1987

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Order Number 8721873

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Iowa State University, 1987

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A kinetic study on the lime-heat treatment of corn for masa production

by

Yung-Ho Chang

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of the
Requirements for the Degree of
DOCTOR OF PHILOSOPHY

Major: Food Technology

Approved:

Signature was redacted for privacy.

In Charge of Major Work

Signature was redacted for privacy.

For the Major Department

Signature was redacted for privacy.

For the Graduate College

Iowa State University
Ames, Iowa

1987

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NOMENCLATURE

a	Spherical-equivalent radius of corn kernel, m.
C	Concentration of water, kg/m^3.
C_i	Initial water concentration in corn kernel, kg H_2O/m^3 corn.
C_s	Saturation concentration of water, kg H_2O/m^3 corn.
D	Water diffusivity, m^2/hr.
D_0	Frequency factor for diffusion, m^2/hr.
E_a	Activation energy, cal/g-mol.
$E_{a,D}$	Activation energy of diffusion process, cal/g-mol.
$E_{a,K}$	Activation energy of gelatinization reaction, cal/g-mol.
e	Equilibrium state.
f	Equilibrium state.
G_0	Absorbance at 630 nm for raw, ungelatinized sample.
G_{100}	Absorbance at 630 nm for autoclaved sample.
i	Initial state.
K	First-order reaction rate constant, 1/hr.
K_a	Apparent reaction rate constant, 1/hr.
K_m	Reaction rate parameter of m-order rate equation, 1/hr.
K_0	Frequency factor for gelatinization reaction, 1/hr.
MC	Moisture content of corn, gm H_2O/100 gm dry-solid.
m	Order of reaction.

Q	Amount of water absorbed by corn, kg.
R	Absorption rate of water, kg/hr.
R_c	Gas constant, 1.987 g-cal/(g-mol)(°K).
r	Radial distance, m.
T	Absolute temperature, °K.
t	Cooking time, hr.
UG	Ungelatinized starch content, %.
V	Viscosity (flow consistency index), $g^n/cm^n sec^{2n-1}$.
WU	Amount of water absorbed by corn, gm H_2O/100 gm dry-solid.
X	Deformation ratio of cooked rice.
α	Gelatinized starch portion.
θ	Cooking time or reaction time, hr.

INTRODUCTION

Corn (Zea mays), consumed in a variety of forms, has been the basic cereal food for centuries in Central America and Mexico. The main form of consumption is the well-known tortilla, made either at home or industrially by cooking corn with lime (Bressani et al., 1958; Bressani and Scrimshaw, 1958; Katz et al., 1974). The recently increasing popularity of Mexican foods and corn-based snacks has generated a multimillion-dollar industry that uses the tortilla as the backbone for most traditional products, such as tacos, nachos and other corn snacks (Bedolla and Rooney, 1982). Thus, the tortilla-making process deserves increasing attention as commercial tortilla plants face the task of converting the traditional method of cooking into a large-scale industrial operation.

The traditional alkali-cooking method of tortilla production was originally developed by Latin American Indians (Katz et al., 1974). Today, even though most commercial plants use relatively sophisticated processing equipment, the basic steps for tortilla production remain relatively unchanged. The optimization of the entire process is determined quite subjectively. Experienced people are relied on to determine the optimum cooking time and to evaluate the properties of the final products (Bedolla and Rooney, 1982). At least one study has shown that the optimization of the process determined in this empirical manner is not necessarily consistent with that determined by a sensory panel (Martinez-Herrera and Lachance, 1979). Moreover, there is little knowledge about the properties of corn that can be used for screening and/or quality control purposes. Therefore, a more objective method for the optimization of the process is needed for quality control and better utilization of various corn hybrids.

Before a method for determining optimum cooking-time can be developed, we need to first learn what physical/chemical properties of corn control the cooking process. Starch is the major component in corn and its derived products; it makes up to 70 to 75% of corn kernels and about 80% of the weight of corn chips (Bedolla et al., 1983). During lime-heat treatment, the energy and alkali solution bring about the gelatinization of starch in corn. Several reports (Bedolla and Rooney, 1982; Khan et al., 1982) also mention that undercooked nixtamals (lime-cooked corns) may not have enough gelatinized starch granules to permit proper masa structure, and that overcooked samples with too high a degree of starch gelatinization may produce masa that is too sticky to be handled. These studies underlined the effect of starch gelatinization on the rheological properties of masa. Thus, the regulation of starch gelatinization should be an important control in the lime-heat processing of corn.

The extent of starch gelatinization is not easily measured analytically, particularly during processing. However, since the gelatinization reaction requires water as one of its reactants, one may be able to monitor the water uptake of corn and relate this uptake to the extent of gelatinization. To do this, a mathematical model is needed to quantitatively analyze the uptake of water during processing. This dissertation will present a study on the kinetics of water diffusion and starch gelatinization during the lime-heat processing of corn, based on the principles of diffusion and chemical reaction kinetics, in order to further understand the changes of corn during lime-cooking.

LITERATURE REVIEW

Traditional Processing of Corn

There are three major steps in the traditional tortilla-making process: lime-heat treatment (nixtamalization) of the corn kernel, the grinding or milling of nixtamal, and the final cooking of masa. Figure 1 shows the outline of the traditional method (Bressani and Scrimshaw, 1958).

Nixtamalization

A great range of processing conditions exist within the traditional method of processing. For example, during nixtamalization the corn kernel is cooked with lime (calcium hydroxide) and water for 20-50 minutes (Cravioto et al., 1945; Bressani et al., 1958). Likewise, the amount of water and lime used varies greatly with different reports, ranging from 120 to 350% (Cravioto et al., 1945; Bressani et al., 1958; Bedolla and Rooney, 1982) and from 0.5 to 5% (Cravioto et al., 1945; Bressani et al., 1958; Matinez-Herrera and Lachance, 1979; Bedolla et al., 1983) of the weight of corn, respectively. The cooking temperature is recognized as the boiling point of the mixture, which is from about 92 to 95°C (Cravioto et al., 1945; Bressani et al., 1958; Bedolla et

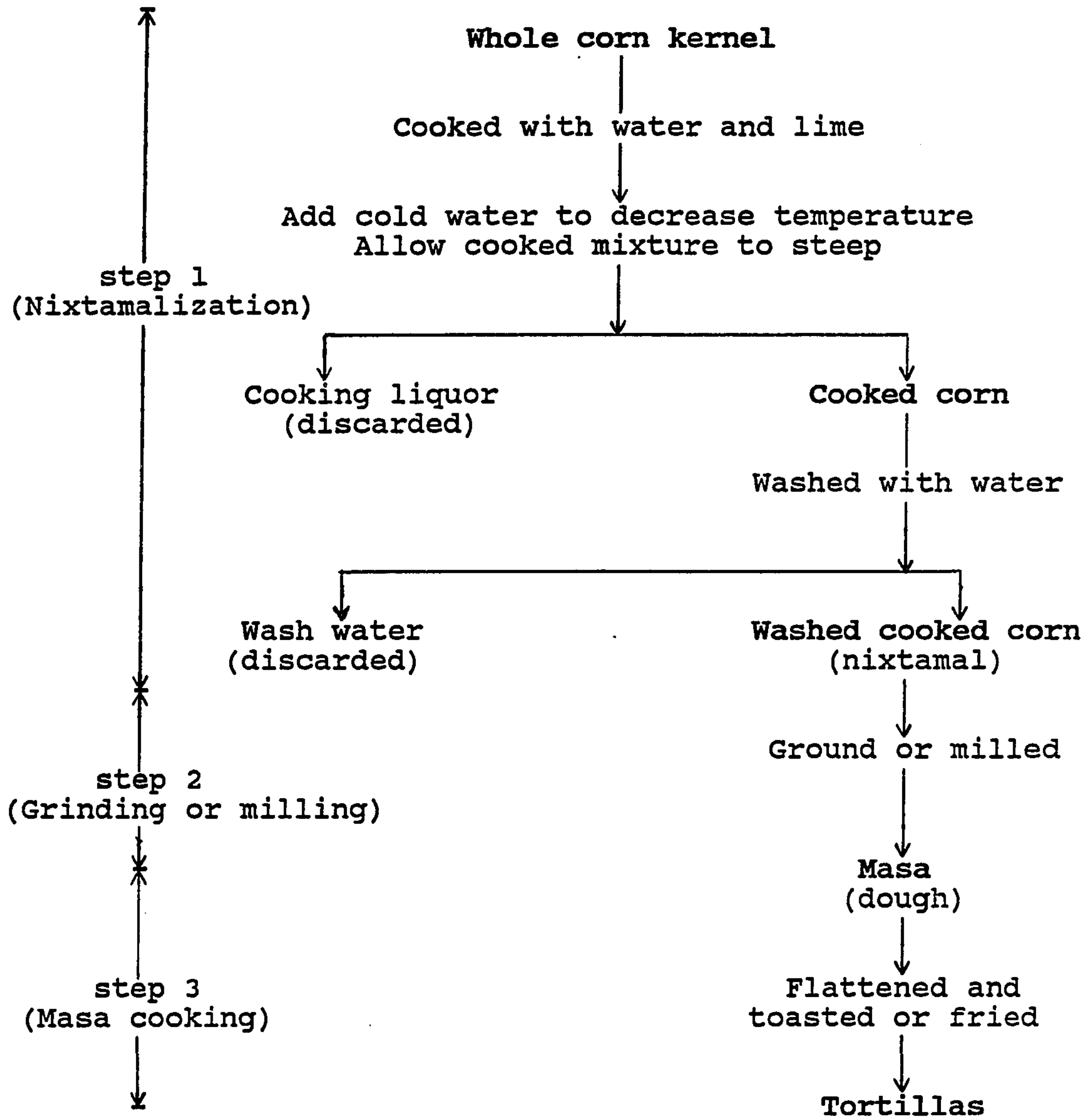


Figure 1. Traditional processing of corn

al., 1983). After cooking, cold water is added to reduce the temperature of the mixture to below 65°C, and then the cooked corn is allowed to steep for 16-18 hr (Cravioto et al., 1945; Bressani and Scrimshaw, 1958; Bedolla and Rooney, 1982). After steeping, the cooking liquor is discarded and the cooked corn is washed three times with tap water. The washed cooked corn is called nixtamal (Bressani and Scrimshaw, 1958).

Grinding or milling

The nixtamal is ground into masa either by hand or machine on a hard surface (Cravioto et al., 1945; Bressani et al., 1958; Bedolla and Rooney, 1982; Khan et al., 1982).

Masa cooking

About 50 gm of masa are patted into flat cakes, 0.2 to 0.3 cm thick and 15 to 20 cm in diameter. The cake is cooked on both sides on a hot iron plate for approximately 5 min to produce the final product (Cravioto et al., 1945; Bressani and Scrimshaw, 1958).

Effects of Lime-heat Treatment on Corn

In traditional processing, corn kernels are exposed to both alkaline and high temperature environments. This causes changes in the composition and the physical-chemical properties of corn.

Nutritive value

Corn is known to be deficient in the essential amino acids lysine and tryptophan (Mitchell and Smuts, 1932; Massieu et al., 1949), and in the B-complex vitamin niacin (Katz et al., 1974). Many efforts have been made to improve the nutritive values of corn-based foods: (1) by genetic means as in the case of Opaque-2 corn (Mertz et al., 1964; Sodek and Wilson, 1971); (2) by addition of limiting amino acids or by protein supplementation (Pushpamma et al., 1972; Bressani et al., 1979; Tonella et al., 1983); and (3) by germination of corn or by fermentation of corn meal (Hasim and Fields, 1979; Hamad and Fields, 1979).

Although alkali-cooking of corn causes the loss of some nutrients (Bressani et al., 1958; Sanderson et al., 1978), the nutritional quality of corn protein can be selectively enhanced by lime processing. This qualitative change probably results from a relative decrease in the solubility of zein, the poorest quality protein fraction in corn, and an increase in the rate of digestibility of most of the essential amino acids found in corn (Bressani and Scrimshaw, 1958).

Not only are the relative amounts of essential amino acids significantly improved by lime processing of corn, but also the availability, in vivo, for both the precursors to niacin and niacin itself appear to be enhanced (Katz et al., 1974). This enhancement is due to the alkaline treatment, which releases niacin from its bound forms, making it more available as a free nutrient (Harper et al., 1958).

Since calcium hydroxide is the usual alkali used to raise the pH value of the cooking solution in traditional processing, the final product (tortilla) contains a large amount of calcium (Cravioto et al., 1945). The increase in calcium content is one of the major nutritional benefits of the alkali-cooking process (Bressani et al., 1958).

Physical-chemical properties

The following are the major changes of the physical-chemical properties of corn noted during lime-heat treatment:

Calcium absorption Depending on the cultivar of corn, the amount of lime used, and the extent of cooking, the amount of calcium absorbed by the corn kernel after the lime-heat treatment could range from about 4.5 to 24 times that of its original calcium content (Cravioto et al., 1945; Trejo-Gonzalez et al., 1982; Morad et al., 1986). In addition to the nutritional benefit mentioned above, the use of lime during the preparation of tortillas also brings about the following benefits. First of all, the presence of lime maintains the pH of the grain-lime-water mixture at 12.4, which is the level of alkalinity necessary to hydrolyze the hemicellulose component of the pericap. Hence, lime treatment assists in the removal of the hull from the corn kernel (Wolf et al., 1953). Secondly, the lime solution provides an alkaline medium that favors the three changes occurring in corn during processing: the change of protein conformation (Bressani and Scrimshaw, 1958), the gelatinization of starch granules (Trejo-Gonzalez et al., 1982; Paredes-Lopez and Saharopulos, 1982), and the release of niacin from its bound forms (Harper et al., 1958). Finally, the absorbed calcium also contributes to much of the flavor of the products made from alkali-cooked corn (Morad et al., 1986).

<u>Dry matter loss</u> In making tortillas the constituents of corn are lost in two ways, either by a physical loss of the grain components during processing or by their chemical destruction due to lime-heat treatment.

The loss of dry matter in nixtamalization comes from lime-treatment, heating, and leaching. The physical loss of solids from raw corn to the nixtamal stage varies from 5 to 14% (Bressani et al., 1958; Khan et al., 1982; Morad et al., 1986), which corresponds to the cooking method used and the extent of treatment. Bressani et al. (1958) also shows that this loss includes about one-third of the ether extractable portion of corn, one-fourth of the crude fiber content, one-tenth of the nitrogen content, and one-fifth to one-half of the vitamin and mineral content.

<u>Water uptake and starch gelatinization</u> After soaking in lime solution at 25°C for 12 hr, corn kernels absorb approximately 45% of their original weight in water. While cooking at 92-95°C with the same ratios of lime and water for 100 min, the corn kernels absorb approximately 90% of their original weight in water (Morad et al., 1986). The higher water uptake of corn during nixtamalization is the result of chemical changes in starch. Generally speaking, when a starch granule in an aqueous environment is heated to a temperature sufficient to furnish the energy needed to break the intramolecular hydrogen bonds of the granule, the starch granule will begin to swell rapidly with progressive hydration, lose birefringence and solubilize. This process is known as gelatinization (Hodge and Osman, 1980). Further

heating causes more loosening of the meshwork, allowing additional water to enter and enlarge the granule furthermore (Smith, 1982). Reports have shown that for nixtamalized corn, the longer the cooking time, the higher the enzyme-susceptible starch value, which is an index of the extent of starch gelatinization (Khan et al., 1982; Morad et al., 1986). Thus, during nixtamalization, the energy and the alkaline solution bring about the gelatinization of starch in corn; consequently, nixtamalized corn picks up more water than corn only soaked at room temperature does.

Lysinoalanine   Toxic compounds, such as lysinoalanine, produced in the alkali treatment of protein-containing foods have been a concern for years (Woodard and Short, 1973; 1977; De Groot et al., 1976). Since lysinoalanine was found in very small amounts in foods prepared under more rigorous conditions than those applied to traditional corn processing (Sternberg et al., 1975), and since the lime treatment of corn has been a processing technique used for hundreds of years (Katz et al., 1974), it is unlikely that the small amount of lysinoalanine resulting from the traditional lime treatment process of corn will have any important physiological consequences in humans (Dworschak, 1980).

Mathematical Models

Even though the phenomenon of starch gelatinization has long been recognized, studies on the kinetics of starch gelatinization are very limited. Currently there is no definitive kinetic model for starch gelatinization since the phenomenon of starch gelatinization itself is still not fully understood.

For studying the kinetics of cooking rice, Suzuki et al. (1976) used a parallel plate plastometer to measure the compressibility of cooked rice. They used the ratio of thickness of the cooked rice grain between the two parallel plates before and after compressing as an indication of degree of cooking. They found that the cooking rate of rice, as measured by the parallel plate plastometer, was a function of the cooking temperature and could be expressed by first-order chemical reaction kinetics. They also found that the activation energy of cooking changed at about 110°C.

According to their analysis, cooking rate may be limited by the reaction rate of the rice components with water at temperatures of 110°C and below. At temperatures above 110°C the cooking rate may be limited by the rate of diffusion of water through the cooked layer to the interface of the uncooked core where the reaction occurs. These hypotheses led them to calculate the reaction rate constant and the diffusion coefficient of water by using the unreacted core model, which assumes symmetric development of a gelatinized layer from the surface to the geometric center. The reaction rate constant, K, was then calculated by the following equation:

$$\mathrm{Ln}\ (1 - \alpha) = -K\theta$$

where α, gelatinized starch portion, was equal to $(X_\theta - X_0)/(X_e - X_0)$, with X_0, X_θ and X_e being the deformation ratios at cooking time 0, θ, and the terminal point of cooking, respectively. They used the value of 0.77 for terminal deformation and a value of 0.12, which was obtained from uncooked rice that has been soaked in water for 30 min, for initial deformation.

In another report, Suzuki et al. (1977) used the weighting method, instead of the deformation method, in a study of the cooking rate equation of rice. Soaking and cooking rates were examined isothermally and were calculated by measuring changes in the weights of rice accompanying soaking and cooking. The same assumptions and a similar mathematical model as those made in the previous report (Suzuki et al., 1976) were used to analyze the data. The results of the cooking rate study were in good agreement with the previous one.

Kubota et al. (1979) studied the gelatinization rate of rice and potato starches under isothermal conditions. Flow behavior of heated starch suspensions as a function of heating temperature were measured using a capillary tube viscometer. An m-th order chemical reaction model was used to analyze the data, and the reaction rate constant (K_m) was calculated from the following equation:

$$\frac{d\alpha}{d\Theta} = K_m (1 - \alpha)^m$$

where

$\alpha = (V_\theta - V_0)/(V_e - V_0)$ = Gelatinized ratio

V_0 = viscosity at initial time, approximated by the observed value after 1 min of mixing with hot water.

V_θ = viscosity at reaction time Θ.

V_e = viscosity at equilibrium state.

Θ = reaction time.

m = order of reaction.

K_m = reaction rate parameter of the m-th order rate equation.

By assuming m=1 (first-order reaction), they found that gelatinization of rice starch was very similar to that which occurred during the cooking of rice (Suzuki et al., 1976; 1977). They also concluded that the gelatinization rate was limited by the chemical reaction rate of starch components with water and/or the physical transforming rate, such as the melting of starch crystalline regions.

The kinetics of water diffusion and starch gelatinization in intact rice kernels during parboiling was studied by Bakshi and Singh (1980). The degree of starch gelatinization was determined using the amylose/iodine blue value method, and the reaction was assumed to be a first-order irreversible chemical reaction. An equation developed by Danckwerts (1950) was used to calculate the absorption rate at which water diffused into rice kernels under the influence of simultaneously occurring starch gelatinization. The influence of temperature on both diffusion and gelatinization was analyzed in terms of Arrhenius-type equations. The diffusion coefficients and reaction rate constants were simulated by using a computer-aided, non-linear optimization technique. They found that the parboiling process was limited by the reaction of starch with water below 85°C and by diffusion of water above 85°C, and that the activation energy for the diffusion-limited process was about half that of the reaction-limited process. They also concluded that the water diffusivity, D, and the reaction rate constant, K, were temperature-dependent, and Arrhenius-type equations were found to relate both D and K to the inverse of absolute temperature.

Wirakartakusumah (1981) observed the gelatinization phenomenon of rice starch by using differential scanning calorimetry (DSC) to estimate the transition energy of starch gelatinization. Since the enthalpy of gelatinization is a linear function of degree of gelatinization, the heat of transition (ΔH) can then be used as a measure of the amount of ungelatinized starch for the calculation of the reaction rate constant. Two systems were examined, the isothermal system and the dynamic system. The isothermal system studies the extent of reaction as a function of time at a given constant temperature. The dynamic system is based on the heat evolution or temperature scanning method using the DSC data. The reaction rate constant was calculated by the following equation:

$$\mathrm{Ln}\ (UG_t - UG_f)/(UG_i - UG_f) = -K_a t$$

where UG_i, UG_t and UG_f are the initial amount, the amount at time t, and the maximum amount at the given temperature, of the ungelatinized starch, respectively. K_a is the apparent rate constant and t is the reaction time. Based on the results, the author concluded that the first-order model adequately described the rate of gelatinization after the lag period when the cooking temperature was greater than 67°C. Therefore, even though the first-order rate model did not describe the rate of gelatinization over the entire range of gelatinization, the model still can be used over limited extents of gelatinization.

Cabrera et al. (1984) studied the kinetics of water diffusion and starch gelatinization during the traditional tortilla-making process at different cooking temperatures and at different water-to-grain ratios. A commercial white corn variety was used and the experiments were carried out in the absence of lime. A mathematical model similar to the one used by Bakshi and Singh (1980) was examined. The results showed that the water-to-grain ratios had no effect on either the extent of starch gelatinization or the amount of water absorbed during the process. They also concluded that in the temperature range studied (70-90°C), the gelatinization reaction controlled the process. Also, the water diffusivity (D) and the reaction rate constant (K) were temperature-dependent, and both D and K followed the Arrhenius-type equation.

Water diffusion and starch gelatinization kinetics during lime cooking of corn was investigated by Herrera et al. (1986) using the unreacted core model proposed by Suzuki et al. (1976; 1977). A yellow dent corn variety was used in this study, which was cooked under different cooking temperatures and with different amount of $Ca(OH)_2$. Cooking rate, hence the degree of gelatinization, was examined through corn radius measurement of alkali-treated corn exposed to different temperatures and calcium hydroxide concentrations. The reaction rate and mass diffusivity were obtained by numerically solving the mathematical equations of the model. From the results obtained, they concluded that cooking rate was limited mainly by the reaction of gelatinization, and the reaction rates for both the diffusion process and the gelatinization reaction increased with increasing temperature.

Table 1 gives the summary of the reported studies on the kinetics of starch gelatinization. The activation energy (E_a) values obtained from the dynamic system of Wirakartakusumah (1981) were much greater than those of the isothermal system, and appeared to be dependent on temperature, i.e., E_a increases with increasing temperature. In the actual cooking process the cooking temperature varies with time; consequently, the rate parameters, which are functions of temperature, also change with respect to time. For better interpretation of the result of kinetic studies, it is recommended that experiments be performed under cooking conditions approaching those anticipated in the actual process.

Table 1. Summary of reported studies on the kinetics of starch gelatinization

	Type of study	Method	Cooking temperature(°C)	Activation energy E_a (Kcal/g-mol)	
				Chem. rxn.	Diffusion
Suzuki et al. (1976)	cooking of rice	rheological-parallel plate plastometer	75, 80, 90,100 110,120,130,150 (isothermal)	19 8.8	- -
Suzuki et al. (1977)	soaking and cooking of rice	weighting method	70,75,80,90,98.5 (isothermal)	20	-
Kubota et al. (1979)	gelatinization of rice and potato starch	rheological-capillary tube viscometer	rice: 70,75,80,85 potato: 60,61,62,63 (isothermal)	14 230	- -

Bakshi and Singh (1980)	diffusion and gelatinization of rough and brown rices	amylose/iodine blue value method		rough rice:	
			50, 60, 70, 80	18.5	7.9
			90,100,110,120 (isothermal)	10.5	15.7
				brown rice:	
			50, 60, 70, 80	24.7	3.8
			90,100,110,120 (isothermal)	9.6	15.5
Wirakartakusumah (1981)	gelatinazation of rice starch	differential scanning calorimetry	65,67,70,73,75 (isothermal)	25	-
			70-75 (non-isothermal)	44-73	-
Cabrera et al. (1984)	diffusion and gelatinization of white corn - water cooking	amylose/iodine blue value method	70,80,85,90 (isothermal)	18 (70-90°C)	10.6-13.7 (80-90°C)
Herrera et al. (1986)	diffusion and gelatinazation of yellow corn - lime cooking	equivalent spherical radius values	70,80,85,90 (isothermal)	-	-

Simplex Search Technique

The simplex search technique is one of the most frequently referred to optimization techniques that can be used for multi-parameter searches, especially the non-linear simplex method originally proposed by J. A. Nelder and R. Mead in 1965 (Adby and Dempster, 1974; Daniels, 1978). Generally speaking, for minimizing an error function of n variables, the simplex method begins by choosing (n+1) parameter vectors to span an n-dimensional space. The geometric figure which is formed by these points is called a simplex, hence the name of the method. For instance, a two-dimensional simplex is a triangle, a three-dimensional simplex is a tetrahedron, a four dimensional simplex is a pentahedron, and so on. An initial guess must be made for the n variables, then the optimization technique is used to adjust the parameters to minimize the error function. The value of the function is calculated at each of these trial points, and a comparison among these calculated values is made. The trial point with the highest value of the function is replaced by a point with a lower value. As the function approaches the minimum, the point of the simplex with the highest value is replaced by a point with a lower value in order to form a new simplex of (n+1) points. This procedure is repeated until the point corresponding to the minimum value of the function is achieved, or the stopping criterion is satisfied (Fan et al., 1971; Daniels, 1978).

Several stopping criteria can be used, one of which is the occurrence of five consecutive values of the function, which can be considered to have the same value according to the accuracy of the computer word-length being used. Another criterion is to compare the standard error of values of the function with a specified value, and then stop the program when the standard error falls below the value (Fan et al., 1971).

Compared with other methods, the simplex method proposed by Nelder and Mead showed more efficiency for function minimization (Nelder and Mead, 1965). This search method was used to solve the problems arising in production planning and inventory control by Fan et al. (1969). For either the production scheduling problem or the personnel and production scheduling problem discussed, the simplex method was shown to be an efficient search procedure for finding the minimum or maximum of a multi-variable function.

Recently, Hsu (1983) used the simplex search method to simulate diffusion parameters of a diffusion model for describing the water movement in legumes during soaking. This search method was able to locate a set of parameters that would provide a minimal error sum of squares between the experimental and theoretical curves.

MATERIALS AND METHODS

Corn

A commercial corn starch (Argo, CPC International Inc., Englewood Cliff, NJ), and four yellow corn hybrids grown in Iowa were used in the development of the modified amylose/iodine blue value method.

A yellow dent corn hybrid grown in South Dakota was used in the study of the hydrothermal cooking of corn in the first part of the cooking experiments.

Nine cultivars of corn were used and classified as samples A to I in the study of the effect of the lime-heat treatment on different hybrids of corn. Among the samples, sample A is a commercial yellow dent corn suitable for dry milling. Sample B is a white corn, and sample C is a commercial yellow dent corn unsuitable for dry milling (Lincoln Grain Inc., Atchison, KS). The other six samples are yellow corn hybrids selected for the purpose of having a wide quality range (Table 2).

For stickiness measurement experiments, a food grade corn grown in Tennessee was used.

All grain samples were cleaned by hand to remove foreign materials, cracked and immature kernels, and to make sure there was no visible mold, staining or insect damage to

Table 2. Properties of corn samples used in lime-cooking experiments[1]

Samples	D_{30}[2] (m^2/hr)	PI[3]	Radius[4] (cm)
A	1.0718E-7	0.368	0.3824
B	1.3641E-7	0.307	0.3918
C	1.2298E-7	0.442	0.3751
D	1.0516E-7	0.266	0.3613
E	0.9223E-7	0.476	0.3896
F	1.0615E-7	0.409	0.4003
G	1.0442E-7	0.399	0.3833
H°	0.7386E-7	0.422	0.3847
I	1.4585E-7	0.429	0.3823

[1] Unpublished data (Hsu, K. H., 1985).

[2] Water diffusivity measured at 30°C.

[3] Pearling index measured after 5 sec of pearling.

[4] Spherical-equivalent radius.

the kernels.

Cooking Procedure

Water-cooking experiments

For the first part of the cooking experiments the procedure was as follows: 500 gm of corn was cooked with 1250 ml of distilled water in a 4000 ml beaker on an electric hot plate. After the contents of the beaker reached boiling, it was held for an additional 25 min. Then, 1250 ml of cold water was added to cool the cooking solution below 65°C, and the cooked corn was allowed to steep for 16 hr. During cooking, continuous stirring was applied using a T-line laboratory stirrer (Talboys Engineering Co., Emerson, NJ).

Lime-cooking experiments

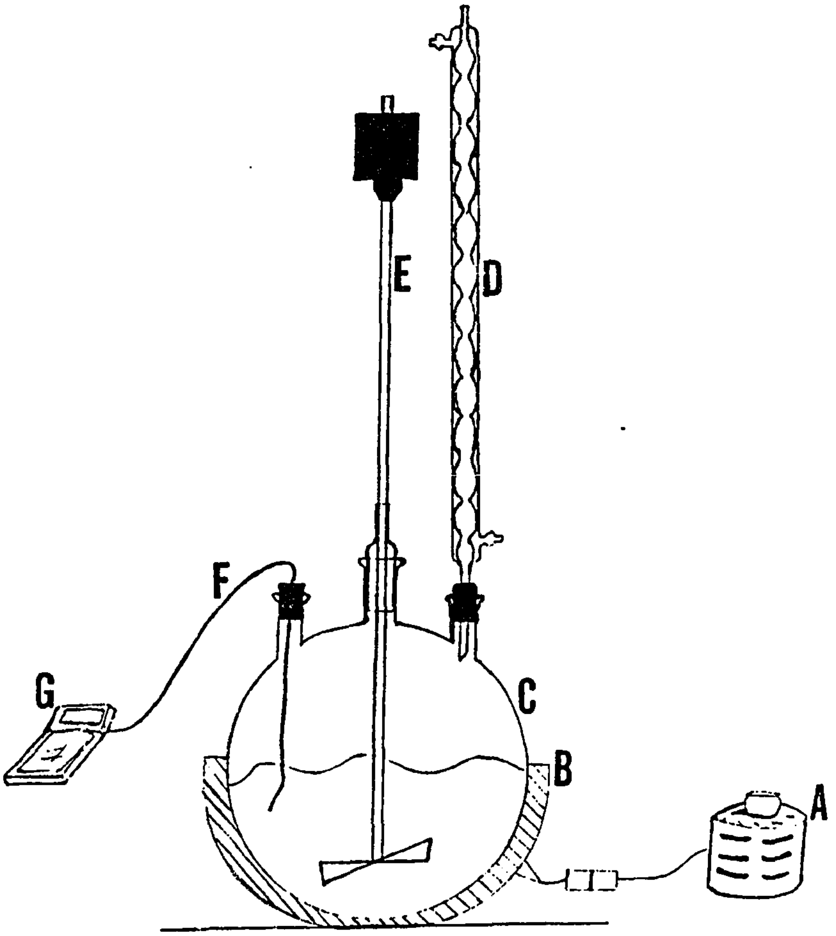
Calcium hydroxide solution, instead of water, was used for the study of the effect of the lime-heat treatment on different cultivars of corn. The amount of calcium hydroxide (reagent grade, Fisher) used was 1% based on corn weight. The cooking process was similar to that described above except that the boiling time, the weight of corn grains, and the amount of cooking solution used were changed to 20 min, 250 gm and 625 ml, respectively; and continuous stirring was applied using a StedFast laboratory stirrer (model SL-300, Fisher Scientific Co., Pittsburgh, PA). Cooking experiment was duplicated for all nine cultivars of corn used.

Stickiness measurement experiments

For stickiness measurement experiments, the same amounts of corn grains, $Ca(OH)_2$, and water as those used in lime-heat treatment of different cultivars of corn were used. The cooking procedure was performed in a three-vertical-neck, round-bottom flask, which was heated by a heating mantle (Glas-Col Apparatus Co., Terre Haute, IN). To avoid the evaporation of water during the long cooking period, a water-cooled condenser was used as shown in Figure 2. A variable autotransformer (type 2PF1010, Staco Energy Products Co., Dayton, OH) was used to control the heating rate. Boiling of the mixture in the flask was reached after 15 min of cooking, and the mixture was held at the boiling point for 10, 20, 30, 40 and 50 min. After the desired cooking time, cold water was added immediately to lower the temperature of the mixture below 65°C. The cooked corn was then allowed to steep for 16 hr at room temperature. Cooking experiment was duplicated for each cooking time.

Figure 2. Cooking apparatus for stickiness measurement experiments

A. Variable autotransformer.
B. Heating mantle.
C. Three-vertical-neck flask.
D. Condenser.
E. StedFast laboratory stirrer.
F. Thermocouple probe.
G. Digital thermometer (model 870, Omega Engineering Inc.).


E
D
F
G
C
B
A

Sampling

Cooking experiments

During cooking studies, samples for water uptake and starch gelatinization determinations were collected from the beaker every 5 min from the beginning of the cooking period until the addition of cold water. Thereafter, two more samples were collected during the steeping process.

Stickiness measurement experiments

For stickiness measurement experiments, after the addition of cold water, about 10 gm of cooked corn were collected for the degree of starch gelatinization determination, and the remainder was used in the stickiness measurement after the steeping process.

Degermination of Corn

Corn samples were prepared for degermination by soaking raw corn kernels in ten times their weight of distilled water for 1 hr at room temperature (30 min for cooked corn), drying the kernels superficially with facial tissues, and tempering them in a jar for 1 hr. Corn endosperms were gently rubbed away from the hulls and germs using a grinding mill (model 4E, Straub Co., Philadelphia, PA) with 0.1 cm in clearance, and were then separated and picked out by hand. After air-drying at room temperature for 24 hr, the endosperms were ground to a powder in a spice mill (coffee and spice mill, model 505, Moulinex Products Inc., Virginia Beach, VA).

Preparation of Totally Gelatinized Corn Samples

For the determination of the degree of gelatinization, commercial corn starch and degermed raw corn flours with a particle size between 60 mesh and 200 mesh U. S. sieves were used and identified as ungelatinized (0% gelatinized) samples. Totally gelatinized corn starch or corn flours (defined as 100% gelatinized) were prepared from the commercial corn starch or the ungelatinized corn flours by autoclaving a 2% slurry at 121°C (15 psi) for 1 hr, and drying the mixture in a freeze-dryer (model USM-15, Virtis Co. Inc., Gardiner, NY).

Temperature of Cooking Solution

Temperature of the cooking solution during processing of corn was detected by a K-type thermocouple probe (Omega Engineering Inc., Stamford, CT), and recorded on a strip chart recorder (recordall series 5000, Fisher Scientific Co., Pittsburgh, PA).

Water Uptake

Samples for water uptake determinations were dried superficially with facial tissue upon the removal from the beaker and weighed. The moisture contents of the samples were determined by drying at 103±1°C for 72 hr (AACC, 1983) in an air oven (model 126G, Fisher Scientific Co., Pittsburgh, PA). The amount of water absorbed by corn at a given cooking time was calculated by the following equation:

$$WU_t = MC_t - MC_0$$

where WU_t= amount of water absorbed by corn at cooking time t,
MC_t= moisture content of cooked corn at cooking time t,
MC_0= moisture content of the raw, uncooked corn sample.

Degree of Starch Gelatinization

Samples for the determination of the degree of starch gelatinization were immersed in ice-water immediately after removal from the cooking mixture. The samples were then degermed and ground according to the procedure described earlier. The ground samples with a particle size between 60 mesh and 200 mesh U. S. sieves were used in the determination of the degree of gelatinization. Two methods were used in the determination of the degree of gelatinization: the modified amylose/iodine blue value method and an enzymic method.

The modified amylose/iodine blue value method

This method is a modification of the colorimetric assay for the degree of starch gelatinization proposed by Birch and Priestley (1973). This method is based on the absorbance of an amylose/iodine blue complex that is formed by the reaction of amylose released during gelatinization and the added iodine reagent. The degree of gelatinization is determined from the ratio of the absorbances of a sample treated with two different concentrations of alkali.

Samples The degree of starch gelatinization of water-cooked corn samples were measured by this method.

Reagents All chemicals used in this method were reagent-grade products from Fisher. Iodine reagent was prepared by dissolving 1 gm of iodine and 4 gm of potassium iodide in 100 ml of distilled water, and it was stored in an amber bottle.

Procedures For the determination of the iodine/blue value, about 0.2 gm of prepared sample was mixed with 98 ml of water, treated with 2 ml of 10M KOH solution and stirred for 10 min. After centrifugation at 580 x g for 10 min (centrifuge model IECHN-SII, International Equipment Co., Needham Hts., MA), 1 ml of supernatant was removed, treated with 0.4 ml of 0.5M HCl solution, and diluted to 10 ml with distilled water. One-tenth ml of iodine reagent was then added and mixed to develop the iodine blue color. The absorbance was then read at 580 nm in a spectrophotometer (Spectronic 20, Bausch and Lomb Inc., Rochester, NY) against a reagent blank. The process was repeated using 95 ml water, 5 ml 10M KOH, and 1 ml 0.5M HCl. The ratio of the two absorbances obtained from each sample was then used to determine the degree of starch gelatinization of that sample.

The enzymic method

The enzymic method used for the determination of the degree of starch gelatinization was based on the procedure of Chiang and Johnson (1977). This method is based on two principles: that gelatinized starch is readily digested by a hydrolytic enzyme (glucoamylase) and that the digestability is proportional to the degree of gelatinization.

Samples The extent of starch gelatinization of the degermed lime-cooked corn flours were measured by this method.

Reagents Sodium acetate buffer was prepared by dissolving 4.1 gm of anhydrous sodium acetate (reagent grade, Fisher) in distilled water making up to 1 L, and adjusting the pH of the solution to 4.5 with acetic acid (reagent grade, Fisher). Twenty-five percent (w/v) trichloroacetic acid (TCA) solution was prepared by dissolving 25 gm of the reagent (reagent grade, Fisher) completely in a small amount of water, and diluting it to 100 ml total volume. A 6% (v/v) o-toluidine reagent (Sigma Chemical Co.) was used for the colorimetric assay of the amount of glucose. The enzyme solution was prepared by dispersing 4 gm of amyloglucosidase from Rhizopus (Specific activity 10,800 u/gm of solid, Sigma Chemical Co.) in 500 ml of sodium acetate buffer and filtering it rapidly through a glass-fiber filter paper (number G6, Fisher brand, Fisher Scientific Co.). The enzyme solution was used within a 2 hr period.

Procedures Twenty mg of ground sample were totally dispersed in 5 ml of distilled water in a 50 ml centrifuge tube. Twenty-five ml of amyloglucosidase solution was added and each tube was incubated in a 40°C water bath for 30 min. Two ml 25% TCA solution was added to inactivate the enzyme and precipitate the enzyme and other proteins. The precipitate was separated from the supernatant by centrifuging at 16,000 x g for 5 min in a centrifuge (model RC2-B, Ivon Sorvall Inc., Newtown, CT). One-half ml of supernatant was mixed with 4.5 ml of o-toluidine reagent in a test tube. The green chromogen was developed by cooking the mixture in boiling water for 10 min. Five ml of glacial acetic acid was added to each tube after cooling with cold water. The absorbance was measured at 630 nm in the Spectronic 20 spectrophotometer against a reagent blank. The extent of starch gelatinization was calculated as:

$$\alpha \% = (S - G_0)/(G_{100} - G_0) \times 100\%$$

where α was the percentage of starch gelatinization of a cooked sample. S, G_0 and G_{100} were the absorbances at 630 nm for that sample, ungelatinized sample (0%), and totally gelatinized sample (100%), respectively.

Equivalent Radius of the Corn Kernel

The corn kernel is not defined by a standard geometric shape. However, for analytic purposes it has been assumed to be a sphere (Cabrera, 1984; Herrera et al., 1986). The spherical-equivalent radius of corn kernels can be determined when the volume occupied by a given number of grains is known.

About 35 gm of raw corn kernels was randomly chosen from each corn sample. The number of kernels was counted and the sample was placed in the sample cup of the pre-calibrated air comparison pycnometer (model 930, Beckman Instruments Inc., Fullerton, CA). The sample cup was clamped and firmly locked. After allowing 15 sec for balancing, the air in the reference chamber and the sample chamber were compressed by turning both reference and measuring handwheels simultaneously or alternately until the reference handwheel rested against the stop. The pointer in the counter was kept on scale during this process in order to maintain equilibrium within the chambers. After 10 sec, the pointer was adjusted to zero with the measuring handwheel, and the sample volume (in cc) was read directly from the counter. The spherical-equivalent radius of the corn sample was then calculated as

$$a = \left(\frac{3V}{4n\pi} \right)^{1/3}$$

where a is the spherical-equivalent radius (cm), V is the measured sample volume (cm^3), and n is the number of the corn kernels used in the measurement.

Stickiness

Stickiness values of masa prepared under different durations of cooking were measured using the modified adhesion test method described by Cagampang et al. (1982).

Samples

Corn kernels were cooked for different times, and allowed to steep for 16 hr as described earlier. After soaking, the cooking solution was discarded and the cooked corn was washed three times with tap water to remove the excess $Ca(OH)_2$ and residual hull from the kernel surface. The nixtamal was ground immediately in a mechanical stone grinder (Glen Mills Inc., Maywood, NJ). Clearance of 0.1 cm between the two plates was used. Stickiness of masa was measured on an Instron testing machine (model 1122, Instron Corporation, Canton, MA) using a test cell (described in the following section). Stickiness measurement was triplicated for each sample prepared with different cooking times. For each measurement 40 gm of masa was used. The masa was kneaded by hand, and was shaped into a cake 1.8 cm thick and 5 cm in diameter using a petri dish.

Test cell

The major component of the test cell was a flat plate, made of plexiglass, 0.6 cm thick and 8 cm in diameter. The plexiglass plate was connected to a small plexiglass square through four plumber's chains (each 16 cm in length). The square plastic was hung on the hook of a 2-kg tension load cell through a metal ring (Figure 3).

Procedures

A 1-kg weight was placed in the center of the plexiglass plate of the test cell, and the entire rig was lowered onto the masa cake. Care was taken to make sure the central axis of the weight compressor, test cell, and sample cake were aligned in one straight line. This allowed the compression force to be distributed evenly over the surface of the sample. When the chains slackened, the weight was

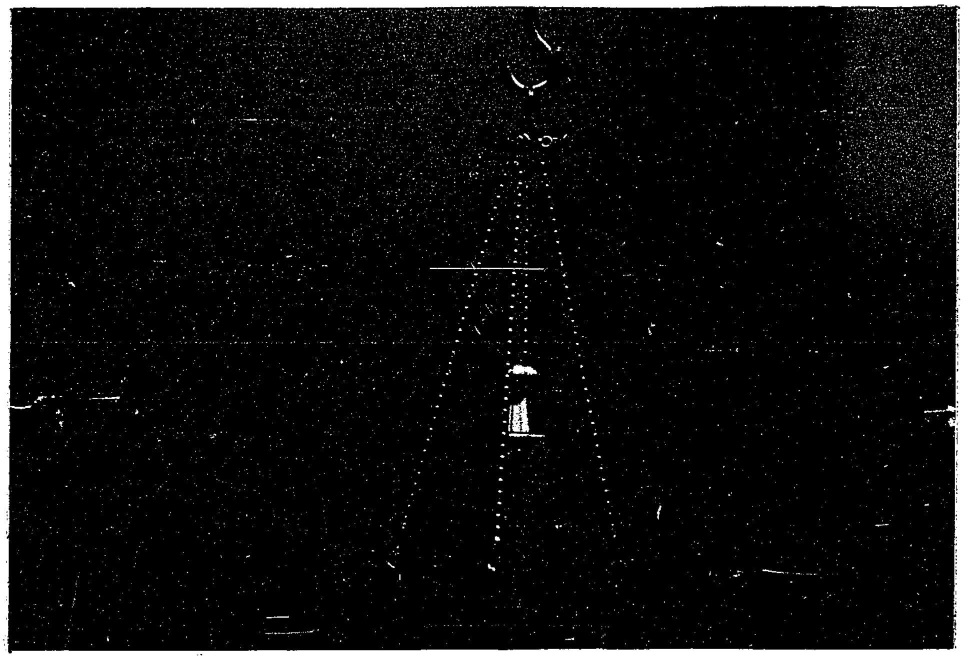
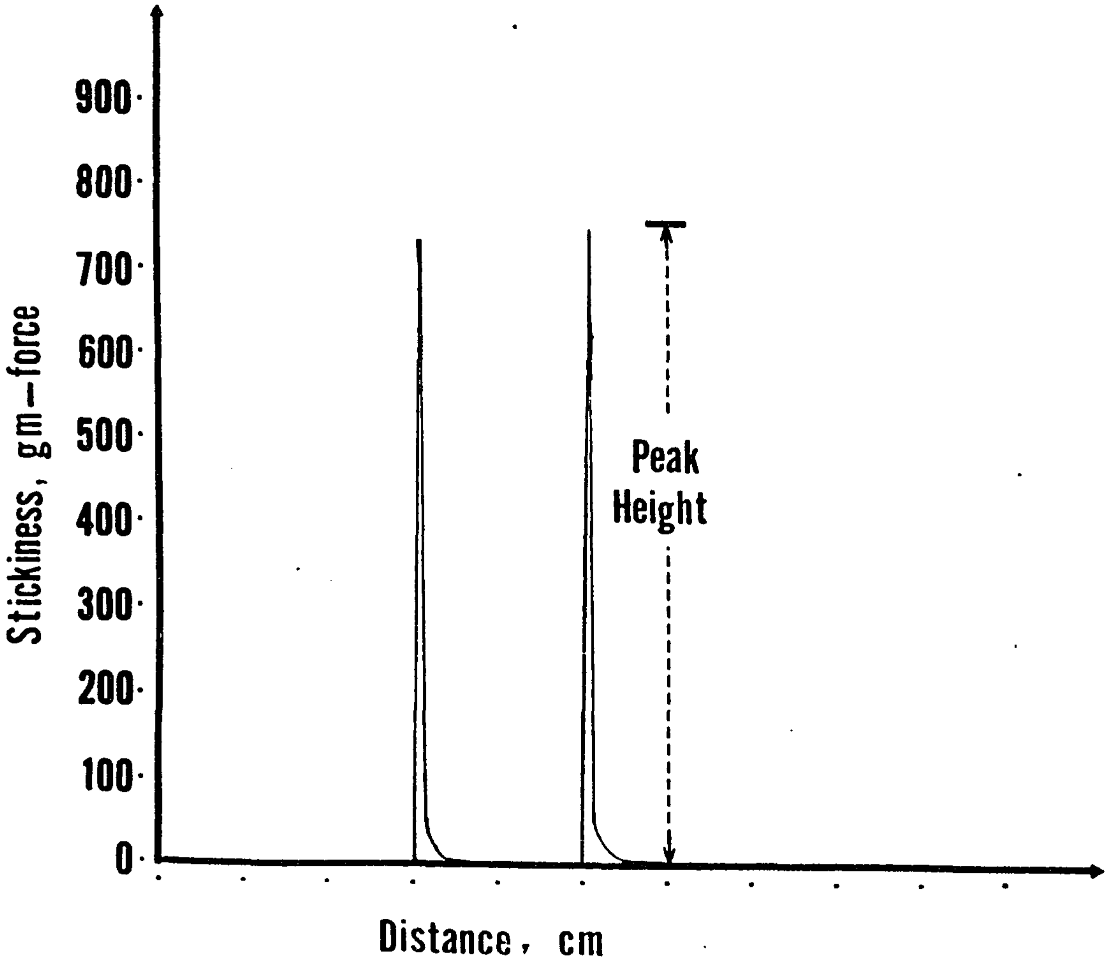


Figure 3. Adhesion test cell mounted in the Instron testing machine model 1122

A. Plexiglass plate.
B. One-kg weight.
C. Plumber's chain.
D. Square plastic plate.
E. Metal ring.
F. Hook of a 2-kg tension load cell.

allowed to remain on the plastic plate for 3 min and then removed. Ten sec after the removal of the weight, the test was run in the tension mode with a 100 mm/min crosshead speed and 20 mm/min recorder chart speed. Figure 4 shows a typical recording of the measurement. The peak height was measured and used as an expression of the stickiness value (adhesion force in grams).

Figure 4. Adhesion peaks of stickiness measurement


900
800
700
600
500
400
300
200
100
0
Stickiness, gm—force
Peak Height
Distance, cm

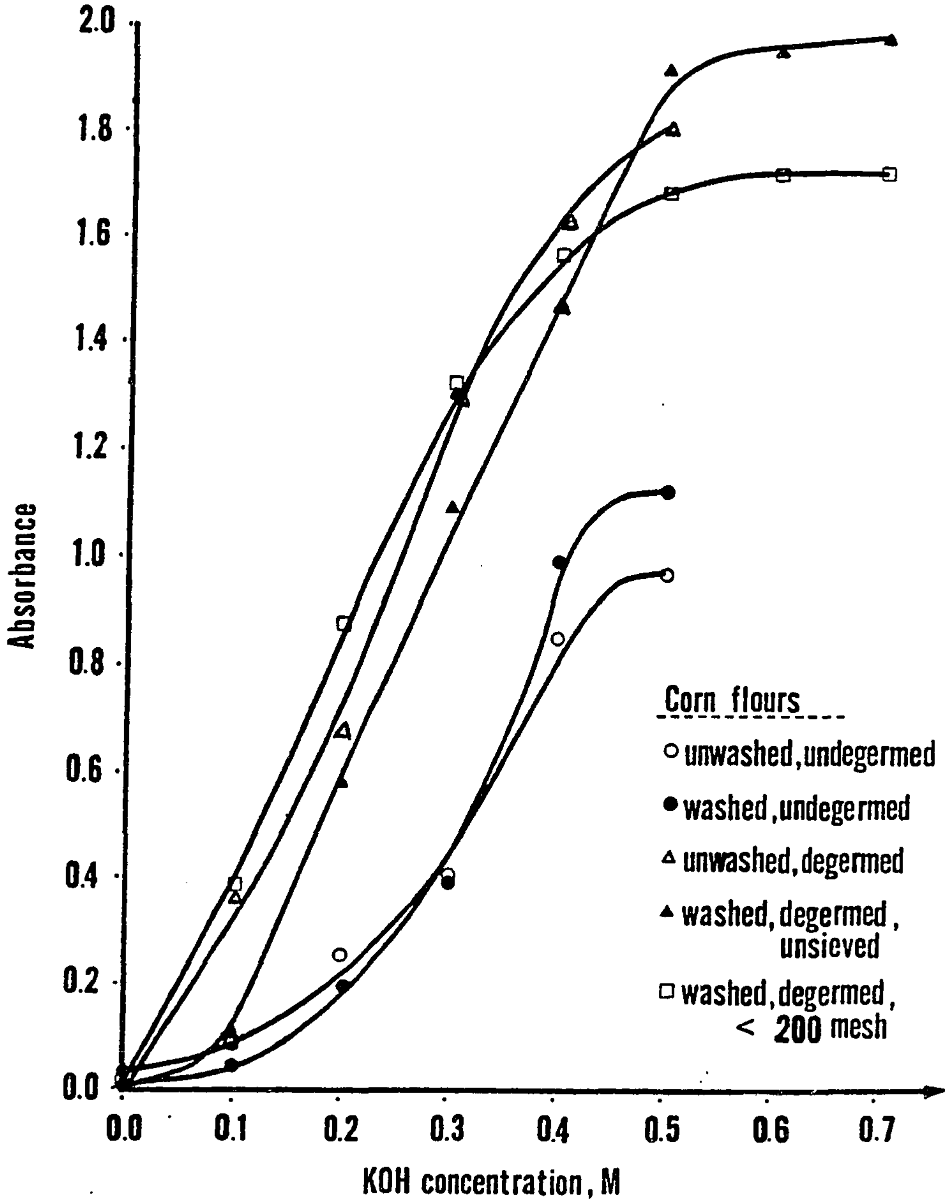
RESULTS AND DISCUSSION

The Colorimetric Method for Determining the Degree of Starch Gelatinization in Water-cooked Corn

Factors affecting determination of degree of gelatinization

The amylose/iodine blue value of cooked corn was initially measured according to the procedure of Birch and Priestley (1973). Results were shown in Figure 5 (undegermed samples). In their study, the authors indicated that the measurement of the amylose/iodine blue value was affected by the amount of damaged starch present in the sample. In our study, during sample preparation, corn kernels were ground in a spice mill, which could create an excessive amount of damaged starch. Therefore, the effect of damaged starch on the iodine blue value was investigated. Ground corn flours, either water-washed at 50°C or unwashed, were treated with different concentrations of potassium hydroxide. The iodine blue values of the samples were then measured. Although damaged starch on the surface of the unwashed rice grains caused erroneous results during Birch and Priestley's determination of degree of starch gelatinization in cooked rice (1973), we found it did not affect the iodine blue values of the raw, whole-kernel corn flours (Figure 5).

Figure 5. Effect of washing and degerming processes on the amylose/iodine blue value of corn flour treated with different concentrations of potassium hydroxide


2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
Absorbance
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
KOH concentration, M
Corn flours
○ unwashed, undegermed
● washed, undegermed
△ unwashed, degermed
▲ washed, degermed, unsieved
□ washed, degermed, < 200 mesh

It was anticipated that during the measurement of the iodine blue value the presence of lipids might cause erroneous results in the measured absorbance. To avoid lipid interference, corn kernels were degermed. The iodine blue values of the degermed ground samples, either water-washed or unwashed, were then measured. Figure 5 shows that even for degermed samples, damaged starch did not show much effect on the iodine blue value, and that the degermed samples had higher values of absorbance than those of undegermed ones. It was also observed that the particle size of the ground sample had some effects on absorbance measurement. The sample with particle sizes that passed 200 U. S. mesh sieve showed a different absorbance from the unsieved sample (Figure 5). Table 3 shows that the degermed corn sample with particle sizes between 60 mesh and 200 mesh U. S. sieves had constant iodine blue values. Samples with particle sizes larger than that range had smaller absorbance values, which could be due to the particle size being too coarse for the completion of the alkali-extraction of amylose. On the other hand, fine grinding could cause damage to the starch granule, which would result in a higher absorbance value. Based on the results shown in Figure 5 and Table 3, degermed ground samples with particle sizes between 60 mesh and 200 mesh sieves were used in the

Table 3. Effect of particle size on the iodine blue value of degermed corn flour treated with 0.2M and 0.7M KOH solutions

	Iodine blue value	
Particle sizes	Treated with 0.2M KOH	Treated with 0.7M KOH
Retained on 35 mesh sieve	0.130	0.936
Passed 35 mesh and retained on 60 mesh sieves	0.160	1.634
Passed 60 mesh and retained on 100 mesh sieves	0.194	1.960
Passed 100 mesh and retained on 200 mesh sieves	0.208	2.000
Passed 200 mesh sieves	0.266	1.954

following experiments. The effect of alkali concentration on the iodine blue value of corn samples with particle sizes between 60 mesh and 200 mesh sieves are shown in Figures 6 and 7, for raw and autoclaved corn flours, respectively. It was observed that the effect of the concentration of potassium hydroxide on each corn sample had the same tendency. Figure 6 also shows that the iodine blue value of raw corn starch or corn flours increases significantly when the concentration of potassium hydroxide is greater than 0.2M, and that the absorbance reaches its maximum when the concentration of potassium hydroxide is 0.5M. For cooked corn samples, the iodine blue value reached at least 85% of its maximum potential under 0.2M KOH treatment and remained at the maximum potential when the concentration of potassium hydroxide was at or greater than 0.5M (Figure 7). The ratio of absorbance obtained under two different concentrations of potassium hydroxide was used to calculate the extent of starch gelatinization (Birch and Priestley, 1973). Based on the results shown in Figures 6 and 7, the ratio of absorbance (0.2M/0.5M) obtained by using the absorbance values of samples treated with 0.2M and 0.5M KOH was optimal to differentiate samples with different degrees of gelatinization. For different corn samples, however, the differentiation between 0.2M and 0.5M absorbance was

Figure 6. Concentration effect of potassium hydroxide on the amylose/iodine blue value of raw corn starch and corn flours with particle sizes between 60 mesh and 200 mesh U. S. sieves

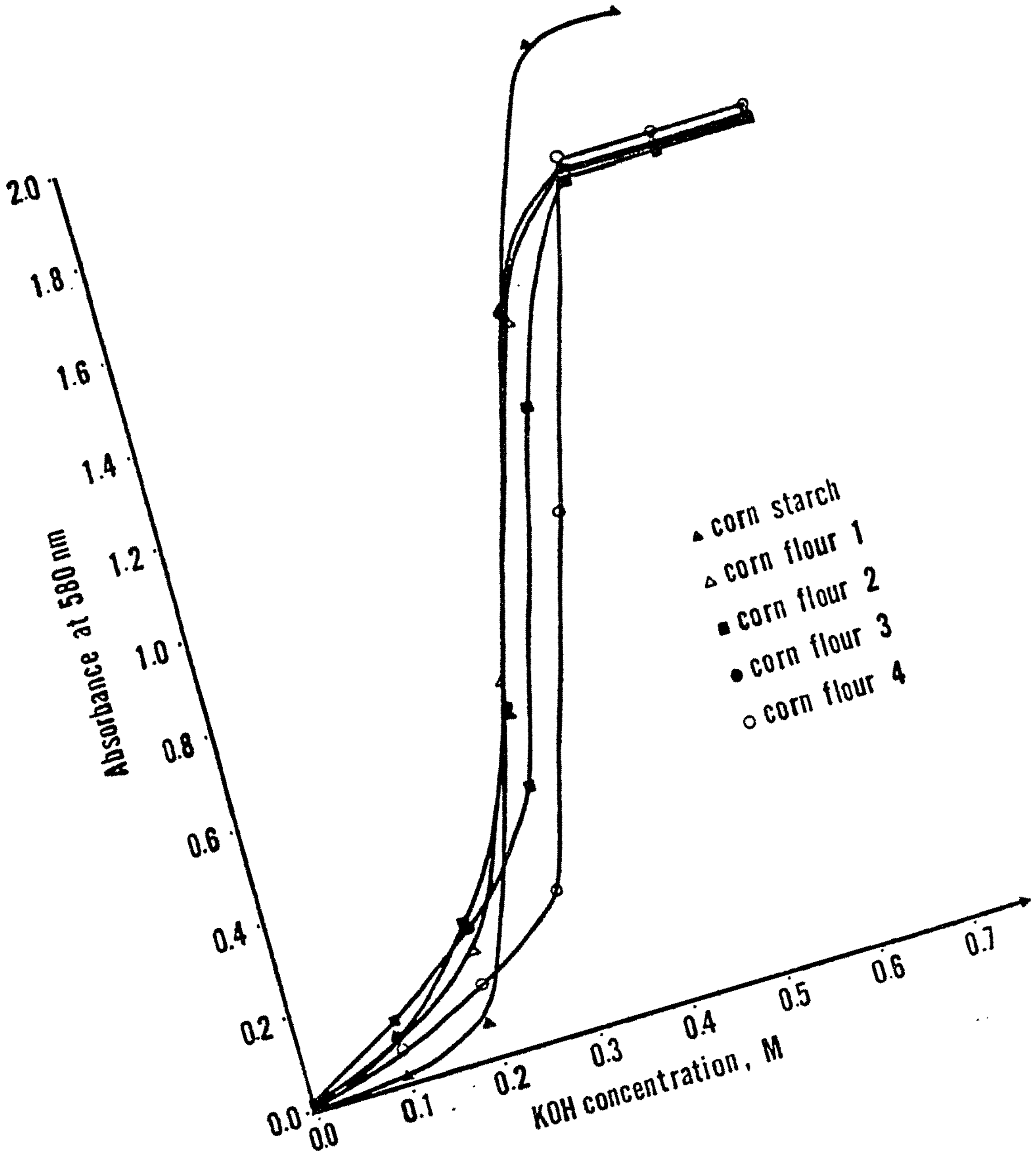
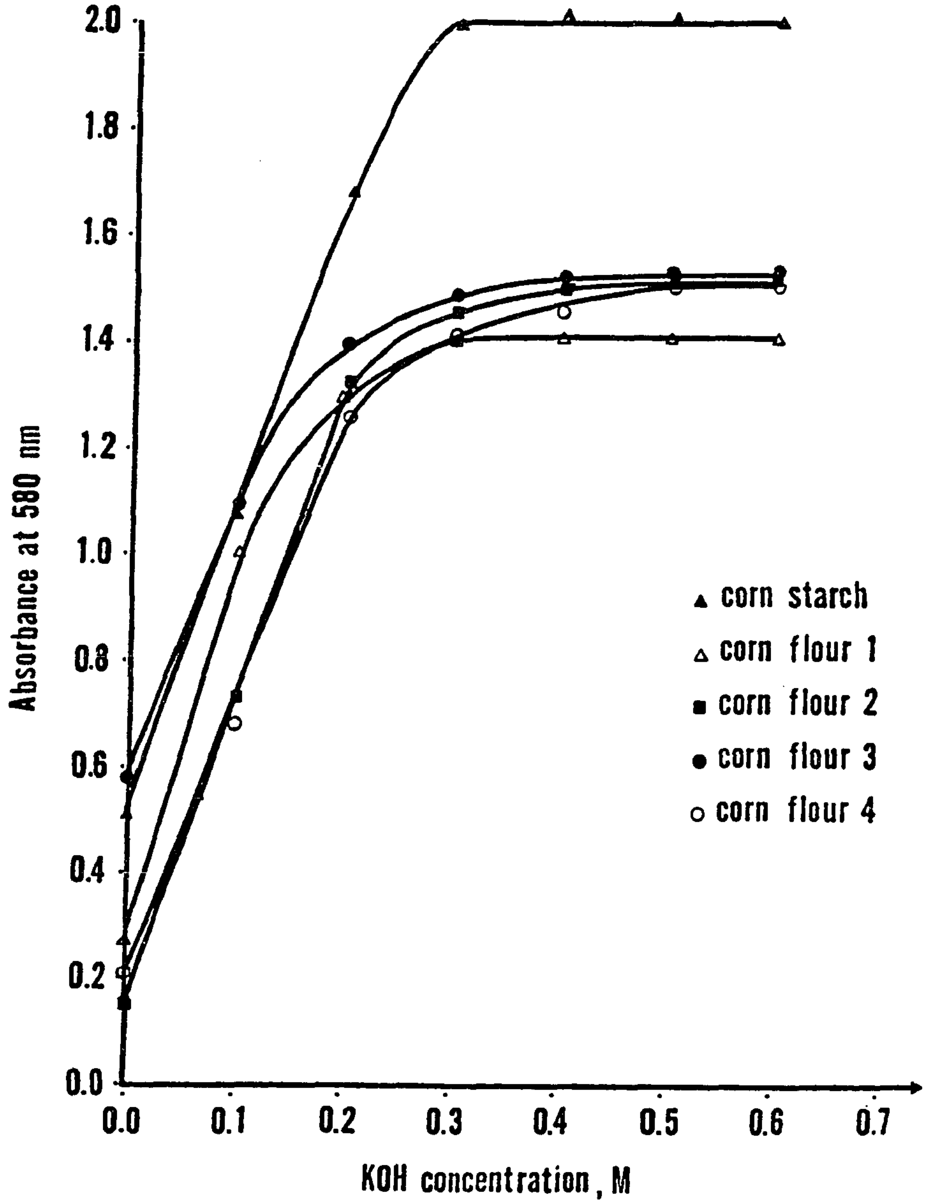

Absorbance at 580 nm
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
KOH concentration, M
▲ corn starch
△ corn flour 1
■ corn flour 2
● corn flour 3
○ corn flour 4

Figure 7. Concentration effect of potassium hydroxide on the amylose/iodine blue value of autoclaved corn starch and corn flours


Absorbance at 580 nm
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
KOH concentration, M
▲ corn starch
△ corn flour 1
■ corn flour 2
● corn flour 3
○ corn flour 4

slightly different. This phenomenon is possibly resulted from different ratios of amylose to amylopectin in different corn samples. This problem can be overcome by normalizing the difference as shown in the following equation:

$$\left[\begin{array}{l}\text{Normalized ratio}\\ \text{of absorbance}\\ \text{of a sample}\end{array}\right] = \frac{\left[\begin{array}{l}\text{Measured ratio}\\ \text{of absorbance of}\\ \text{the sample}\end{array}\right] - \left[\begin{array}{l}\text{Measured ratio}\\ \text{of absorbance of}\\ \text{raw corn}\end{array}\right]}{\left[\begin{array}{l}\text{Measured ratio}\\ \text{of absorbance of}\\ \text{autoclaved corn}\end{array}\right] - \left[\begin{array}{l}\text{Measured ratio}\\ \text{of absorbance of}\\ \text{raw corn}\end{array}\right]}$$

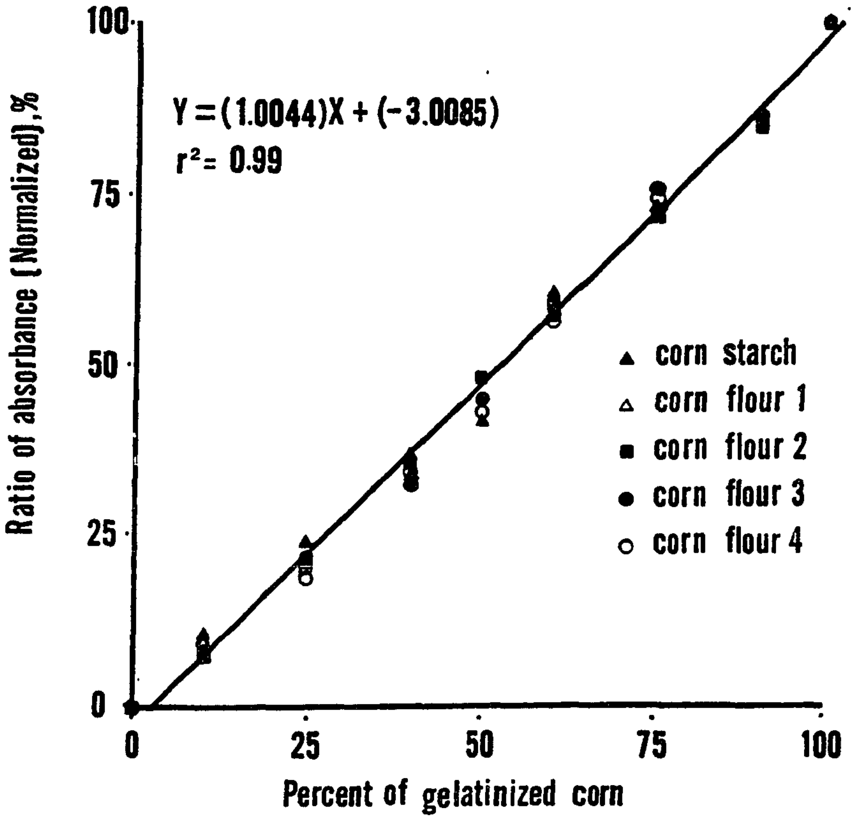
Standard curve

By applying such a technique to samples with different degrees of gelatinization, which were obtained by mixing raw (ungelatinized) and autoclaved (100% gelatinized) corn samples, a standard curve can be constructed. Table 4 shows the regression results of such plots for the samples of corn starch and corn flours. The high coefficients of determination ($r^2 \geq 0.99$) justify the application of this technique. Moreover, both the regression coefficients and the intercepts of the five regression lines show no significant differences ($p<0.05$) between different corn samples. Therefore, after normalization the differences in the differentiation between 0.2M and 0.5M absorbance values for different corn samples can be removed. Figure 8 shows the regression line obtained by pooling the four corn flour

Table 4. Determination coefficients, regression coefficients and intercepts of regression lines of the normalizaton ratio of absorbance for corn starch and corn flours

Sample	Determination coefficient (r^2)	Regression coefficient (b)	Intercept (a)
Corn starch	0.990	0.984	-1.460
Corn flour 1	0.997	1.011	-3.084
Corn flour 2	0.996	1.002	-2.744
Corn flour 3	0.994	1.017	-3.919
Corn flour 4	0.992	1.016	-4.008

Figure 8. Normalized ratio of absorbance for mixtures of raw and autoclaved corn starch and corn flours


Y = (1.0044)X + (-3.0085)
r^2 = 0.99
▲ corn starch
△ corn flour 1
■ corn flour 2
● corn flour 3
○ corn flour 4
Ratio of absorbance (Normalized),%
100
75
50
25
0
0
25
50
75
100
Percent of gelatinized corn

samples and one corn starch sample. This regression line, having a high coefficient of determination (r^2=0.99) and a slope close to 1 (b=1.004), was then used in determining the change of degree of starch gelatinization during hydrothermal processing of corn accompanied with the modified iodine blue value method.

Hydrothermal Processing of Corn

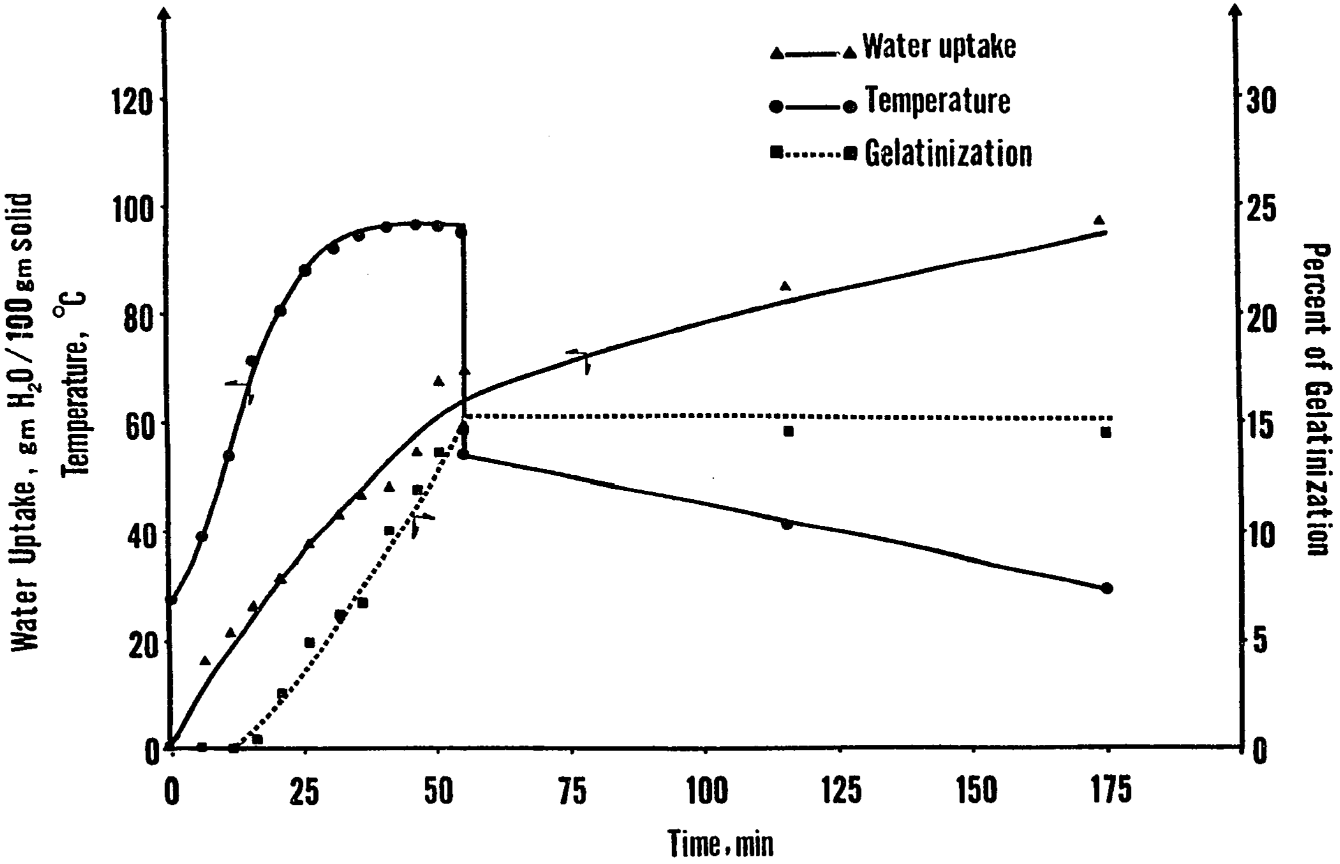
Heating, water uptake, and degree of gelatinization curves

The temperature of the cooking solution, the water uptake value, and the degree of gelatinization of water-cooked corn, with respect to time, are shown in Figure 9. This figure shows that after 15 min of cooking (68°C), the starch in the corn began to gelatinize; and after the addition of cold water (temperature below 65°C), the extent of gelatinization of the cooked corn remained relatively unchanged.

Simultaneous diffusion and reaction

Since the gelatinization reaction requires water as one of its reactants, the extent of gelatinization can also be estimated by analyzing the water uptake data. The water uptake of corn during processing can be considered as the

Figure 8. Normalized ratio of absorbance for mixtures of raw and autoclaved corn starch and corn flours


Water uptake
Temperature
Gelatinization
Water Uptake, gm H_2O/100 gm solid
Temperature, °C
Percent of Gelatinization
Time, min
0
20
40
60
80
100
120
0
5
10
15
20
25
30
0
25
50
75
100
125
150
175

diffusion of a substance (water) into a medium (corn kernel) in which the absorbed substance reacts simultaneously with a component (starch) of the medium. For the development of a mathematical model the following assumptions were made: (a) the amount of water absorbed by corn is equal to the amount of water contributed by concurrent diffusion and gelatinization processes; (b) the starch gelatinization reaction follows first-order chemical reaction kinetics; (c) the reaction rate constants for both processes are independent of concentration; (d) Fick's Law of diffusion holds true for the diffusion of unreacted water within the corn kernel; and (e) the geometric shape of the corn kernel is spherical, and the effect of change in volume of the kernel during cooking and steeping is negligible. Based on these assumptions, the non-steady state of water absorption can be mathematically described in spherical coordinates as follows (Bakshi and Singh, 1980):

$$\frac{\partial C}{\partial t} = D \left(\frac{\partial^2 C}{\partial r^2} + \frac{2\partial C}{r\partial r} \right) - KC$$

with initial and boundary conditions:

$C = \text{finite}$ at $r = 0,\ t \geq 0$

$C = C_s$ at $r = a,\ t > 0$

$C = C_i$ at $t = 0,\ 0 \leq r \leq a$

where
C= concentration of water in corn kernels, kg/m^3.
t= reaction time, hr.
D= diffusivity, m^2/hr.
r= radial distance, m.
k= first-order reaction constant of the gelatinization reaction, 1/hr.
C_s= the saturation concentration, which is the concentration of water in a corn kernel when the kernel reaches its maximum water uptake, and which can be defined as the weight of water (in kg) present per cubic meter of corn.
C_i= initial water concentration in the corn kernel, kg-water per cubic meter of corn kernel.

Solutions to this type of problem have been proposed by Danckwerts (1950). He has shown that the rate at which a solute is absorbed into a sphere at a constant temperature and under the influence of a simultaneously occurring first-order chemical reaction, can be described as:

$$R= 8\pi aDC_s \sum_{n=1}^{\infty} \frac{Ka^2+ Dn^2\pi^2 \, \mathrm{Exp}[\ -t(\ K + (Dn^2\pi^2)/a\ )]}{Ka^2 + Dn^2\pi^2}$$

where
R = absorption rate of solute, kg/hr.
a = radius, m.
D = diffusivity, m^2/hr.
C_s= saturation concentration, kg/m^3.
K= reaction rate constant, 1/hr.
t = reaction time, hr.

The total amount of water absorbed by corn, Q, after a given reaction time, t, can then be calculated as

$$Q = \int_0^t R \, dt$$

Since in our study, the temperature of the cooking solution does not remain constant, the diffusivity (D) and the reaction rate constant (K) become functions of temperature. Hence, the rate of absorption (R) does not remain constant during the cooking process and the above integral will have to be determined graphically or numerically.

The dependence of D and K on temperature can generally be expressed in Arrhenius forms (Bakshi and Singh, 1980; Hsu, 1983):

$$D = D_0 \, \mathrm{Exp}(-E_{a,D}/R_c T), \text{ and}$$

$$K = K_0 \, \mathrm{Exp}(-E_{a,K}/R_c T)$$

where D_0 = frequency factor for diffusion, m^2/hr.
$E_{a,D}$ = activation energy of diffusion, cal/g-mol.
R_c = gas constant, 1.987 g-cal/(g-mol)(°K).
T = absolute temperature, °K.
K_0 = frequency factor for gelatinization, 1/hr.
$E_{a,K}$ = activation energy of gelatinization reaction, cal/g-mol.

To complicate the situation, it has been reported by several researchers that the activation energy for both D and K changes between 70-100°C (Suzuki et al., 1976; Bakshi and Singh, 1980). This phenomenon can be explained as follows. In the low temperature range both the temperature and the small amount of water around starch granules will limit the extent of starch gelatinization. Therefore, diffusion is the major process occurring in the low temperature range. As soon as sufficient heat and water are presented, the situation becomes more feasible for gelatinization to take place. The activation energy for the gelatinization reaction decreases and gelatinization becomes the dominant reaction in the high temperature range. Also, the gelatinized starch inhibits the mass transfer of water and causes the activation energy to increase for diffusion in the high temperature range. However, even with these complications, the diffusion and reaction rate parameters can still be determined from absorption data like those shown in Figure 9. This is done by using the simplex pattern search scheme (see Appendix) to locate a set of parameters that will provide a best-fit curve, which minimizes the sum of the square of errors between the predicted and the experimental data. Table 5 summarizes the result of such a calculation. The water uptake and starch gelatinization curves in Figure 9 were the results of simulation based on the estimated parameters.

Calculated degree of starch gelatinization in water-cooked corn

The estimated rate parameters in Table 5 were used to calculate the degree of gelatinization (α) by the following

Table 5. Rate parameters obtained by the simplex pattern search scheme for water-cooking

Sample	Temperature range (°C)	D_0 (m^2/hr)	$E_{a,D}$ (cal/g-mol)	K_0 (1/hr)	$E_{a,K}$ (cal/g-mol)
Corn cooked in water	< 84.6	0.0158	7073	3.755E18	31500
	> 84.6	2.5300	10680	3.605E04	8564

equation:

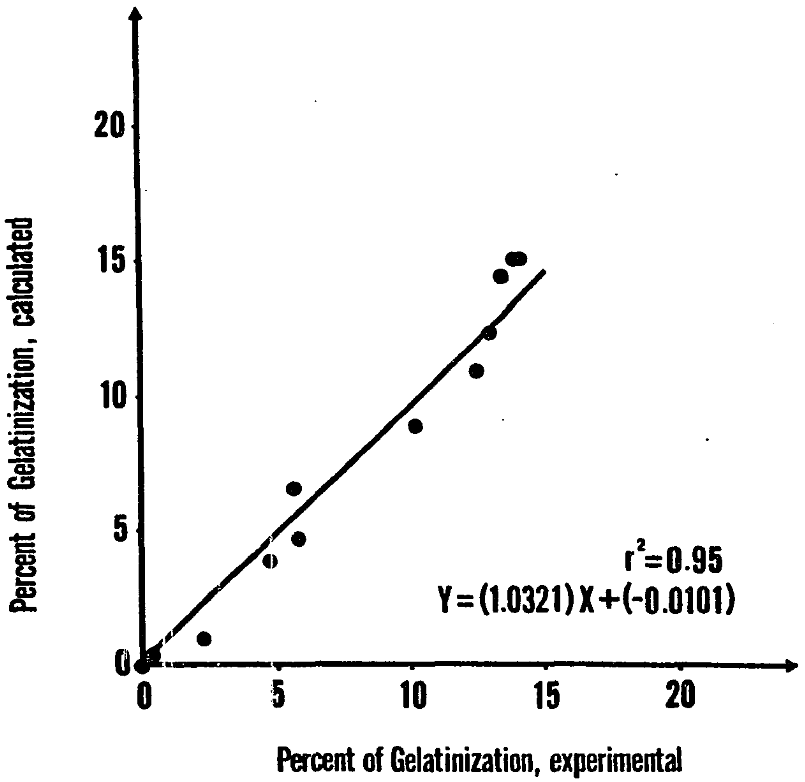
$$\mathrm{Ln}\ (\ 1 - \alpha\ ) = -\int_{0}^{t} K\ dt$$

Again, this integration can only be done graphically because the reaction rate constant (K) does not remain constant during the cooking process. The calculated degree of starch gelatinization was compared to that experimentally measured by the amylose/iodine blue value method used for water-cooked corn (Figure 10). A determination coefficient of 0.95 indicates that the two are very well correlated. The close correlation also indicates that the developed quantitative analysis model can be used to estimate the extent of starch gelatinization in water-cooked corn based on the water uptake data.

Lime-heat Treatment on Different Hybrids of Corn

Due to the interference of Ca^{+2} ions in the formation of the amylose/iodine blue complex (Radley and Tripp, 1953), the degree of starch gelatinization of the sample cooked in lime solution can not be determined by using the amylose/iodine blue value method. Therefore, the enzymic method proposed by Chiang and Johnson (1977) was used to

Figure 10. Calculated percent of starch gelatinization of water-cooked corn versus that experimentally determined by using the modified amylose/iodine blue value method



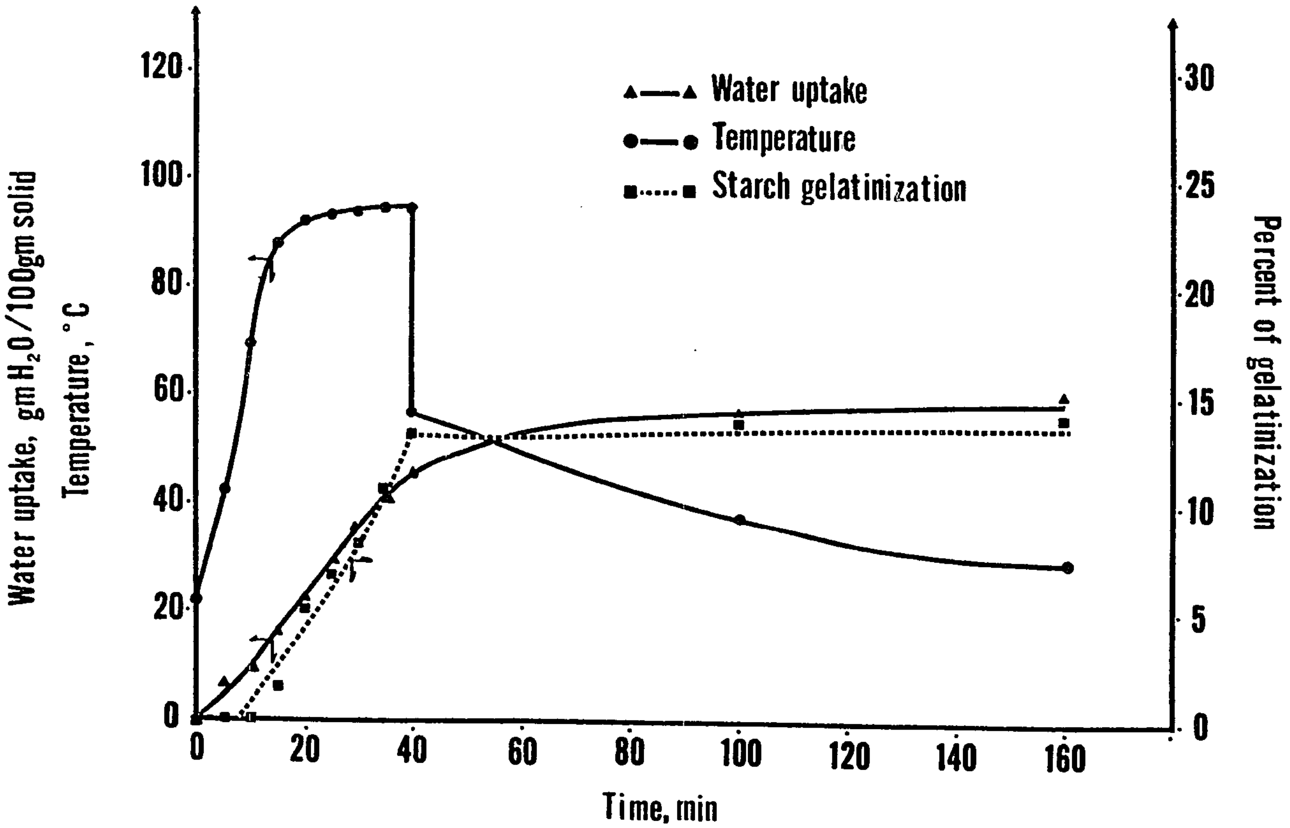
r² = 0.95
Y = (1.0321) X + (-0.0101)
Percent of Gelatinization, calculated
0
5
10
15
20
Percent of Gelatinization, experimental
0
5
10
15
20

measure the extent of starch gelatinization in lime-cooked samples. The degerming and sieving of samples remained unchanged. The agitation condition used for the lime-cooking study was also different from that used for the water-cooking one. In the water-cooking study, a high-speed, low-torque stirrer was used for agitating during the cooking process. The high-speed stirrer tended to break up the corn kernels and the breakage of corn kernels created more surface area for reaction and mass transfer to take place. This could cause greater sensitivity of the diffusion and reaction toward temperature change. To avoid this problem a low-speed, high-torque stirrer, which did not break up corn kernels as much as the high-speed one, was used in the lime-cooking study.

Heating, water uptake, and degree of gelatinization curves

Figure 11 shows typical curves of the temperature change of the cooking solution, the water uptake, and the extent of starch gelatinization of corn during the lime-cooking process. The curves in this graph show the same tendency as those in Figure 9. It was observed that the rate of temperature increase for the cooking solution was similar, with or without the presence of $Ca(OH)_2$. Due to the higher breakage of corn kernels during cooking and

Figure 11. Typical water uptake curve, temperature history of cooking solution, and starch gelatinization curve for lime-cooked corn


Water uptake
Temperature
Starch gelatinization
Water uptake, gm H_2O/100gm solid
Temperature, °C
Percent of gelatinization
Time, min
0
20
40
60
80
100
120
140
160
0
20
40
60
80
100
120
0
5
10
15
20
25
30

longer cooking time of water-cooking study, the water-cooked corn showed higher water uptake than that of lime-cooked corn (Figures 9 and 11). Figure 11 indicates that once the temperature of the cooking solution was raised to greater than 70°C, gelatinization in the starch of the cooked corn became measurable by the enzymic method. Again, after the addition of cold water, temperature of the cooking solution dropped down to below 65°C and the extent of starch gelatinization remained relatively unchanged. Data for the nine cultivars of corn used, all showed similar types of curves as those shown in Figure 11.

Rate parameters for the lime-cooking system

The same mathematical model used in the water-cooking study was used to analyze the data of the lime-cooking study. For each cooking experiment, the simplex pattern search scheme was again used to locate a set of parameters that would provide the best-fit curves to the water uptake and starch gelatinization data. Table 6 summarizes the estimated rate parameters for the nine cultivars of corn. The water uptake and starch gelatinization curves in Figure 11 were the results of simulation for sample D based on the estimated parameters.

Table 6. Rate parameters obtained by the simplex pattern search scheme for lime-cooking

Sample	Temperature range (°C)	D_0 (m^2/hr)	$E_{a,D}$ (cal/g-mol)	K_0 (1/hr)	$E_{a,K}$ (cal/g-mol)
A	< 90.7[bc,1]	1.254E-2[d]	7623[a]	7.139E14	23900
	> 90.7	1.307E07	21850	16115[d]	7849[a]
B	< 93.9[ab]	1.709E-2[b]	7612[a]	1.468E12	21170
	> 93.9	2.759E10	28045	15290[d]	7841[a]
C	< 77.0[e]	1.611E-2[c]	7613[a]	2.527E14	24190
	> 77.0	1.162E07	20800	13980[e]	7863[a]
D	< 91.0[bc]	1.252E-2[d]	7624[a]	8.898E13	24030
	> 91.0	2.948E05	19720	16080[d]	7833[a]

E	$< 88.2^{d}$	1.132E-2^{e}	7632^{a}	3.302E13	23170
	> 88.2	7.846E03	17250	15370^{d}	7859^{a}
F	$< 92.2^{b}$	1.066E-2^{f}	7634^{a}	4.814E12	20640
	> 92.2	9.840E04	17485	18345^{c}	7823^{a}
G	$< 92.1^{b}$	1.220E-2^{d}	7626^{a}	3.627E13	21460
	> 92.1	1.683E05	18745	24335^{b}	7830^{a}
H	$< 88.9^{cd}$	1.053E-2^{f}	7616^{a}	8.449E13	23505
	> 88.9	1.433E09	26542	15365^{d}	7881^{a}
I	$< 96.5^{a}$	1.781E-2^{a}	7617^{a}	5.534E13	22070
	> 96.5	4.276E08	23546	27695^{a}	7833^{a}
LSD	3.6803	0.385E-3	27.839	1138.8	63.374

---

[1] For each column, means with the same letter are not significantly different at the 5% level (LSD).

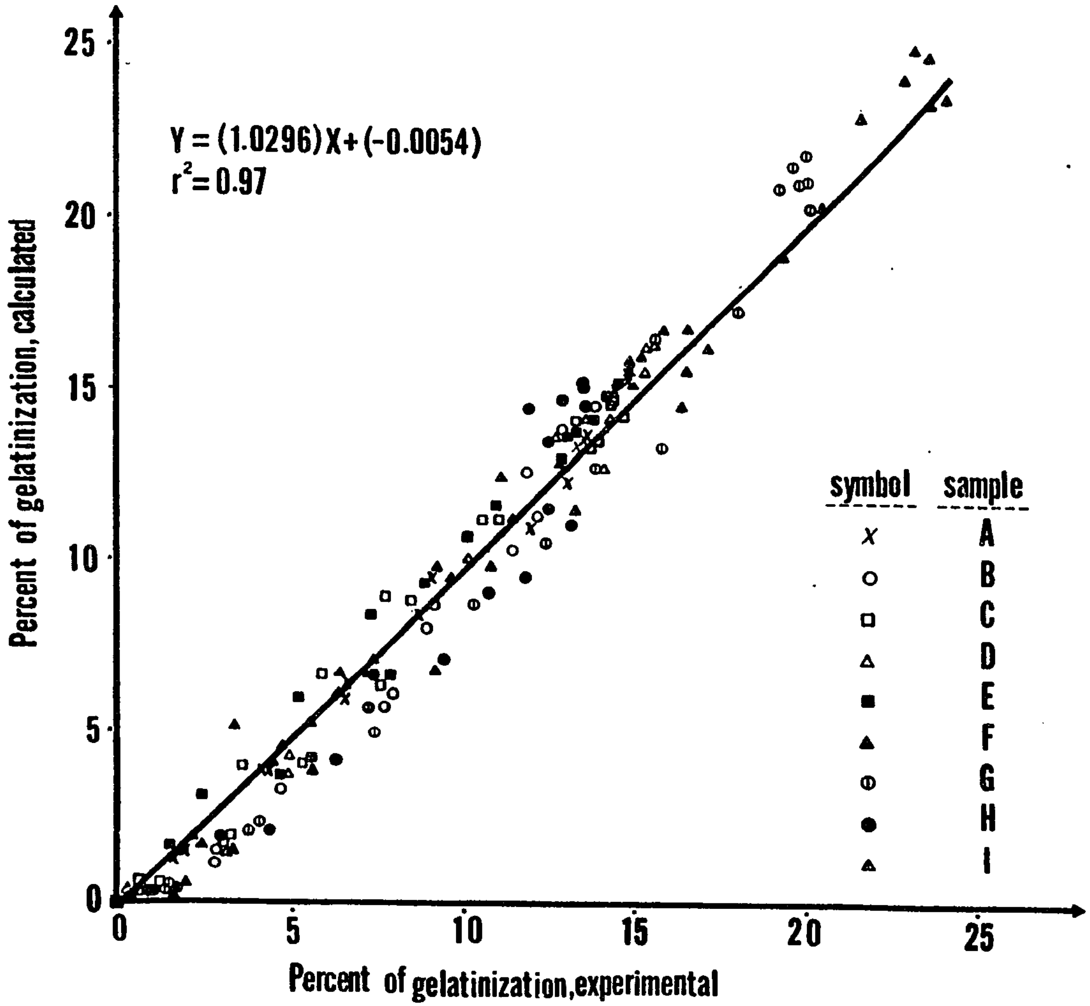
Calculated degree of starch gelatinization in lime-cooked corn

Reaction rate parameters shown in Table 6 were used to calculate the degree of gelatinization using the rate equation previously mentioned. The calculated degree of gelatinization of the nine cultivars of corn were then compared to the experimentally measured ones as shown in Figure 12. The close correlation (r^2=0.97) indicates that this quantitative model based on the principles of diffusion and chemical reaction kinetics is capable of predicting the extent of starch gelatinization during lime-heat processing of corn once the physical parameters are known.

Rate parameters and water uptake of corn

Results in Table 6 show that, with the exception of sample C, the change in activation energies of diffusion and gelatinization processes due to starch gelatinization for the corn samples were all estimated to be between 88 and 97°C. The activation energy of gelatinization ($E_{a,K}$) at the high temperature range was estimated as about one-third of that at the low temperature range and the activation energy of diffusion ($E_{a,D}$) at the low temperature was also estimated as about one-third of that at the high temperature range. The results show that the diffusion process

Figure 12. Calculated percent of gelatinization of lime-cooked corn samples versus those experimentally determined by using the enzymic method


Y = (1.0296)X + (-0.0054)
r² = 0.97
Percent of gelatinization, calculated
Percent of gelatinization, experimental
0
5
10
15
20
25
symbol sample
x A
○ B
□ C
△ D
■ E
▲ F
⦶ G
● H
▲ I

dominates water uptake of corn in the low temperature range, as does the gelatinization reaction in the high temperature range. Therefore, D_0 and $E_{a,D}$ values at the low temperature range and also K_0 and $E_{a,K}$ values at the high temperature range are important factors in determining water uptake of corn. Comparison among the nine cultivars of corn shows that there is no significant difference among the $E_{a,D}$ values at the low temperature range. The same is true for the $E_{a,K}$ values at the high temperature range. However, the D_0's at the low temperature range and the K_0's at the high temperature range showed greater variations (Table 6).

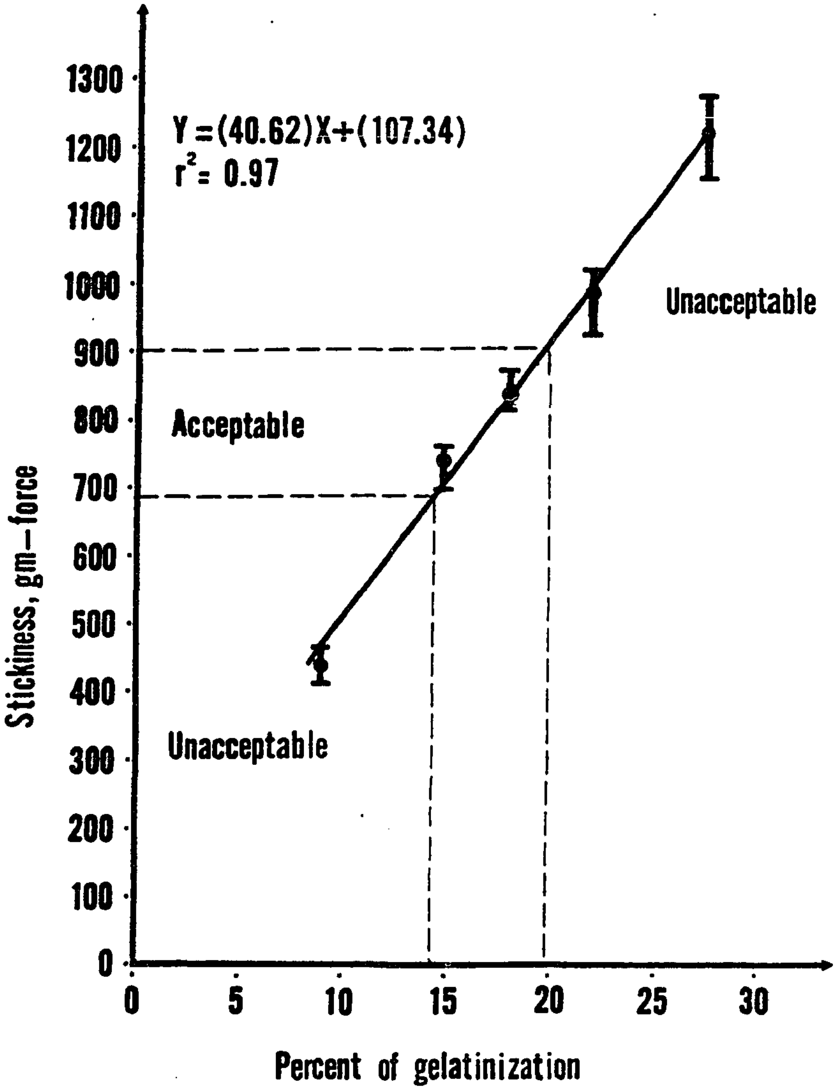
These results indicate that the response of the diffusion process to temperature change is similar for all the nine cultivars of corn. The same is true for the response of the gelatinization reaction to temperature change. Therefore, the differences in the D_0 values at the low temperature range and the K_0 values at the high temperature range account for the differences observed in the water uptake and the degree of gelatinization when the corn samples are processed under the same conditions. These results are not unreasonable since the same types of diffusion process and gelatinization reaction occurred in the same kind of material (corn). Therefore, the materials have similar response to temperature change and the differences among the materials are expressed by the different values of D_0 at the low temperature range and K_0 at the high temperature range.

Extent of Starch Gelatinization and Stickiness Values of Masa Prepared from Lime-cooked Corn

The rheological properties of masa, such as plasticity, cohesiveness, and stickiness have a direct effect on the sensory characteristics of the final product. Several reports mention that a positive relationship exists between the time required to cook the corn and the extent of gelatinization of its starch (Morad et al., 1986; Khan et al., 1982; Bedolla and Rooney, 1982). However, none of the reports have studied the relationship between the rheological properties of masa and the extent of gelatinization of its component starch. Moreover, no report has yet established an optimum range of starch gelatinization for consistent, high quality masa production. This portion of the study was performed to establish the relationship between the stickiness value of masa and the extent of gelatinization of its starch and to find a suitable range for the extent of starch gelatinization in the production of masa with a consistent quality level.

The corn was cooked for 10, 20, 30, 40 and 50 min and the extent of starch gelatinization of the cooked corns and the stickiness values of the masa prepared from the cooked corn were determined. The extent of gelatinization of corn cooked for different lengths of time were then compared with the stickiness value of the masa made from the corn (Figure 13). It was found that there was a positive linear relationship (r^2=0.97) between the extent of starch gelatinization and the stickiness value of the masa prepared from the lime-cooked corn. It was also found that the range of degree of gelatinization in the preparation of masa dough with acceptable stickiness for handling was from 14 to 20% of total starch gelatinization. When the sample was cooked for less than 20 min, the starch was not sufficiently gelatinized to permit proper masa structure; therefore, the sample easily fell apart during the compression phase of stickiness measurement procedure. On the other hand, when the corn was cooked for 40 min or more, the masa prepared from the corn became too sticky to be properly handled. For the sample cooked for 50 min, the degree of starch gelatinization was so high and the masa so sticky that the sample adhered to the aluminum foil, the petri dish, and the shaping knife; and it could not be shaped properly for measurement. These characteristics caused a higher

Figure 13. Stickiness value of masa prepared under different cooking times versus the extent of gelatinization of its component starch


Y=(40.62)X+(107.34)
r²= 0.97
Acceptable
Unacceptable
Unacceptable
Stickiness, gm—force
Percent of gelatinization
0
100
200
300
400
500
600
700
800
900
1000
1100
1200
1300
0
5
10
15
20
25
30

variation of the stickiness value for this sample.

Results indicate that masa dough with desired range of stickiness can be produced through the control of the extent of gelatinization in its starch.

CONCLUSIONS

1. The developed mathematical model is useful for simulating the changes that take place during the water-cooking or lime-cooking of corn. Experimentally determined property values predicted the degree of starch gelatinization accurately in the first-order kinetic model.

2. The critical temperatures, at which activation energies of diffusion and gelatinization change their values, for the nine cultivars of corn studied show variations among samples. However, there is no significant difference among the activation energies of diffusion ($E_{a,D}$) at the low temperature range. The same is true for the activation energies of gelatinization ($E_{a,K}$) at the high temperature range.

3. The values of diffusivity (D_0) and the reaction rate constant (K_0) determine the differences in water uptake and starch gelatinization among samples.

4. From the stickiness measurement experiments, it was found that the range of degree of starch gelatinization in the preparation of suitable masa dough was between 14 to 20% of total starch gelatinization. Twenty to 30 min cooking time for the sample studied was found to produce this degree of starch gelatinization.

RECOMMENDATIONS

Since the values of diffusivity (D_0) and the reaction rate constant (K_0) determine the differences in water uptake and starch gelatinization among different corn samples during lime-heat processing for tortilla production, the measurement of these parameters are critical. However, these parameters are not easily measured analytically. For practical purposes, other physical properties of corn (eg. density, flintiness, etc.) that can be readily measured should be considered and statistical correlation work should be conducted to relate these readily measured properties to water diffusivity and the reaction rate constant in order to have the benefit of the developed mathematical model fully realized.

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ACKNOWLEDGEMENTS

I would like to express my deepest appreciation to my major professor, Dr. Kenneth Hsu for his guidance and patient assistance throughout the entire course of this study. I would also like to thank the other members of my POS committee, Dr. Charles Hurburgh, Dr. Lawrence Johnson, Dr. Allen Kraft, Dr. Mark Love and Dr. Lester Wilson for their interest and help in this dissertation.

I am sincerely grateful to Dr. Curtis L. Knipe for allowing me to use the 2-kg load cell for the measurement of the stickiness values of masa doughs. Thanks was also due to my lab-mates Steven Fox and Kurt Kuipers helped me with my English throughout my study at ISU.

My deepest gratitude is to my family, especially my parents, for their support and understanding.

APPENDIX

Computer Program Used for Parameter Simulation

```
// JOB
/*JOBPARM  BIN=005
//S1  EXEC  FORTH
//FORT.SYSIN  DD  *

      IMPLICIT REAL*8(A-H,O-Z)
      DIMENSION FX(10),D(10)
      COMMON DATA(15,4),AB(15),GL(15),L
      L=12
      LL=L-1
      READ(5,1)((DATA(I,J),J=1,4),I=1,L)
    1 FORMAT(4D10.4)
      DO 4 I=1,L
      WRITE(6,5)(DATA(I,J),J=1,4)
    4 CONTINUE
    5 FORMAT(4(10X,D10.4))
    7 FORMAT(20X,D10.4)
      ALPHA=1.0
      BETA=0.5
      GAMMA=2.0
      FX(1)=0.1253D-1
      FX(2)=0.7630D4
      FX(3)=0.2305D5
      FX(4)=0.1951D5
      FX(5)=0.1614D5
      FX(6)=0.7814D4
      FX(7)=0.9100D2
      D(1)=.01*FX(1)
      D(2)=.001*FX(2)
      D(3)=.01*FX(3)
      D(4)=.01*FX(4)
      D(5)=.01*FX(5)
      D(6)=.001*FX(6)
      D(7)=.01*FX(7)
      EPSI=1.0D-4
      N=7
      K=N+2
      ITOUT=5
      ITMAX=300
      CALL SIMPX(FX,FY,N,D,ITOUT,ITMAX,EPSI,ALPHA,
      BETA,GAMMA)
      CALL OBJN(FX,YY,N)
      DO 20 I=1,K
      WRITE(6,7)FX(I)
```

```
     20 CONTINUE
        WRITE(6,15)
     15 FORMAT(2X,' TIME(MIN)',2X,' TEMP. C. ',2X,
        'EXP. W. U.',2X,'CAL. W. U.',2X,'EXP. D. G.',
        2X,'CAL. D. G.'/1X,75(1H-))
        DO 10 I=1,LL
        WRITE(6,25)DATA(I,1),DATA(I,2),DATA(I,3),
        AB(I),DATA(I,4),GL(I)
     10 CONTINUE
     25 FORMAT(6(2X,D10.4))
        STOP
        END


        SUBROUTINE SIMPX(FX,FY,N,D,ITOUT,ITMAX,EPSI,
        ALPHA,BETA,GAMMA)
        IMPLICIT REAL*8(A-H,O-Z)
        DIMENSION X(15,10),FX(10),Y(15),D(10)
   1003 FORMAT(3X,65(1H*))
   1004 FORMAT(5X,18H**INITIAL POINT ..)
   1005 FORMAT(12X,2HX(,I3,4H) = ,D11.4)
   1006 FORMAT(5X,5HFY = ,D11.4,15H, EPSI USED IS ,
        D11.5,2H .)
   1007 FORMAT(5X,20H**INITIAL SIMPLEX ..)
   1008 FORMAT(8X,5HPOINT,I3,3H ..)
   1009 FORMAT(10X,3HY= ,D11.4,1H.)
   1010 FORMAT(20X)
   1011 FORMAT(5X,5HOY = ,D11.4,9H  ITER = ,I4,
        10H  NOPT. = ,I4,10H  NOCVN = ,I4)
   1012 FORMAT(7X,8HNORFT = ,I4,4X,8HNOEXP = ,I4,
        10H  NOCNT = ,I4,10H  NOCUT = ,I4)
   1013 FORMAT(7X,24HCURRENT SEARCHED DATA ../10X,
        3HY =,D11.4,1H,)
   1014 FORMAT(10X,2HX(,I3,4H) = ,D11.4,1H,,5X,
         3HOX(,I3,4H) = ,D11.4,1H,)
   1015 FORMAT(7X,8HYMEAN = ,D15.8,9H ,  SY = ,
         D15.8,2H .)
   1016 FORMAT(5X,24H**CUT STEP-SIZES TIMES  ,
         I3,2H .)
   1018 FORMAT(5X//5X,17HOPTIMAL RESULTS..//)
   1019 FORMAT(7X,7HNOPT = ,I4,10H   ITER = ,I4,
        10H  NOCVN = ,I4/7X,8HNORFT = ,I4,
        10H  NOEXP = ,I4,10H  NOCNT = ,I4,7X,
        8HNOCUT = ,I4)
   1020 FORMAT(7X,14H* OPTIMAL Y = ,E11.4,8H,  YM = ,
        E11.4,7H, SY = ,E11.4,2H ,)
   1022 FORMAT(5X,63(1H*))
   1023 FORMAT(5X,26H** ITERATION NO. EXCEEDED ,I5,
```

```
          2H .)
     1025 FORMAT(5X,20H...SIMPLEX SEARCH...)
          WRITE(6,1025)
          MULT=1
          NOPT=0
          NOCUT=0
          NOCVN=0
          ITER=0
          NORFT=0
          NOEXP=0
          NOCNT=0
          FN=N
          NM=N+1
          CALL OBJN(FX,YF,N)
          LOCAT=1
          IWAY=1
          GO TO 510

C     SET UP INITIAL SIMPLEX .
C         THIS PROCEDURE FOR DETERMINING THE INITIAL
          SIMPLEX PRODUCES A PARTICULAR CONFIGURATION
C         OF THE SIMPLEX.  THE PROCEDURE MAY NEED TO
C         BE MODIFIED TO PRODUCE OTHER SIMPLEX
          CONFIGURATIONS.

        2 DO 6 J=1,N
          DO 3 I=1,J
        3 X(I,J)=  FX(J)-D(J)
          FJ=J
          X(J+1,J)=  FX(J)+FJ*D(J)
          IF(J-N)4,6,6
        4 JM=J+2
          DO 5 I=JM,NM
        5 X(I,J)=  FX(J)
        6 CONTINUE
          WRITE(6,1010)
          DO 8 I=1,NM
          DO 7 J=1,N
        7 FX(J)=X(I,J)
          CALL OBJN(FX,YF,N)
          DO 76 J=1,N
       76 X(I,J)=FX(J)
        8 Y(I)=YF
          INI=1

C     REARRANGE ORDER (OVERALL) .

        9 I=1
```

```
      NS=N+1
   10 IF(Y(I)-Y(NS))13,11,11
   11 YTEM=Y(NS)
      Y(NS)=Y(I)
      Y(I)=YTEM
      DO 12 J=1,N
      FX(J)=X(NS,J)
      X(NS,J)=X(I,J)
   12 X(I,J)=  FX(J)
   13 IF(NS-I-1)15,15,14
   14 NS=NS-1
      GO TO 10
   15 I=I+1
      IF(I-N-1)16,17,17
   16 NS=N+1
      GO TO 10
   17 IF(INI) 65,65,501
  501 LOCAT=2
      IWAY=2
      GO TO 120

C   COMPUTE THE CENTROID.

   18 DO 20 J=1,N
      PXT=X(1,J)
      DO 19 I=2,N
   19 PXT=PXT+X(I,J)
   20 X(N+2,J)=PXT/FN

C   **MAKE REFLECTION MOVE .

      DO 21 J=1,N
      X(N+3,J)=X(N+2,J)+ALPHA*(X(N+2,J)-X(N+1,J))
   21 FX(J)=X(N+3,J)
      CALL OBJN(FX,YF,N)
      DO 77 J=1,N
   77 X(N+3,J)=FX(J)
      Y(N+3)=YF
      NOPT=NOPT+1
      LOCAT=3
      IWAY=3
      GO TO 500
   22 IF(Y(N+3)-Y(1))29,23,23
   23 IF(Y(N+3)-Y(N))24,26,26
  244 IWAY=7
   24 DO 25 I=1,N
   25 X(N+1,I)=X(N+3,I)
      Y(N+1)=Y(N+3)
```

```
      ITER=ITER+1
      NORFT=NORFT+1
      GO TO 100
   26 IF(Y(N+3)-Y(N+1))27,49,49
   27 DO 28 I=1,N
   28 X(N+1,I)=X(N+3,I)
      Y(N+1)=Y(N+3)
      ITER=ITER+1
      NORFT=NORFT+11
      GO TO 49

C    **MAKE EXPANSION MOVE .

   29 DO 30 J=1,N
      X(N+4,J)=X(N+2,J)+GAMMA*(X(N+3,J)-X(N+2,J))
   30 FX(J)=X(N+4,J)
      CALL OBJN(FX,YF,N)
      DO 78 J=1,N
   78 X(N+4,J)=FX(J)
      Y(N+4)=YF
      NOPT=NOPT+1
      LOCAT=4
      IWAY=4
      GO TO 500
   31 IF(Y(N+4)-Y(1))32,244,244
   32 DO 33 I=1,N
   33 X(N+1,I)=X(N+4,I)
      Y(N+1)=Y(N+4)
      ITER=ITER+1
      NOEXP=NOEXP+1
      GO TO 100

C    **MAKE CONTRACTION MOVE .

   49 DO 50 J=1,N
      X(N+5,J)=X(N+2,J)+BETA*(X(N+1,J)-X(N+2,J))
   50 FX(J)=X(N+5,J)
      CALL OBJN(FX,YF,N)
      DO 79 J=1,N
   79 X(N+5,J)=FX(J)
      Y(N+5)=YF
      NOPT=NOPT+1
      LOCAT=5
      IWAY=5
      GO TO 500
   51 IF(Y(N+5)-Y(N+1))52,60,60
   52 DO 53 I=1,N
   53 X(N+1,I)=X(N+5,I)
```

```
          Y(N+1)=Y(N+5)
          ITER=ITER+1
          NOCNT=NOCNT+1
          NOCVN=NOCVN+1
          GO TO 110

C     **CUT DOWN STEP-SIZES .

       60 DO 62 I=2,NM
          DO 61 J=1,N
          X(I,J)=(X(1,J)+X(I,J))/2.0
       61 FX(J)=X(I,J)
          CALL OBJN(FX,YF,N)
          DO 80 J=1,N
       80 X(I,J)=FX(J)
       62 Y(I)=YF

C     **REARRANGE ORDER (OVERALL ) .

          INI=0
          GO TO 9
       65 NOCUT=NOCUT+1
          NOPT=NOPT+N
          NOCVN=NOCVN+1
          LOCAT=6
          IWAY=6
          GO TO 120
      100 NOCVN=0

C     **REARRANGE ORDER ( SHOT-DOWN ).

      110 IOR=N
      111 IF(Y(IOR+1)-Y(IOR))112,120,120
      112 YTEM=Y(IOR+1)
          Y(IOR+1)=Y(IOR)
          Y(IOR)=YTEM
          DO 113 J=1,N
          FX(J)=X(IOR+1,J)
          X(IOR+1,J)=X(IOR,J)
      113 X(IOR,J)=FX(J)
          IF(IOR-1)120,120,114
      114 IOR=IOR-1
          GO TO 111

C     **TEST FOR OPTIMALITY .

      120 FNM=NM
          YM=Y(1)
```

```
      DO 121 I=2,NM
  121 YM=YM+Y(I)
      YM=YM/FNM
      SY=(Y(1)-YM)**2
      DO 122 I=2,NM
  122 SY=SY+(Y(I)-YM)**2
      SY=(SY/FN)**0.5
      IF(LOCAT-6) 123,500,123
  123 IF(LOCAT-2) 500,500,124
  124 IF(SY-EPSI) 125,125,18
  125 LOCAT=8
  500 IF(NOPT-ITMAX) 505,505,560
  505 GO TO (510,520,530,530,530,540,560,560),LOCAT
  510 WRITE(6,1004)
      DO 511 I=1,N
  511 WRITE(6,1005)I,FX(I)
      WRITE(6,1006)YF,EPSI
      WRITE(6,1003)
      GO TO 2
  520 WRITE(6,1007)
      DO 521 I=1,NM
      WRITE(6,1008)I
      DO 522 J=1,N
  522 WRITE(6,1005)J,X(I,J)
      WRITE(6,1009)Y(I)
  521 WRITE(6,1022)
      WRITE(6,1010)
      GO TO 18
  530 IF(NOPT-ITOUT*MULT) 533,531,531
  531 MULT=MULT+1
      IF(NOPT-ITOUT*MULT) 532,531,531
  532 WRITE(6,1011)Y(1),ITER,NOPT,NOCVN
      WRITE(6,1012)NORFT,NOEXP,NOCNT,NOCUT
      WRITE(6,1015)YM,SY
      WRITE(6,1013)YF
      DO 534 IN=1,N
  534 WRITE(6,1014)IN,FX(IN),IN,X(1,IN)
      WRITE(6,1003)
  533 IWAY=IWAY-2
      GO TO (22,31,51,123,18),IWAY
  540 WRITE(6,1016)NOCUT
      GO TO 123
  560 IF(LOCAT-8) 561,562,562
  561 WRITE(6,1023)ITMAX
      GO TO 563
  562 WRITE(6,1018)
  563 WRITE(6,1019)NOPT,ITER,NOCVN,NORFT,NOEXP,
      NOCNT,NOCUT
```

```
      WRITE(6,1020)Y(1),YM,SY
      DO 565 I=1,N
  565 WRITE(6,1005)I,X(1,I)
      WRITE(6,1003)
      DO 564 I=1,N
  564 FX(I)=X(1,I)
      FY=Y(1)
      RETURN
      END


      SUBROUTINE OBJN(X,YY,N)
      IMPLICIT REAL*8(A-H,O-Z)
      DIMENSION R(15),T(15),GK(15),X(10)
      COMMON DATA(15,4),AB(15),GL(15),L
      AB(1)=0.0
      GL(1)=0.0
      SSED=0.0
      SSEK=0.0
      LL=L-1
      CO=1883.83
      S=0.0
      AUC=0.0
      PI=3.1416
      A=0.3751D-2
      CR=1.987
      TCR=(X(7)+273.0)*CR
      X(8)=X(1)*DEXP(-X(2)/TCR)/DEXP(-X(4)/TCR)
      X(9)=X(5)*DEXP(-X(6)/TCR)/DEXP(-X(3)/TCR)
      DO 80 J=1,N
      IF (X(J) .LE. 0.0) X(J)=0.1
   80 CONTINUE
      MFLAG=0
      DO 10 I=1,L
      T(I)=DATA(I,2)+273.0
      RT=CR*T(I)
      IF (MFLAG .EQ. 1) GO TO 20
      IF (DATA(I,2) .GT. X(7)) GO TO 20
      PD=-X(2)/RT
      DD=X(1)*DEXP(PD)
      PK=-X(3)/RT
      RK=X(9)*DEXP(PK)
      GO TO 30
   20 MFLAG=1
      IF (DATA(I,2) .LT. X(7)) GO TO 45
      PD=-X(4)/RT
      DD=X(8)*DEXP(PD)
      PK=-X(6)/RT
```

```
      RK=X(5)*DEXP(PK)
   30 DO 40 J=1,20
      EE=DD*J*J*PI*PI
      E1=(RK+EE/(A*A))*DATA(I,1)/60.0
      RN=RK*A*A+EE*DEXP(-E1)
      RD=RK*A*A+EE
   40 S=S+RN/RD
      R(I)=8.0*PI*A*DD*CO*S
      S=0.0
      GK(I)=RK
      GO TO 10
   45 PD=-X(4)/RT
      DD=X(8)*DEXP(PD)
      PK=-X(3)/RT
      RK=X(9)*DEXP(PK)
      GO TO 30
   10 CONTINUE
      DO 50 I=2,LL
      IF (DATA(I,1) .EQ. 100.0) GO TO 60
   70 AB(I) =(DATA(I,1)-DATA(I-1,1))*(R(I)+R(I-1))/
      0.029+AB(I-1)
      ERRD=AB(I)-DATA(I,3)
      GO TO 55
   60 R(I-1)=R(L)
      GO TO 70
   55 SSED=ERRD*ERRD+SSED
   50 CONTINUE
      DO 100 I=1,8
      IF( GK(I+1) .LT. GK(I) ) GO TO 110
      AUC=AUC+GK(I)/12.0+( GK(I+1)-GK(I) )/24.0
      GO TO 120
  110 AUC=AUC+GK(I+1)/12.0+( GK(I)-GK(I+1) )/24.0
  120 GL(I+1)=1.0-DEXP(-AUC)
  100 CONTINUE
      AUC=AUC+GK(10)+( GK(12)-GK(10) )/2.0
      GL(10)=1.0-DEXP(-AUC)
      AUC=AUC+GK(11)+( GK(10)-GK(11) )/2.0
      GL(11)=1.0-DEXP(-AUC)
      DO 130 I=2,LL
      ERRK=GL(I)-DATA(I,4)
      SSEK=ERRK*ERRK+SSEK
  130 CONTINUE
      YY=SSED+SSEK
      RETURN
      END

/*
```

```
//GO.SYSIN  DD  *
  (DATA)
//
```