With the use of the concept of relative acid efficiency, that is, the ratio of acid required to achieve a given specific rate with starch to the amount of acid required to give the same specific rate with flour, the relationship shown in Fig. 3 was developed. In this figure,

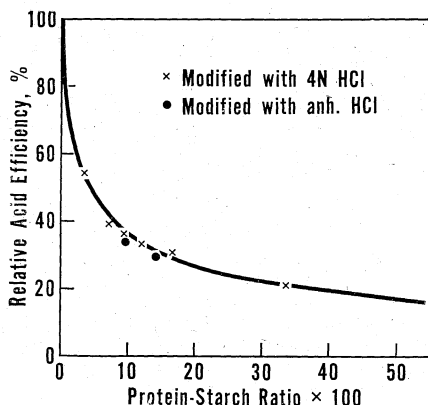


Fig. 3. Protein reduces the effectiveness of the acid.

not only are the data from the hard and soft flours from the present studies plotted, but also the data of Rankin (1), which cover a wider range of protein content and type and were obtained by a wet acid spray process. The correlation is thus a general one which is independent of factors such as temperature and acid concentration.

The curve drawn in Fig. 3 is the line  $(100/E - 1) = 7.4 P^{0.64}$ .  $E$  = relative protein efficiency, the amount of acid for a given specific rate with starch, divided by the amount of acid for the same specific rate with flour, times 100.  $P$  = protein-starch ratio, the protein content of the flour (% m.f.b.) divided by 100 minus the protein content.

Given the protein content of a flour, the efficiency can be calculated from this equation and thus the amount of acid necessary to give a desired modification rate predicted by reference to the appropriate

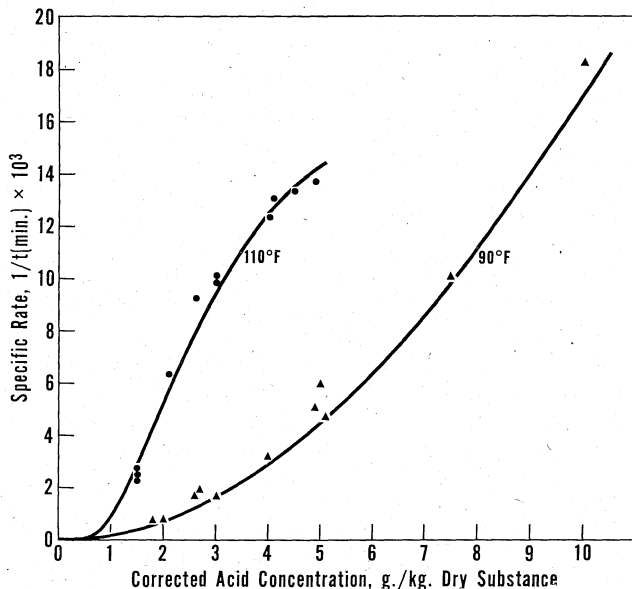


Fig. 4. When corrected for protein, kinetics for flours follows the pattern of starch.

specific rate curve for starch. The amount of acid for the flour is obtained by dividing the amount of acid required for starch by the efficiency for the flour.

The starch reference curves calculated by multiplying the concentrations of acid in the flours by the efficiency, together with the starch data (100% efficiency), are shown in Fig. 4. This figure illustrates that the pattern followed by the kinetics is relatively independent of the substrate after the acid concentrations have been corrected for protein effects.

The shapes of the curves in Fig. 4 are not easily explainable. Increased acid above the minimum required at 90°F. appears to greatly increase the specific rate over a wide range. With only 20°F. increase in temperature, the rate of increase of specific rate with increasing acid slows down after only a relatively small amount has been added. One possible explanation for this phenomenon is that the amount of sorbed (and thus reactive) acid may be limited as the temperature increases. Despite some uncertainty in interpretation, the relationships developed are a step forward in achieving good design and optimum operation of the acid-modification process.

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