

EFFECT OF HEAT TREATMENTS ON  
WHEAT STARCH SUSPENSIONS

by

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B. S., Kansas State University, 1965

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A MASTER'S THESIS

submitted in partial fulfillment of the  
requirements for the degree

MASTER OF SCIENCE

Department of Grain Science  
and Industry

KANSAS STATE UNIVERSITY  
Manhattan, Kansas

1967

Approved by:

  
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TABLE OF CONTENTS

INTRODUCTION . . . . .	1
REVIEW OF LITERATURE . . . . .	1
The Structure of Starch . . . . .	1
Hydrolysis of Starch . . . . .	5
Effect of Heat on Starch . . . . .	8
Separation of Starch Hydrolysis Products . . . . .	15
MATERIALS AND METHODS . . . . .	16
RESULTS AND DISCUSSION . . . . .	20
Effect of Heat Treatment on Sugar Production . . . . .	23
Ratio of Glucose to Maltose Following Heat Treatments . . . . .	26
Concentration of Total Reducing Sugars . . . . .	27
Effect of Heat Treatment on pH and Total Acidity . . . . .	30
SUMMARY AND CONCLUSION . . . . .	35
ACKNOWLEDGMENT . . . . .	36
LITERATURE CITED . . . . .	37

## INTRODUCTION

Starch by its very nature and occurrence is an important substance. A great deal of research has been done on starch and its properties and components under many and varied conditions. Much of this research has been concerned with the effect of heat treatments on starch and the changes that occur as a result of the variation of the temperature of the heat treatments. Most of this research has been done at temperature levels below 100° C. This temperature involves the range of starch gelatinization. The starch properties that are effected most at these temperature levels are the film and paste formation. Another area of a great deal of research has been starch decomposition by various means such as acid or enzyme hydrolysis. There has been a great deal of interest in the amount of hydrolysis, the reactions under different conditions, and the products formed. This investigation was undertaken to relate heat treatment of starch in water to the degree of hydrolysis.

## REVIEW OF LITERATURE

### The Structure of Starch

Raw starch is composed of minute granules. Natural starch is regarded as being made up of biological or chemical micelles (8). Sponsler (57) reported that in the starch granule there is, within limits, a regular and fairly uniform arrangement of atoms. He also stated (56) that the starch granule is built up of units arranged in concentric layers and that the structure is neither strictly amorphous nor crystalline. Starch is a

colloidal micellar structure (44). Leach et al. (35) stated that whenever linear segments of either branched or linear molecules parallel one another, hydrogen bonding forces pull the chains together into associated crystalline bundles or micelles. A long linear chain may conceivably pass through a number of such micellar areas, or the outer fringe branches of a branched molecule may participate in several separate micelles. Hence, these crystalline areas act to hold the granule together. In the spaces between the micelles, the chains and branches are more disordered and hence less densely packed. Kerr (27) reported that the short branched chains were joined together to form a large laminated molecule.

The variety of the starch and its environment during development perhaps may have much more to do with shape of the granule than any chemical reactions (54). The molecules of amylose and amylopectin form a coiled structure. Heyn (19) reported that in the starch granule, the macromolecules of starch form, long coiled polymer crystals or aggregates extending in the radial direction of the grain. Leach et al. (35) also stated that starch molecules are arranged in a radial fashion. Starch granules have what is called a hilum. The hilum is thought to be the nucleus around which the granule appears to have grown. When observed under a polarizing light, the granules light up brightly except for an interference pattern in the form of a "Maltese Cross", whose lines intersect at the hilum. Some starches show pronounced "oyster shell" striations arranged concentrically around the hilum while it is entirely absent in other starches. Reychler (50) reported that starch grains possess two hila.

Natural starch consists of two fractions (3, 37, 51, 63). The fractions are now called amylose and amylopectin. There was some confusion as to the

naming of amylose and amylopectin for some time. It was even doubted that amylopectin existed. The amount of these two fractions vary with the variety of the starch and the environment under which the cereal is grown. This led to most of these disagreements. When it was agreed that amylopectin did exist, it was called beta-amylose and amylose was called alpha-amylose due to the difference in solubilities (27). Now it is known that in most cases, amylopectin is the major component of most cereal starches. The contents of various starches were determined by Bates et al. (2) using potentiometric titrations with iodine. They found that amylose ranged from 0% in waxy rice starch, waxy sorghum and waxy barley to 34% in lily bulb. Also Nishimura (42) found amylopectin in different varieties of cereals ranged from 65% to 85%.

Amylose is the linear fraction of starch. It consists of long unbranched chains of 300 to 400 glucopyranose units joined together by alpha-1,4 glucosidic linkages (39). Attack by alpha-amylase on amylose gives rise to a mixture of dextrans, whereas attack by beta-amylase gives pure maltose in almost quantitative yield (63). Meyer (41) reported that amylose from corn starch can be separated into fractions of different solubilities. The molecular weight of these fractions varying from 13,000 to 60,000. The mean molecular weight is 44,000. It has a polymerization degree of 270. By methylation, Meyer (41) showed that only one end group is present and there is, therefore, no branching.

The physical and chemical properties of amylose are different than those of amylopectin. Amylose is only slightly soluble in cold water. It gives a blue color when treated with iodine. Amylose shows an exaggerated tendency to retrograde and to precipitate out of solution on cooling. It also has high absorption on cellulose, high degree of crystallization in

certain alcohols, and the ability to absorb large amounts of iodine in titration (47).

Amylopectin is the branched fraction of starch. It is made up of repeating chain lengths of about 25 glucose units. These chains are combined to form a branched structure (39). The glucose residues which are situated at each point of branching are substituted not only on carbon-4 but also on carbon-6. Isolation of the alpha-1,6 disaccharide, isomaltose, from the products of incomplete hydrolysis of amylopectin establishes the constitution of the branch points. When amylopectin is treated with alpha-amylase, it undergoes random rupture of the alpha-1,4 linkages and yields a mixture of branched and unbranched oligosaccharides in which alpha-1,6 linkages are abundantly present (63). The branches themselves are combined in such a way that the free reducing groups of the glucose unit of a branch are linked through the sixth hydroxyl group of the glucose in an adjacent branch, or alpha-1,6 glucosidic linkage, thus forming a ramified structure (40). In Meyer's (41) studies, he found amylopectin to have a molecular weight of 500,000 and a polymerization degree of more than 3,000.

Amylopectin is soluble in water and forms a colloidal solution. It gives a red-brown color with iodine (47). Bates et al. (2) suggested that the affinity of iodine varies inversely with the degree of branching and directly with the length of the chain. Amylopectin has a limited conversion of up to about 64% with beta-amylase and it also has a slight tendency to retrograde (41).



## Hydrolysis of Starch

Starch is one of the major sources of commercial sugars. Because starch is a polymer of glucose as discussed previously, the products of the hydrolysis of the starch are of great commercial value. Hydrolysis may either be partial or complete and is usually done by acid or enzyme hydrolysis or both.

As early as 1811, a Russian chemist, Kirchoff (28) discovered that heating starch with dilute sulfuric acid transformed the starch into sugar, although, his object was to prepare a light colored substitute for gum arabic. The starch sugar is identical with grape sugar or glucose as was established by de Saussure (11).

Attempts to study the mechanism of the reaction have been complicated mainly by three factors: 1) failure to recognize and appreciate the importance of the secondary reactions; 2) a lack of suitable analytical methods to study the system of reactions; 3) and a lack of knowledge concerning the chemical nature of the starch. The result was that most of the early work, in common with many other phases of starch chemistry, is of little value and is of interest mainly to the historian (26).

The amylases are as ancient as life itself. The use of amylases coincides in the beginning with the discovery that an intoxicating beverage resulted from the fermentation of cereal grains. The earliest known records of the preparation of malt, date back to 7000 B. C. and that beer brewing was an established craft by 5000 B. C. The early knowledge of the mechanism of starch-sugar transformation was very meager (26). The foundation for the scientific approach to the problem of enzymatic starch degradation lies in

the discovery of diastase by Kirchoff (29).

Cowie and Greenwood (10) examined the effect of 0.2M hydrochloric acid at 45° C. on the granular structure of potato starch, a tuber starch. They observed that, under the conditions used, there was no swelling of the granules, whose birefringent properties were also unchanged. It was interpreted as meaning that acid treatment preferentially affected the amorphous rather than the crystalline region of the granule. They also found that, in the granule, amylopectin was degraded at a considerably faster rate than amylose. Since the hydrolysis rate must be a minimum rate and alpha-1,6 linkages are more resistant to acid hydrolysis than alpha-1,4 linkages, they decided that amylopectin, must be far more accessible to attack than amylose and must therefore, be more associated with amorphous regions than amylose. They interpreted their data as meaning that acid modification of the granule took place in two stages, a rapid attack on amorphous regions followed by a slower attack on the more crystalline areas.

Swanson and Cori (58) found that amylose was hydrolyzed more easily by acid than a dextrin containing mainly alpha-1,6 glucosidic linkages and that the alpha-1,4 glucosidic linkages had the same stability whether in a linear or a branched molecule. They interpreted this to mean that the alpha-1,6 glucosidic linkages is more stable to acid hydrolysis than the alpha-1,4 glucosidic linkage.

Freudenberg and Kuhn (16) proceeded on the assumption that hydrolysis is a monomolecular reaction involving the scission of equivalent alpha-1,4 glucosidic linkages. They applied a statistical treatment to predict the  $W(n)_{\max}$  maximum weight fraction of a polymer during random degradation. The



following equation was derived:

$$W(n)_{\max} = \frac{nZa_{\max}}{N} = n \left( \frac{2}{n+1} \right)^2 \left( \frac{n-1}{n+1} \right)^{n-1}$$

Za is the number of chains of length n, n is the number of units per chain, and N is the total number of units.

Enzymes capable of catalyzing the hydrolysis of starch are widely distributed in nature, occurring in the digestive secretions of animals and within the cells of most animals, plants, and microorganisms. The enzymes of this class can be divided into the following groups according to their action patterns; alpha and beta-amylase, and glucoamylase. Alpha-amylase found virtually in every type of living cell, effect a rapid fragmentation of the whole starch molecule by cleaving the alpha-1,4 linkages more or less at random and bring about a slow, though eventually extensive, conversion of starch to reducing sugars. Beta-amylase found primarily in plant materials, promotes a rapid hydrolysis of the outer chains of starch molecules to maltose, but since this enzyme cannot hydrolyze an alpha-1,6 linkages, a high-molecular-weight limit dextrin remains. Glucoamylase initially discovered in microorganisms, but also present in animal tissues, bring about a complete hydrolysis of starch directly to glucose.

The hydrolysis of starch and oligosaccharides by enzymes involves the addition of the elements of water to a glucosidic bond. In the enzymic reactions, the catalysis occurs on the surface of the enzyme molecule. Initially, some of the functional groups at the active site of the enzyme molecule must interact with the functional groups of the substrate molecules

to form the enzyme-substrate complex. In the complexes, the glucosidic-bond oxygen has been protonated by hydrogen ions from amino or imidazole groups of the enzyme and the electron deficient center at C-1 of the bond attracts electrons from donor groups such as hydroxyl groups. The resulting strained structure is cleaved on the C-1 carbon side of the bond forming a carbonium ion intermediate and a neutral glucosyl fragment. The final step involves the addition of a hydroxyl ion or a water molecule to the carbonium ion intermediate. With some enzymes, the last step occurs with inversion of configuration and with others by retention of the original configuration at C-1. Other mechanisms for hydrolysis have been postulated such as the double displacement mechanism for the alpha-amylase reaction. The experimental verification of these mechanisms is difficult to achieve (62).

#### Effect of Heat on Starch

A great deal of research has been done in the field of starch suspensions in water and the effect of temperature on these suspensions. As an aqueous suspension of starch is slowly heated, the granules lose their birefringence before swelling becomes pronounced. As heating is continued, the granules swell until they can no longer be distinguished under the microscope. Following the swelling the suspension gains in viscosity (54). This swelling process is called gelatinization. There have been many studies made on gelatinization and the effect of variables such as percent water, the varieties of cereals, the length of heating, and even the environment effects within varieties. Gelatinization was defined by Labanov and Lovacheva (33) as a process of breaking down the native structure of the starch granule, the

degree of which depends on the relationship between the amount of starch and water, temperature, and length of heating. Hollo<sup>1</sup> and his co-workers (20) stated that the pasting of starch proceeds in several stages of morphological changes in starch granules by heating to 100° C. These changes end with the starch in a nearly molecularly dispersed state. These changes are accompanied by alterations of physical constants such as viscosity, light refraction, and absorption. In some further work Hollo<sup>1</sup> et al. (21) proposed a mechanism of gelatinization; (a) before granules of starch are altered physically, a certain amount of starch dissolves, (b) amylose dissolves out of the granules in two granules in two stages. In the swelling stage, the free or unbound amylose and the amylose having a lower degree of polymerization go into solution. In the dispersion stage, the bound amylose and amylose having higher degree of polymerization go into solution, (c) amylopectin does not begin to dissolve until the stage of full dispersion has been attained, Lepeshkin (36) reported that the swelling of starch in cold water is purely physical and completely reversible. He also reported that the swelling of starch in hot water involves two processes: (1) a chemical reaction between water and the polysaccharides of starch leading to the formation of hydrates and (2) a swelling in water of the product thus formed. The absorption of water by these hydrate compounds was ten times greater than that of starch in cold water. Tiebackx (59) stated that the viscosity of starch solution is proportional to its amylopectin content. Ceason (7) reported that the viscosity of a starch solution depends on the swelling of the starch cells.

Much specific information concerning the swelling of starch has been recorded. Dox and Roark (13) tested 13 varieties of corn starch and observed swelling of these starches in a range of 65.1° C. to 71.1° C. Katz and his

co-workers (22) reported that the swelling of wheat starch occurs in two stages. The first stage of the paste formation was reached when wheat starch is heated at  $60^{\circ}$  C. -  $62.5^{\circ}$  C. in the presence of adequate water or with limited water to  $100^{\circ}$  C. The second stage appeared upon heating the wheat starch with adequate water at  $90^{\circ}$  C. -  $100^{\circ}$  C. In the first stage, the starch granule was swollen. In the second stage, the starch grain changed to a sac filled with a thin starch solution.

Pyler (48) investigated the secondary viscosity behavior of five cereal starches and potato starch. He found that removal of the natural lipids caused the disappearance of the secondary viscosity increase. A secondary viscosity increase was not observed in the waxy starches since they did not contain amylose. Increasing the concentration of the starch caused a decrease in the time required to reach the secondary peak, while increasing the temperature caused an increase in the time to attain the secondary peak. It was concluded that the secondary viscosity peak was due to a secondary swelling of the individual starch granules. The lipids were thought to be present as the amylose fatty acid complex, which forced the amylose molecules to assume a constricted helical conformation, effectively tightening the molecular network of the granule. Addition of energy destroyed the complex, allowing the amylose molecules to expand, and the granules to undergo secondary swelling.

Most of the work done on the effects of heat treatments alone on starch have been done at temperatures below  $100^{\circ}$  C. A notable exception was the work of Bryce and Greenwood (4, 5, 6) who heated starch in the dry state as high as  $400^{\circ}$  C. They found that starches heated to these temperatures gave volatile products and a pyrolytic residue. The condensable products of



potato starch pyrolyzed at 300° C. were: carbon dioxide, acetaldehyde, furan, propionaldehyde, acetone, acrolein, 2-methylfuran, butyraldehyde, methyl ethyl ketone, 2, 5-dimethylfuran, valeraldehyde, methyl propyl ketone, and diethyl ketone. The non-condensable products were: nitrogen, methane, and carbon monoxide. The pyrolytic residue was a condensed syrup consisting of 1,6-anhydroglucose and furfural.

The experiments of Bryce and Greenwood suggested that during pyrolysis of starch at elevated temperatures, there is a rapid breakdown of the molecular structure at a temperature around 220° C. - 230° C. rather than a steady random decomposition. The appearance of 1,6-anhydroglucose at the temperature indicated the breakage of the alpha 1,4-glucosidic linkages was occurring. After scission, the direct loss of water would result in the formation of the 1,6-anhydroglucose sugar, while isomerization of the ring must also occur in some manner prior to the loss of water to account for the extensive formation of the furanose form of the sugar. On the basis of the yields of pyrolytic residue, the thermal stability was: isomaltose greater than amylopectin and maltose greater than glucose and amylose which suggested that the alpha-1,6 bonds are more stable to pyrolysis than the alpha-1,4 bonds.

Lanning and Barham (34) thought that starch might dissolve or disperse in some polar solvents at temperatures at or above 110° C. as the result of a breakdown of hydrogen bonds. However, in their experiments, starch did not dissolve or disperse, as such, in any of the solvents tested. They found that cornstarch undergoes pyrolysis in absolute ethyl alcohol at temperatures above 110° C. to form alcohol soluble products.

Their experiments were made at various temperatures between 110° C. and 230° C. using a rocker type autoclave equipped with pyrex glass and

stainless steel liners. All air was removed from the reactor by allowing the solvent to boil a short time before sealing the autoclave. The starch used was defatted by dioxane and thoroughly dried in a vacuum oven. Corn-starch was heated over a temperature range from 115° C. to 229° C. The time was also varied. The results showed that slight pyrolysis took place at 192° C. in absolute ethyl alcohol. However, the starch was almost completely changed to an alcohol-insoluble product about 227° C. if enough time was allowed.

The insoluble residues in each experiment were tested with iodine and examined microscopically. The granule modification was shown by the disappearance of the "Maltese Crosses" and the reduction of the starch granule size. The results showed that some dextrin was formed and that modification of the granule began at 192° C. The alcohol-soluble product was dark brown, had a sharp bitter taste, and had a definite characteristic odor. The solubility tests showed that the alcohol-soluble product behaved like an alcohol, and had solubility characteristics different from those of the original starch. Various qualitative chemical tests were made on the products. The products from the experiments at 227° C., 228° C., 229° C. for different times all gave the same results. From the qualitative tests, they concluded that the product was not starch. The product may have been an unsaturated compound. The product had reducing groups and no free aldehyde groups or ketones. The product had active hydroxyl groups, but phenols and enols were not present. Low molecular weight alcohols probably were not present. Iodine tests on the alcohol-insoluble residues showed that dextrans were formed.

Acetone was not nearly as effective in converting starch into a soluble



product as absolute alcohol. The residue gave no starch iodine test and was not dextrin or starch. This residue was partly soluble in water and insoluble in alcohol and ether. The qualitative tests performed were the same as the alcohol products. The results of these qualitative tests were the same with the exception that phenols and enols were present. Trisobutylene converted very little starch to a soluble solid. At temperatures above  $200^{\circ}$  C. starch readily lost water to form pure carbon.

Perez (45) investigated the moisture-temperature relationship in starch gelatinization. Five cereal starches, including wheat, corn, waxy corn, non-glutinous sorghum, and German rice were analyzed for beta-amylase susceptibility and maximum hot-paste viscosity changes following pre-heat treatment at two temperature levels,  $100^{\circ}$  C. and  $200^{\circ}$  C., using five moisture levels of 29%, 38%, 52%, 68%, and 99%.

The pre-heat treatment at  $100^{\circ}$  C. consisted of heating the suspensions in an autoclave for five minutes. The resultant suspensions were further dispersed in a blender to insure a uniform suspension and beta-amylase susceptibility was determined by the ferricyanide reduction method. The hot-paste viscosity pre-heat treatment was the same as previously stated but the resultant suspensions were not further dispersed. The maximum hot-paste viscosity was recorded with a Brabender amylograph.

For the pre-heat treatment at  $200^{\circ}$  C. stainless steel tubes hermetically sealed by means of a steel cap with a lead gasket were used as containers. The heating was done in an oven for five minutes. At the end of the heating time, the starch suspensions were transferred from the tubes and treated as described before for beta-amylolysis. For the hot-paste viscosity determination, the same tubes were used. At the end of the five minutes

heating period, the tubes were allowed to cool to room temperature. The starch paste was then transferred from the tubes and treated as described before.

The results indicated that heating at both 100° C. and 200° C. caused uneven gelatinization of the starch mass if insufficient water was present. When the starches were heated at 100° C., the beta-amylase action on the starches increased, and the maximum hot-paste viscosity decreased as the moisture was increased. At 200° C., both beta-amylase susceptibility and maximum hot-paste viscosity decreased for all starches except waxy corn.

In some later work Perez (46) investigated the effects of moisture, time of heating, and temperature of heating on the gelatinization and pasting properties of high amylose, unmodified, and high-amylopectin corn starches. The starches were suspended in 20%, 40%, 60%, 80% moisture. The suspensions were heated for 5, 10, 15, 20, and 30 minutes at 80° C., 100° C., 200° C., and 250° C. Beta-amylolysis determinations were made using the ferricyanide reduction method. Maximum hot paste viscosities were measured with the Brabender Amylograph.

The results indicated that beta-amylolysis of all starches increased as the moisture, time of the heat treatment, and temperature of the heat treatment was increased. Availability of the starches to beta-amylase varied inversely with the amylose content of the granule when treated at any temperatures. At any given temperature, the beta-amylolysis of the starches increased as the moisture and time of the heat treatment was increased, except at 250° C. for 30 minutes. In this case, the starch polymer was apparently destroyed. The maximum hot-paste viscosity of the starches decreased as the temperature and time for heating were increased. The maximum hot-paste viscosity of the

high-amylopectin starch decreased, progressively, as the moisture content was increased, the effect becoming more marked as both time and temperature of the heating were increased. The starches containing significant amounts of amylose showed an increase of the maximum hot-paste viscosity when the moisture content was 40% or above.

### Separation of Starch Hydrolysis Products

There have been many methods used to separate the products resulting from starch hydrolysis. The most widely used have been the chromatographic methods. Column, paper, and even gas chromatography may be used.

Column chromatography was the first of these methods used in the separation of enzymatic hydrolysis products. Ulman (60) used  $Al_2O_3$  to selectively separate, by absorption, the products of enzymatic action on starch. Nordin (43) used Sephadex G-75 to separate starch dextrans. He found resolution according to molecular size. Whelan and his co-workers (61) used a charcoal-celite column to separate maltodextrans with increasing concentrations of ethyl alcohol to elute the larger dextrans. Salem (52) also used a charcoal-celite column to separate the oligosaccharides from corn syrup using increasing concentrations of ethyl alcohol. More sophisticated techniques of separation were employed by Durso et al. (14) and Salem (52) who used an automatic fraction collector for the collection of fractions.

Another technique for the separation of oligosaccharides has been paper chromatography. Several methods have been used. Commerford et al. (9) used a solvent of n-propyl alcohol, ethyl acetate, and water in a 14:2:7 (v/v) ratio using Whatman 3mm paper. Descending chromatography was used and the

paper was developed two or three days. Dimler et al. (12) used butyl alcohol, pyridine, and water in a 6:4:3 (v/v) ratio or fusel oil, pyridine, and water in a 1:1:1 (v/v) ratio to separate the products of starch hydrolysis. Salem (52) separated oligosaccharides with a solvent of butanol, pyridine, and water in a 6:4:3 (v/v) ratio using Whatman No. 4 filter paper. The chromatograms were developed sixteen to twenty-four hours.

Gas chromatography was used by Bryce and Greenwood (4, 5, 6) to separate the volatile products from the pyrolysis of starch. It was the objective of this investigation to observe what would happen to starch suspensions subjected to extreme heat in the presence of water. Previous investigations of starch hydrolysis have used acids or enzymes. In this investigation, starch in water was subjected to heat treatments of extreme temperatures to determine the nature of the degradation products.

#### MATERIALS AND METHODS

This investigation was performed on wheat starch. A one percent suspension of this starch in de-ionized water was subjected to a heat treatment for one hour. The temperature ranged between 150° C. and 250° C. in 10° C. increments. The resulting solutions were analyzed by various means.

The wheat starch was extracted from a Hard Red Winter Wheat flour milled on the Kansas State University pilot mill. Two methods were attempted to extract the starch from the flour. The first method attempted was by suspending the flour in water and blending the suspension in a Waring Blendor. The suspension was centrifuged and the gluten fraction and intermediate fraction, containing protein and some starch, was discarded. The third



fraction was retained. This fraction was resuspended and recentrifuged several times until there was no gluten or protein fraction remaining. This method was discarded because it was suspected that the blender blades were causing excessive starch damage. The second method used was the laboratory modification of the well known Martin commercial method as recently cited by Wolf (64). The method entailed making a stiff dough ball of flour and water. The dough ball was aged at room temperature for one hour. The starch was washed from the dough ball by kneading it with the addition of distilled water. This washing process was continued until most of the starch was washed out. The starch slurry was centrifuged and the gluten layer and intermediate fraction discarded. The starch was resuspended and recentrifuged and the protein discarded. This process was repeated until no more protein could be removed. The starch was air-dried at  $40^{\circ}$  C. -  $45^{\circ}$  C. under a forced-air draft. This method was preferred because it removed most of the damaged and small starch granules.

The starch was defatted by modifying a method as described by Schoch (53). The air-dried starch was placed in a four liter Erlenmeyer flask to which was connected a 3-foot condenser. The starch was suspended in 85% (by volume) aqueous methanol. The mixture was then refluxed for two hours. The mixture was agitated occasionally to prevent bumping. After reflux, the hot suspension was filtered rapidly on a large Büchner funnel, and the starch cake was washed on the filter with several portions of hot 85% aqueous methanol. The wet cake was then broken up and returned to the flask and resuspended in 85% aqueous methanol and refluxed for two hours again. This process was repeated three times. After washing, the filtered starch was resuspended in distilled water, with stirring for 30 minutes, followed

by filtering. This washing process was repeated three times. The cake was broken up and air-dried at  $40^{\circ}$  C. -  $45^{\circ}$  C. in a forced-air draft.

De-ionized water was the suspending agent used in this investigation. This water was prepared from distilled water. The distilled water was passed through an ion exchange resin twice at a slow rate. The resin was Fisher Rexyn AG501.

The heat treatments were performed in stainless steel tubes six inches in length and 0.5 inches inside diameter. The starch suspension was hermetically sealed in the tubes by means of a steel cap with a lead gasket.

The temperature of the heat treatments were measured with a copper-constantan thermocouple. The function of the thermocouple was immersed in silicon oil in a short peice of stainless steel tubing through the side of one of the tubes containing the starch suspension. The potential difference of the EMF of the copper and the constantan was measured with a Leads and Northrup millivolt potentiometer.

Perez (45) showed that the higher the percent water in a starch suspension, the greater the effect of heat treatment had on the starch. One percent suspension of wheat starch in water was used in this investigation. In order to have adequate material ten tubes, each containing 25 mls. of the one percent starch suspensions were used at each temperature level. The suspension (25 mls.) allowed for a small amount of head space in each tube. They were sealed and placed on a rack in the oven. The heat treatments were performed for one hour at the desired temperature level in a National Micro Oven equipped with a fan for air movement.

Two solvent systems and two different filter papers were investigated. It was decided to use N-propanol-ethyl acetate-water 6:1:3 (v/v) rather than



Buthanol-ethanol-water because of the faster development time and better separation. Whatman No. 1 rather than Whatman No. 4 filter paper was used because it gave better resolution. The reference used for sugar identification by chromatography was a one percent corn syrup solution. This was prepared from a corn syrup having a Dextrose Equivalent of 43. Also, a commercial maltose was used for the second reference.

The chromatograms were developed with silver nitrate. The silver nitrate was prepared by adding 0.1 mls. of a saturated silver nitrate to 20 mls. of acetone. Water was added dropwise until the silver nitrate was dissolved. The paper chromatograms were dipped in the silver nitrate solution and allowed to dry for three to four minutes. The papers were then dipped in a 0.4 % sodium hydroxide in methanol. When the spots were developed, the papers were dipped in a 5% sodium thiosulfate fixing solution and washed with water and dried.

Total acidities of the resulting solutions were determined by titrating 25 mls. aliquots of the combined solutions with 0.1N sodium hydroxide to a pH 7.0.

The concentration of the total reducing sugars in the heat treated starch solutions was determined by the Folin and Wu method (18).

A determination of the concentration of the glucose and maltose produced during the heat treatment of the starch suspension was determined. This was determined by spotting a known amount of the heat treated solutions on a paper and developing the chromatogram. Also known concentrations of glucose and maltose were spotted on the papers. The densities of the known and unknowns were determined with a model 520-A Photovolt Multiplier densitometer with a Model 42-A Varicord variable response recorder. The areas under the curves were compared.

## RESULTS AND DISCUSSION

It was known from previous work by Perez (45, 46) that the heat treatment of starch suspensions affected the pasting properties and beta-amylase susceptibility of the resulting suspensions. In this investigation a one percent suspension of wheat starch was subjected to a heat treatment for one hour at the desired temperature level. A temperature range of 150° C. to 250° C. in 10° C. increments was investigated. Pronounced changes in the starch suspensions were observed between 150° C. and 200° C.

The physical appearance of the solutions resulting from the heat treatment reflect the changes in the starch as the temperature of the heat treatment was varied. As the temperature of the heat treatment was increased, more of the starch went into solution and the solutions became clearer. Also, as the temperature of the heat treatment was increased, the solutions became succeeding a darker brown in color. All the solutions after the heat treatments had a characteristic odor of caramelization. At the 150° C. and 160° C. heat treatments, the odor was very slight. This odor became more pronounced as the temperature of the heat treatments were increased.

The effects of heat treatment on the color of starch suspensions as shown by the optical density at 280m $\mu$  is summarized in Table 1 and Fig. 1. These data indicate a sharp increase in the color of the starch suspensions when heated between 180° C. and 190° C.

Table 1. Effect of heat treatment of starch suspensions on optical density of solutions.

Temperature of the Heat Treatment (°C)	Optical Density
150	0.026
160	0.112
170	0.200
180	0.292
190	0.600
200	0.625

These data suggest that browning and/or carmelization took place as a result of the heat treatment.

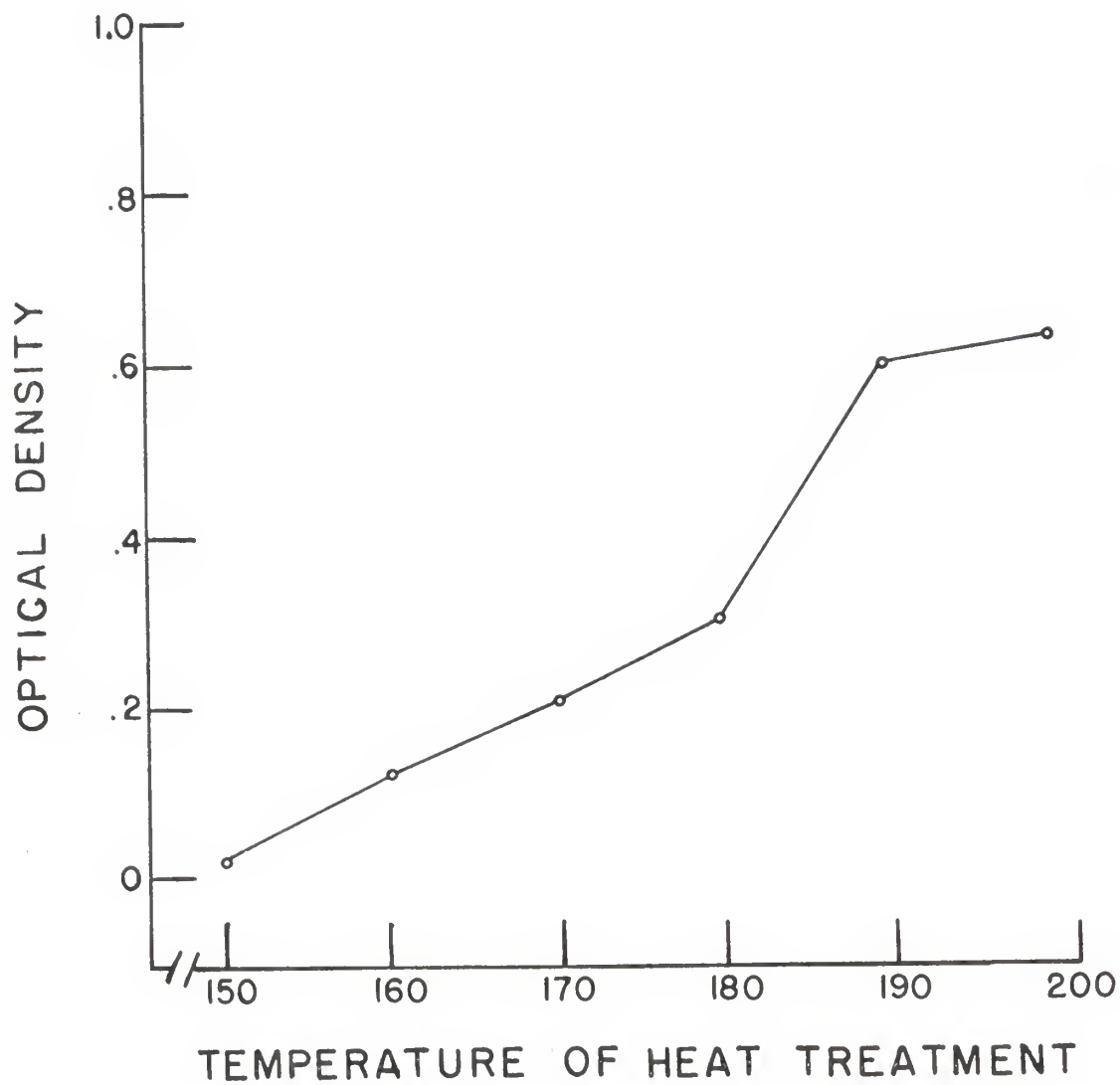


Fig. 1. Effect of temperatures of heat treatment ( $^{\circ}\text{C}$ ) on color of solutions.

## Effect of Heat Treatment on Sugar Production

The observation of the changes in the color and the caramelization odor of the heat starch suspensions, suggested that hydrolysis of the starch had taken place.

Analysis by paper chromatography of the heated solutions showed evidence that the heat treatments caused hydrolysis of the starch with the formation of various oligosaccharides. The distribution of the oligosaccharides in heat starch suspensions are shown in Fig. 2 and are summarized in Table 2.

In all cases, the effects of the heat treatments at 150° C. and 160° C. were undetected by paper chromatography. No reducing sugars were detected on the paper chromatograms for these heat treatments. The partial breakdown of the starch began at 170° C. Heat treatment of the starch suspension at 170° C. caused production of a homologous series of reducing sugars from G<sub>1</sub> to G<sub>5</sub> and some higher oligosaccharides. The heat treatment at 180° C. produced homologous series of oligosaccharides ranging from G<sub>1</sub> to G<sub>5</sub> and higher. Also present were mannose or fructose, isomaltose, furfural, 5-hydroxymethyl furfural, and a reducing sugar that was not identified. The heat treatment at 190° C. caused an almost complete breakdown of the starch polymer. The only products present were glucose, a small amount of maltose. Also, mannose or fructose, furfural, 5-hydroxymethyl furfural, and an unidentified reducing sugar. The heat treatments at 200° C. caused the complete breakdown of the starch polymer. There was no glucose or glucose polymers present. The only reducing substances were furfural and 5-hydroxymethyl furfural. The heat treatments beyond 200° C. gave the same results.

# DISTRIBUTION OF OLIGOSACCHARIDES FOLLOWING HEAT TREATMENTS



Fig. 2. Chromatogram showing effect of temperature of heat treatment (°C) on sugar production.



Table 2. Distribution of oligosaccharides in heated starch suspensions.

Reducing Substance	R <sub>G</sub>
Maltopentose	0.21
Maltotetrose	0.32
Maltotriose	0.50
Maltose	0.71
Isomaltose	0.82
Glucose	1.00
Fructose or Mannose	1.07
Unidentified	1.44
5-Hydroxymethyl furfural	1.67
Furfural	1.93

### Ratio of Glucose to Maltose Following Heat Treatments

The ratio of glucose to maltose in the various heat treated samples was determined in order to have a measure of the degree of hydrolysis which had occurred.

Table 3. Concentration of glucose and maltose following heat treatment.

Temp. of the Heat Treatment (°C)	Glucose Mg %	Maltose Mg %	Glucose + Maltose	Glucose/ Maltose
150	-----	-----	-----	-----
160	-----	-----	-----	-----
170	255.1	583.8	838.9	.44
180	427.4	432.9	860.3	.99
190	412.9	93.8	560.7	4.40
200	-----	-----	-----	-----

Since the chromatograms representative of the heat treatments showed that hydrolysis of the starch did not take place until 170° C. was reached, the concentrations of glucose and maltose were only determined for the 170° C., 180° C., and 190° C. heat treatments. The data in Table 3 shows that hydrolysis of the wheat starch suspension occurred as a result of the heat treatment. Most of the starch was hydrolyzed to glucose and maltose.

### Concentration of Total Reducing Sugars

The concentration of the total reducing sugars of the starch solutions following heat treatment were determined as milligram percent of glucose.

Table 4. The mean concentration of total reducing sugars present in the starch solution following heat treatment.

Temperature of the Heat Treatment (°C)	Mg. % of the Reducing Sugars in Dextrose Equivalents
150	7.0
160	8.3 *
170	150.8 *
180	411.3 *
190	347.2 *
200	231.6

LSD<sub>.05</sub> = 29.417

\* Denotes significance at 5% level.

Table 5. The analysis of variance of the mg. % glucose of the final solution following heat treatment.

Source of Variation	Degrees of Freedom	Sum of Squares	Mean Squares	F
Temp.	5	864483	172997	316.5*
Susp. same Temp.	12	6555	546	1.2
Reps. same Susp. same Temp.	<u>18</u>	<u>8454</u>	470	
Total	35	879492		

\* Denotes significance at 5% level.

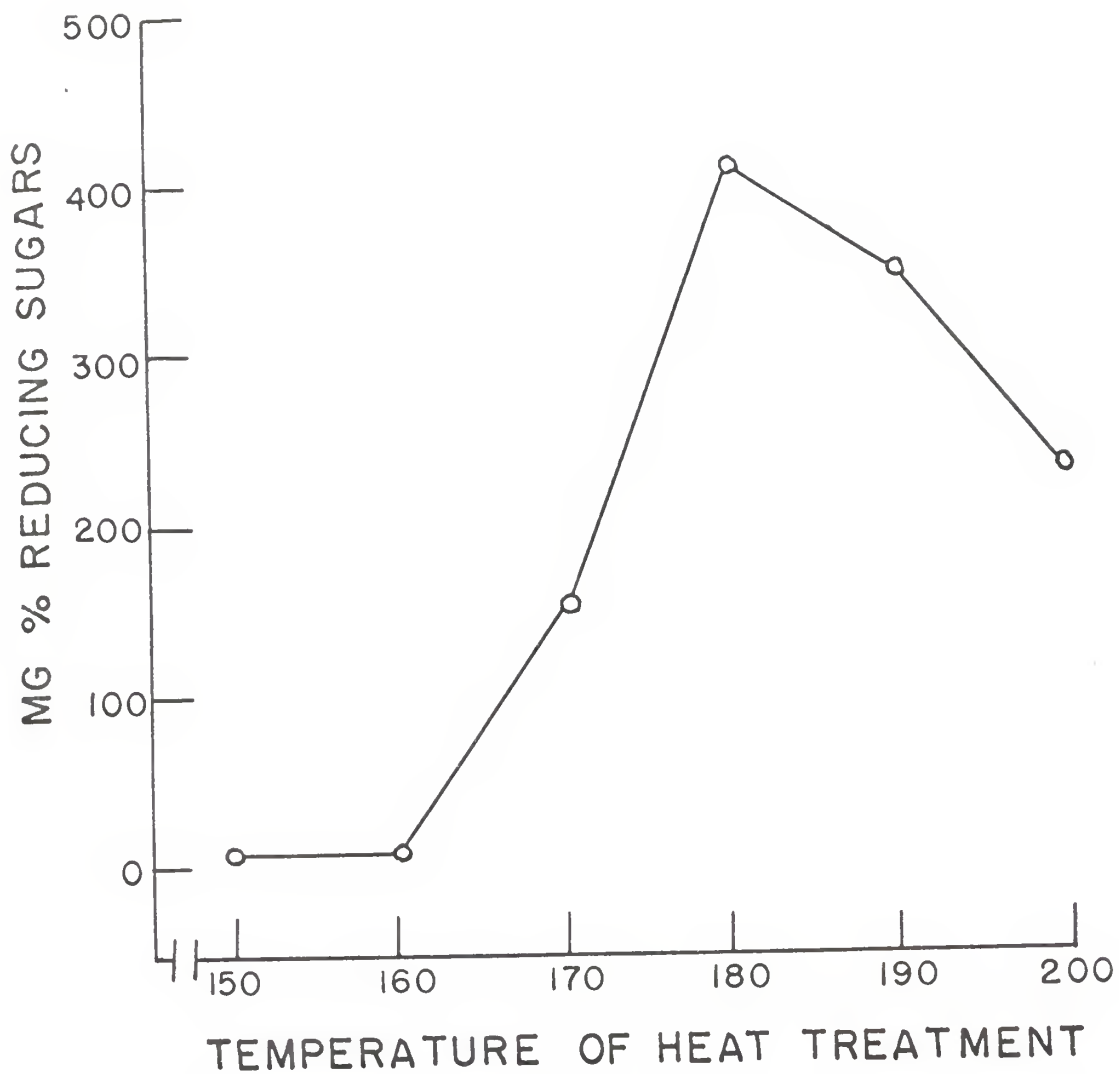


Fig. 3. Effect of temperatures of heat treatment (°C) on reducing sugars.

The statistical model of this investigation was a nested classification. The main variable was the temperature. The suspensions prepared for each experiment were the treatments within the temperature. In this case, the suspension effect was a measure of the homogeneity. The suspension effect was random for each fixed temperature.

The expected mean squares of the model for a nested design are not listed. These expected mean squares are the criteria for the F ratio to test the significance of the effects.

It was found that the concentration of the reducing sugars were small following the heat treatments at 150° C. and 160° C. These reducing sugars were probably long chain dextrans with only one or two reducing groups per chain. The concentration of the reducing sugars in the starch solutions from the heat treatments at 170° C. to 200° C. was too strong to perform the test directly from the solution. Five mls. of these solutions were diluted 50 mls. for analysis of the reducing sugars. There was a large increase in the concentration of the reducing sugars after heating the starch suspensions to 170° C. or higher. The analysis of variance indicates that the temperature of the heat treatments had a significant effect on the production of the reducing sugars. The LSD's show that there was not a significant change in the reducing sugars until the temperature was between 160° C. and 170° C. All levels of the heat treatment were significant beyond 170° C. Heating to 190° C. and 200° C. caused a reduction in the reducing sugars indicating that the reducing sugars were being destroyed at the elevated temperatures.

Effect of Heat Treatment on pH and  
Total Acidity

The effect of heat treatments on the pH and total acidities of the starch solutions are shown in Table 6.

Table 6. Mean pH and mean total acidities of the starch solution following heat treatment.

Temperature of the heat treatment (°C)	Mean pH	Mean total acidities (microequivalents of NaOH)
150	6.07 *	-----
160	5.47 *	0.20
170	4.38 *	1.28 *
180	3.79 *	10.90 *
190	3.18	39.00
200	3.18	45.08
210	3.17	49.10
220	3.10	44.10
230	3.10	41.90
240	3.17	40.90
250	3.11	38.40

LSD<sub>.05</sub> (pH) = .46

LSD<sub>.05</sub> (total acidity) = 6.31

\* Denotes significance of 5% level.



Table 7. Analysis of variance of pH of the final solution following heat treatment.

Source of Variation	Degrees of Freedom	Sum of Squares	Mean Squares	F
Temp.	5	218	44.0	64.2 *
Susp. same Temp.	12	8	0.7	5.2 *
Reps. same Susp. same Temp.	<u>162</u>	<u>21</u>	0.13	
Total	179	247		

\* Denotes significance at 5% level.

Table 8. Analysis of variance of the total acidities of the final solution following heat treatment.

Source of Variation	Degrees of Freedom	Sum of Squares	Mean Squares	F
Temp.	5	12791	2548	101.4 *
Susp. same Temp.	12	302	25	207.1 *
Reps. same Susp. same Temp.	<u>18</u>	<u>2</u>	0.12	
Total	35	13095		

\* Denotes significance at the 5% level.

The mean pH of the starch suspensions before heat treatment was 6.6. As the temperatures of the heat treatment were increased, the pH decreased and the total acidities increased. The analysis of variance indicates that the temperature of the heat treatments had a significant effect on the production of acids. The suspensions effect was also significant. This might indicate that the suspensions were not homogeneous or that they reacted differently during the replication. The LSD's of the pH means show that the production of acid was sufficient to cause a significant change in the pH from 150° C. to 190° C. The LSD's of the total acidities show that there was a significant increase up to heat treatments of 190° C., but did not change significantly above that temperature. These changes are illustrated in Tables 6, 7, and 8 and Figs. 4 and 5.

It has been shown previously that the starch suspensions underwent browning and/or caramelization reactions as the suspensions were subjected to the heat treatments. As these reactions took place, organic acids were produced as a by-product. These acids could account for the decrease in pH and increase in total acidities. As the temperatures of the heat treatment were increased, the starch suspensions underwent further browning and/or caramelization resulting in the formation of additional acids. As the starch was hydrolyzed into glucose, the glucose was broken down into 5-hydroxymethylfurfural and furfural with the production of additional acids.

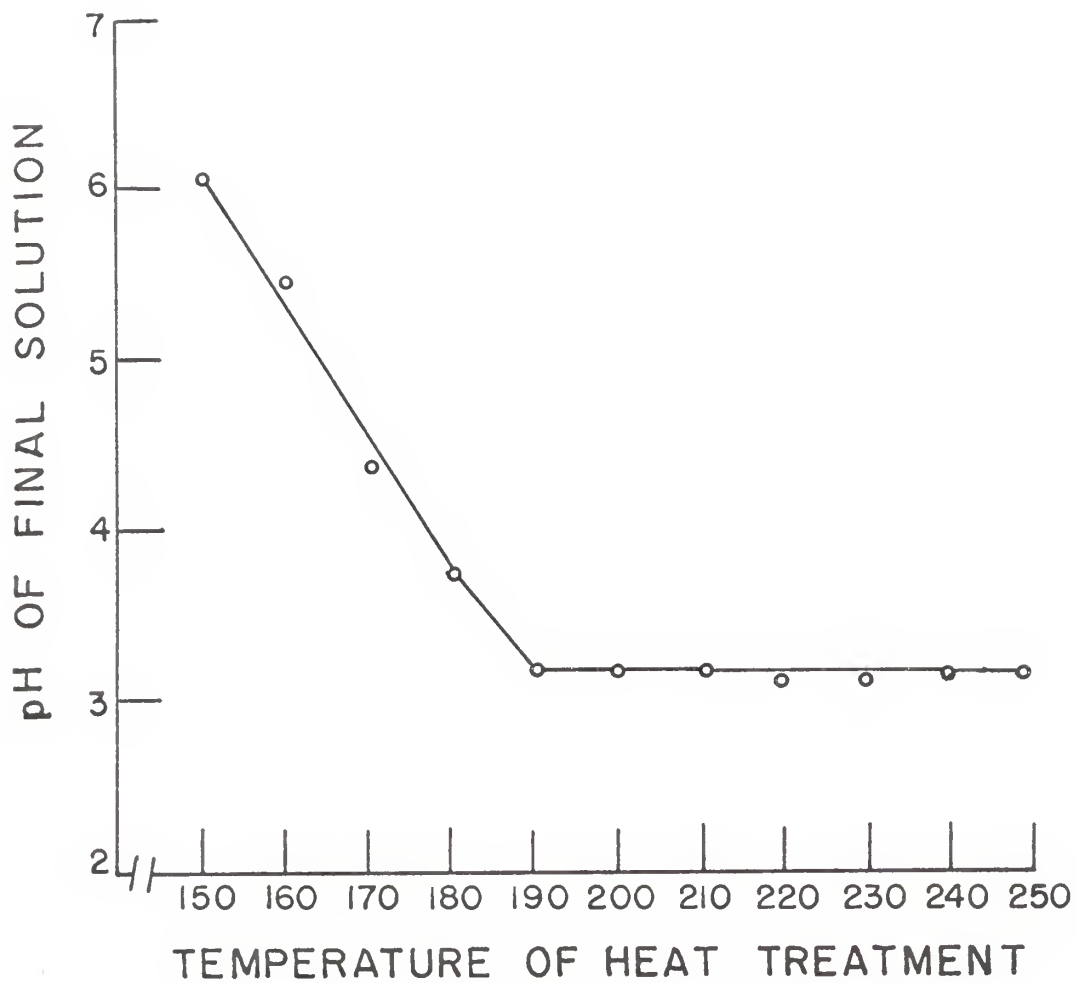


Fig. 4. Effect of temperatures of heat treatment ( $^{\circ}\text{C}$ ) on pH.

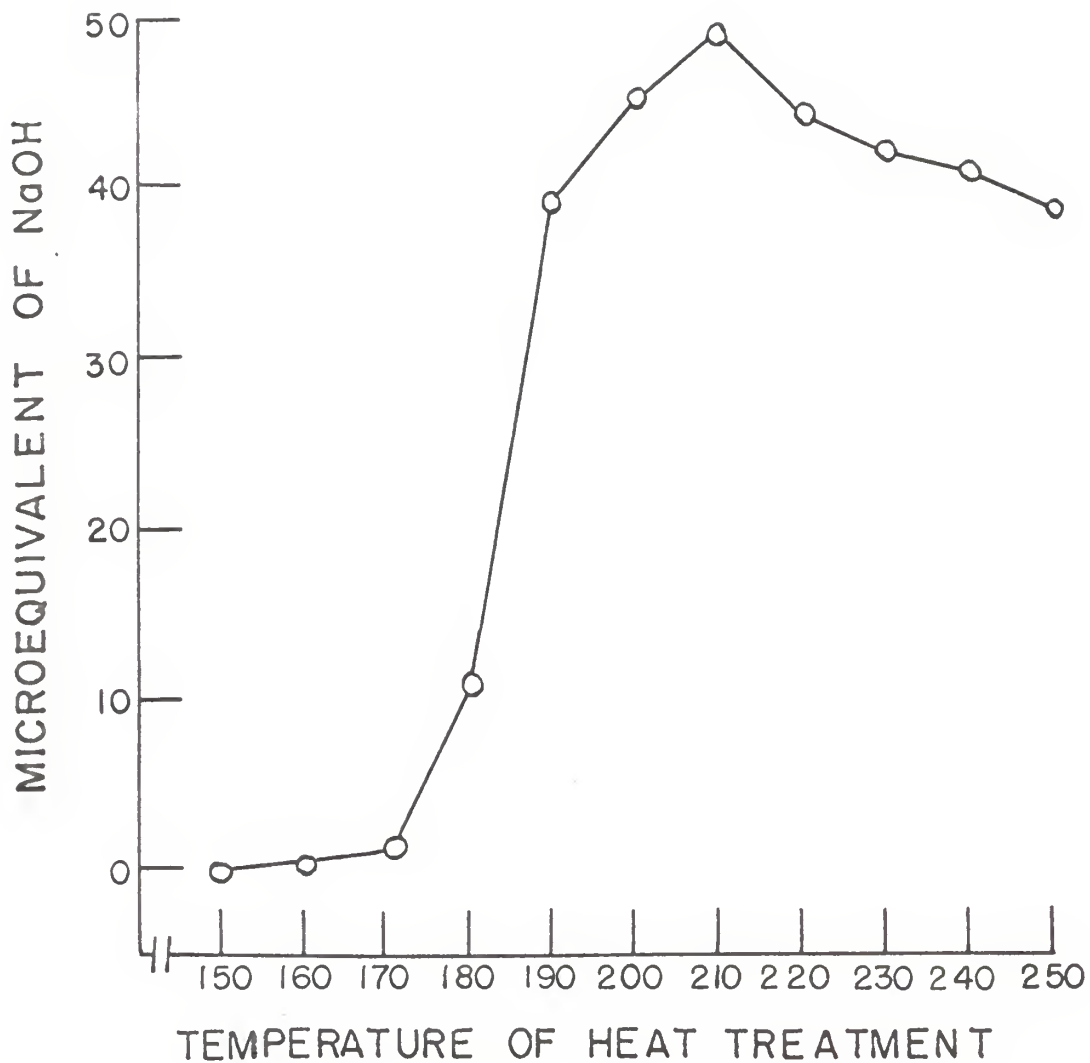


Fig. 5. Effect of temperatures of heat treatment ( $^{\circ}\text{C}$ ) on Total acidity.

## SUMMARY AND CONCLUSIONS

The effect of heat treatments on a one percent wheat starch suspension was investigated. The wheat starch was suspended in pure distilled water and was held at the desired temperature level for one hour. The temperature of the heat treatments investigated were 150° C. to 200° C. and some determinations were made as high as 250° C. The temperature was varied in 10° C. increments. The effects of the heat treatment were followed by paper chromatography and by the physical and chemical changes in the solutions resulting from the heat treatment.

It was found that the starch underwent hydrolysis. As the temperature of the heat treatments were increased, the amount of hydrolysis increased. The optimum temperature for hydrolysis was 180° C. At this temperature, the starch was broken down to the maximum number of products obtained. Beyond this temperature, the starch polymer was completely broken down and the glucose destroyed.

The heat treatments of the starch suspensions caused a browning and/or caramelization reaction to occur. A by-product of these reactions are organic acids. These acids catalyzed a hydrolysis of the starch. As the temperature of the heat treatments were increased, more acids were produced and an increasing number of alpha-1,4 bonds were broken in a random order. This hydrolysis was continued until the starch was converted to oligosaccharides.

## ACKNOWLEDGMENTS

The author wishes to acknowledge his gratitude to his major professor, Dr. John A. Johnson, for his assistance and advice during this investigation and in the preparation of the manuscript. Appreciation for the use of the research facilities is extended to Dr. William J. Hoover, Head of the Grain Science and Industry Department. Appreciation is also extended to the other members of the staff of the Grain Science and Industry Department for their help during this investigation.

The author also wishes to acknowledge his indebtedness to Quaker Oats Company, Barrington, Illinois, for the financial assistance which made this research possible, and for the consultation given by their research staff.

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EFFECT OF HEAT TREATMENTS ON  
WHEAT STARCH SUSPENSION

by

JACK EDWARD CALENTINE

B. S., Kansas State University, 1965

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AN ABSTRACT OF A MASTER'S THESIS

submitted in partial fulfillment of the

requirements for the degree

MASTER OF SCIENCE

Department of Grain Science  
and Industry

KANSAS STATE UNIVERSITY  
Manhattan, Kansas

1967

An investigation was conducted of the effect of heat on one percent wheat starch suspensions. Wheat starch was suspended in pure distilled water and the temperatures of the heat treatment varied from 150° C. to 250° C. The temperature was varied in 10° C. increments. The starch suspensions were hermetically sealed in stainless steel tubes and held at the desired temperature level for one hour. The effects of the heat treatment were determined by physical and chemical changes in the solutions.

The results showed that the starch underwent hydrolysis producing oligosaccharides. As the temperatures of the heat treatment were increased, the extent of hydrolysis increased. In general, as the temperatures of the heat treatments were increased, the color of the solutions became a darker brown, the pH decreased, the total acidity increased, and the concentration of the reducing sugars increased. The optimum temperature for the starch hydrolysis was 180° C. At this temperature the maximum amount of oligosaccharides was obtained from the starch. At 190° C. mainly glucose remained with little maltose and no measurable amount of higher oligosaccharides. At temperatures of 200° C. and above, glucose was converted to other products and 5-hydroxymethylfurfural and furfural. It is likely that browning and/or caramelization reactions produced organic acids which catalyzed the hydrolysis of the starch producing oligosaccharides.