

Characteristics of Alkali-Extracted Starch Obtained from Corn Flour

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ABSTRACT

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Characteristics of starches obtained from corn flour by an alkali extraction method were investigated and compared with those of commercial corn starch. Of the variables studied, alkali concentration had the most effect, extraction temperature had some effect, and steeping time had no significant effect on the characteristics of the alkali starches. The protein content of most of the alkali starches was significantly different from that of commercial starch, but the sodium content of all alkali starches was higher than that of commercial starch. The alkali starches had lower pasting temperatures and higher viscosity after 15 min holding

at 95°C than those of commercial starch as determined by a Brabender amylograph. Starches extracted using lower alkali concentration had lower peak temperature and lower onset temperature of gelatinization than those extracted at higher alkali concentration as determined by differential scanning calorimetry. The X-ray diffraction pattern, birefringence, morphology, and enzymatic hydrolysis characteristics of alkali starches were similar to those of commercial starch. The alkali starches absorbed more moisture than the commercial starch at a given water activity.

The increases in demand for starch and its conversion products, in production costs, and in Environmental Protection Agency regulations have caused many corn processors to evaluate methods other than conventional wet milling using sulfur dioxide for obtaining starch.

Mistry and Eckhoff (1992) have studied the alkali debranning of corn and subsequent dry milling as a less-energy-intensive method of fractionation and as a way to enhance germ recovery from dry milling. Products from the dry-milling industry such as fine grits and flour have been used as a source of starch for the production of alcohol, chemicals, and products used in pharmaceuticals (Maisch 1987). Extraction of starch from endosperm pieces could result in a lower-cost method of obtaining starch.

Several methods have been proposed and developed to extract starch from cereal flours using alkali treatment (Dimler et al 1944, Crozier 1959, Phillips and Sallans 1966, Fellers et al 1969, Johnston et al 1971, Wu and Sexson 1976). The starch extraction method developed by Dimler et al (1944) for wheat flour was the most effective method so far to obtain starch in high yield and purity. They used 0.50–1.0% alkali solutions to extract starch from wheat flour. This method also was applied to corn flour (Dimler et al 1944) to extract corn starch. However, the yield (maximum 67% on flour dry basis) and purity (0.5–1% protein content) of the starch extracted from corn flour was lower than that obtained from wheat starch. A modified alkali extraction process was developed (Mistry 1991) that extracted starch from corn flour with higher yields and purity than those of the earlier alkali processes and than those from commercially obtained corn starch. This modified method uses lower alkali concentrations (<0.5%) than those used by Dimler et al (1944).

Alkali has been used to produce modified starches and starch products having properties different from those of native corn starch (Yeates et al 1965, Lancaster et al 1966, Krochta et al 1988). Several studies have been reported that investigated the behavior of starch when reacted with alkali solutions (Mangels and Bailey 1933; Leach et al 1959, 1961; Medcalf and Gilles 1966; Lancaster and Conway 1968). Strong alkali solutions have varying effects on starch, such as granule swelling, increased viscosity, and gelatinization.

The conditions for alkali extraction of starch are significantly different from those used for starch modifications. Conditions generally have shorter exposure times and lower alkali concentrations. No studies have been reported to investigate the properties and characteristics of starch resulting from alkali extraction. The objectives of this study were to investigate characteristics of alkali-extracted starches using the amylograph, differential scanning calorimetry (DSC), the X-ray diffractometer, birefrin-

gence, vapor sorption isotherms, scanning electron microphotographs, and enzymatic hydrolysis and to study the effect of alkali extraction parameters (alkali concentration, extraction temperature, and extraction time) on starch characteristics.

MATERIALS AND METHODS

Materials

Degerminated yellow corn flour (Lauhoff Grain Co., Danville, IL), approximately composed of 80.0% starch, 11.0% moisture, 6.0% protein, 2.0% fat or oil, 0.5% fiber, and 0.5% ash; sodium hydroxide (reagent grade pellets, Fisher Chemicals, Fair Lawn, NJ); and food grade corn starch (A. E. Staley Manufacturing Co., Decatur, IL) were used in this investigation.

Starch Extraction from Corn Flour

Starch samples were prepared using the alkali extraction method developed by Mistry (1991) and using eight different extraction conditions (Table I). These conditions were designed on the basis of a review of literature and preliminary laboratory studies. A full factorial experimental design was used with two levels of alkali concentration (0.1 and 0.4%), two levels of temperature (25 and 55°C), and two levels of time (30 and 90 min).

Aqueous sodium hydroxide (NaOH) was prepared (0.1 or 0.4%, w/v) by dissolving NaOH pellets in 600 ml of distilled water. With the solution in a constant-temperature water bath (25 or 55°C), corn flour (100 g, dry basis) was accurately weighed and added to 600 ml of the alkali solution with continuous agitation

TABLE I
Sample Identification, Alkali Extraction Conditions, and Protein and Sodium Contents of Starches from Corn Flour^a

Sample Identification	Extraction Conditions		Time (min)	Protein ^b (% dry basis)	Sodium ^c (ppm)
	Alkali Concentration (%)	Temperature (°C)			
Flour	6.45	24
Commercial starch	0.35 d	561 f
Starch 1	0.1	25	30	0.74 b	1,003 d
2	0.1	25	90	0.56 c	871 d
3	0.1	55	30	0.19 e	889 d
4	0.1	55	90	0.10 f	906 d
5	0.4	25	30	0.31 d	3,371 b
6	0.4	25	90	0.54 c	3,886 a
7	0.4	55	30	0.82 a	2,319 c
8	0.4	55	90	0.55 c	3,239 b

^aEach value represents the mean of two replicates. Mean comparisons followed by the same letter are not significantly different ($P < 0.05$) within the same column.

^bLSD = 0.07.

^cLSD = 178.

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to obtain uniform dispersion. The corn flour to steep water ratio of 1:6 was found to effectively disperse protein with a minimum loss of starch (Wu and Sexson 1976). After 30 or 90 min of steeping, the flour was ground 5 min in a blender (Waring, New Hartford, CT) at high speed and was screened (using a 200-mesh screen) to remove fibrous materials. The tabling method was used to separate starch from the flour slurry. The slurry was pumped at 180 ml/min on a 10-ft-long, 4-in.-wide galvanized trough having a 1-in. slope. The starch that settled on the table was washed twice with 500 ml of distilled water to remove residual protein and other nonstarch components. After drying overnight on the table, the starch was scraped off and dried in a forced-air oven at 49°C for 24 hr. The solids content of the starch was determined by drying a 20-g sample of dried starch for an additional 2 hr at 103°C.

The experiment was replicated to obtain a total of 16 samples. For comparison, commercial starch and unextracted corn flour were tested using the methods described below. The flour, commercial corn starch, and alkali-extracted starch samples were analyzed for protein content by the micro-Kjeldahl method (AACC 1983) and for sodium by emission-spectroscopic analysis (AOAC 1980).

Amylograms

The amylograms of the corn flour and the starch samples were obtained using a Brabender Viscoamylograph (model P110, C. W. Brabender Instruments Inc., South Hackensack, NJ). A sample of 30 g of flour or starch (dry basis) was placed in a Waring blender containing 360 ml of buffer solution, pH 5.30–5.35. Buffer was prepared using AACC approved method 22-10 (AACC 1983). To this, 3.6 g (0.8%, v/v) of carboxymethylcellulose was added and mixed into a slurry on low speed to avoid foaming. The carboxymethylcellulose was used to increase the sensitivity to swelling of starch granules (Tipples 1980). The slurry was poured into the amylograph cup, and the blender bowl was rinsed with an additional 100 ml of the buffer solution that was then poured into the cup. The Brabender amylograph was run at 75 rpm, and viscosity was measured in Brabender units by heating the starch slurry from 50 to 95°C at a rate of 1.5°C/min. (The Brabender amylograph does not measure true viscosity nor an apparent viscosity; it gives only a numerical value related to an apparent viscosity. "Viscosity" is used in the text in lieu of any appropriate term.) The slurry was held for 30 min at 95°C, cooled to 50°C at the same rate, and then held for 30 min at 50°C.

Endotherms

The endotherms of flour, commercial corn starch, and alkali starches were obtained for a temperature range of 55–145°C at a scan rate of 16°C/min using a differential scanning calorimeter (Perkin Elmer DSC 1, Norwalk, CT). DSC pans (for volatile samples) were used to seal 10–20 mg of starch suspension (starch-water ratio = 1:2), and an empty pan was used as a reference. The endotherms were analyzed to obtain data according to the method of Wootton and Bamunuarachchi (1979).

X-Ray Diffraction Patterns

The X-ray diffraction patterns of the starch samples were monitored by X-ray crystallography in a Rigaku D-Max X-ray diffractometer (Rigaku, Danvers, MA) equipped with a monochromator that selects the radiation from a copper target generated under 45 kV and 20 mA. Before analysis with a diffraction angle (2 θ) from 5 to 45° at a scan speed of 8°/min, the starch samples were equilibrated for 12 hr over a saturated potassium nitrate solution (water activity, 0.93) at room temperature.

Birefringence

A 1% starch suspension prepared in distilled water was observed at $\times 40$ magnification under a bright field microscope (Nikon Instruments, Melville, NY) equipped with polarizer and analyzer lenses. All of the samples were observed for polarization crosses, and the entire slide was scanned to monitor the crosses. The purpose of scanning was to look for granules not showing crosses

because of alkali gelatinization of granules. Some granules that did not show a polarization cross were ruled out as mechanically damaged because of milling. This was confirmed by staining the granules with Congo red dye, in which only the damaged granules picked up the red dye (S. A. Watson, *personal communication*).

Vapor Sorption Isotherms

Dried starch samples were equilibrated against 11 saturated salt solutions at 25°C (Stokes and Robinson 1949, Greenspan 1977) to obtain a sorption isotherm over the water activity range of 0.33–0.97. This was performed in proximity equilibration chambers (Lang et al 1981) that were modified by placing a weighing bottle containing the sample in a well in the middle of the saturated salt solution. Equilibration moisture content was determined from the weight gain by the sample. Duplicate determinations were made and, since there was low deviation (standard deviation was <0.1%, $P < 0.05$) from the means, only averages are presented.

Scanning Electron Microphotographs

The morphology of the flour, commercial starch, and selected alkali starches was examined using a scanning electron microscope (ISI-DS-130, International Scientific, Inc., Livonia, MI) according to the procedure of Aguilera et al (1980). The mounted samples were observed in the lower stage using an accelerating voltage of 12 kV and 30° stage tilt.

Enzymatic Hydrolysis

Commercial starch and alkali starch no. 4 were hydrolyzed using α -amylase and glucoamylase enzymes (Genencor International, Chicago, IL). The maltose and glucose production were monitored using high-performance liquid chromatography (HPLC). A 20% starch suspension (w/w, dry basis) was prepared in distilled water, and the pH was adjusted to 6.0 using hydrochloric acid or calcium hydroxide. The suspension was liquified by adding α -amylase at the rate of 0.1 ml/100 g of dry starch and holding it for 30 min in a 90–95°C water bath. The liquefaction step was performed only as a method of preparing the raw corn starch powder for the saccharification reaction. Other than the monitoring of glucose and maltose, there was no attempt to optimize and study the hydrolysis process and the hydrolysate. The liquified starch was cooled, and pH was adjusted to 4.35. Glucoamylase was added at the rate 0.1 ml/100 g of dry starch, and the suspension was placed in a water bath at 60°C for saccharification. Samples were drawn every 2 hr until 6 hr of saccharification and then at 12 and 48 hr. Samples then were filtered through Whatman no. 1 paper, and a 1:10 dilution was prepared using deionized distilled water. The diluted samples were stored in the freezer until they were analyzed in the high-performance liquid chromatograph.

HPLC was used to analyze the products of the hydrolysis using a Dionex system (Sunnyvale, CA). The system was equipped with a Dionex CarboPac PA-1 column (4 \times 250 mm) with anion exchange resin. Detection was performed using a pulsed amperometric detector equipped with a gold working electrode having

TABLE II
Linear Gradient for Starch Hydrolysate Analysis

Time (min)	Mobile Phase, ^a %		
	1	2	3
0	100	0	0
5	80	20	0
25	46	54	0
35	30	70	0
37–40	0	100	0
40–42	0	0	100
42–50	100	0	0

^a Flow rate of 1 ml/min. Mobile phase 1, 150 mM NaOH; mobile phase 2, 150 mM NaOH with 0.5M sodium acetate; mobile phase 3, 1.0M NaOH.

an output range of 3,000 nA. Separation of the hydrolysate was performed at a flow rate of 1 ml/min using 150 mM NaOH as mobile phase 1, 150 mM NaOH containing 0.5M sodium acetate as mobile phase 2, and 1.0M NaOH as mobile phase 3. The optimum separation and retention time accuracy was obtained using a linear gradient as shown in Table II.

After the diluted samples were filtered through 0.22- μ m membrane GS-type filters (Millipore Corp., Bedford, MA), they were injected into the column. The column was equilibrated at initial conditions for 30 min between each injection. A Spectra-Physics SP 4290 integrator (Spectra-Physics, San Jose, CA) was used to record and integrate the area of each peak. External carbohydrate standards (Sigma Chemical Co., St. Louis, MO) were employed for identification and quantification of maltose and glucose peaks using retention time and peak area. The concentration of glucose and maltose (in milligrams per liter) in the experimental samples was calculated on the basis of the area of the external standard in the HPLC analysis and also on the dilution factor of the injected sample.

Analysis

The test data were statistically analyzed to determine the least significant difference between the extraction conditions and the commercial starch at a 5% significance level. Corn flour also was analyzed for similar characteristics for comparison. Flour data were not included in the statistical analysis because flour and starches are completely different products.

RESULTS AND DISCUSSION

The protein contents of most of the alkali starches (Table I) were significantly different from each other and from that of the commercial starch. Starches 1 and 7 had relatively high protein contents. The lower levels of the extraction conditions used for starch 1 did not completely disperse the protein in the flour. This resulted in poor separation of starch and protein, leaving more protein with the starch. The high levels of extraction conditions used for starch 7 resulted in increased viscosity of the steeped flour slurry. This caused difficulties in starch separation, and thus more protein settled with the starch. Starch extracted at low alkali concentration and high temperature had the lowest protein contents (starches 3 and 4). However, at high alkali concentration, it was the opposite. Higher extraction time, alkali concentration, and temperature (starches 2, 6, and 8) had no significant effect on the protein content.

All alkali starches had significantly higher sodium content than that of the flour and the commercial starch (Table I). Low alkali-extracted starches had almost twice the sodium content of commercial starch, whereas the high alkali-extracted starches were

about four to six times higher in sodium content. Lancaster and Conway (1968) indicated that absorption of alkali by starch was a function of alkali concentration in the solution. At low alkali concentrations, the extraction temperature and time had no significant effect on the sodium content of the alkali-extracted starches. However, starches extracted at high alkali concentration (starches 5–8, Table I) had significantly different sodium contents.

Amylograms

The amylograph data (Table III) indicated that the initial pasting temperatures of all alkali starches, except starch 1, were significantly lower than those of the flour and the commercial starch. All extraction conditions used had no significant effect on the pasting temperature of most of the starches. The alkali extraction process slightly lowered the initial pasting temperature of extracted starches. These findings corresponded with the results of the study by Anker and Geddes (1944) on the effect of chemical gelatinizing agents on amylograph viscosity curves of wheat starch. The reagents they used (including NaI and NaSCN) caused a decrease in the pasting temperature and an increase in maximum viscosity. They attributed this effect to the anions of the reagents (I^- and SCN^-) associated with the starch in dilute solutions. Within a Hofmeister or lyotropic series of anions, the effect of the hydroxyl (OH^-) ion was found to be maximum, i.e., gave the highest viscosity of starch suspension, among the concentration-viscosity characteristics of starches (Mangels and Bailey 1933).

The peak height of alkali starches 3 and 4 was significantly higher than that of flour and commercial starch (Table III). Low-temperature extracted starches, in general, had lower peak height than that of high-temperature extracted starches. The extraction time had no significant effect on the peak height. The peak temperature for all samples occurred at 95°C. However, all of the alkali starches (except starch 8) reached the peak 3 min after the temperature first reached 95°C. Thus, the alkali starches had sustained viscosity longer than the commercial starch. The viscosity of alkali starches after 15 min of holding at 95°C was much higher than that of both flour and commercial starch. The setback of the heated alkali starch paste extracted at low alkali concentration was higher than that of commercial starch and generally lower than that of starch extracted at a higher alkali concentration. The setback results indicated that the cooled paste viscosity of some alkali starches was more than that of the commercial starch. Thus, in other words, alkali starch had very little granular structure failure compared with that of commercial starch. Extraction time had no significant effect on the setback of starches extracted at low alkali concentration. However, the effect was mixed for high alkali-extracted starches.

The amylograph curve for commercial starch (Fig. 1C) indicated

TABLE III
Amylograph Data^a of Flour, Commercial Starch, and Alkali-Extracted Starches

Sample Identification	Initial Pasting Temperature ^b (°C)	Peak Height ^c (BU)	Peak Temperature ^d (°C)	15-Min Height ^e (BU)	Setback ^f (BU)
Flour	71.00	240	95 (3.5)	230	245
Commercial starch	70.25 b	512 b–d	95 a (1.5)	365 h	325 c
Starch 1	71.00 a	555 b	95 a (3.5)	515 f	465 a
2	69.50 c	570 b	95 a (3.5)	542 e	470 a
3	69.50 c	637 a	95 a (3.0)	605 c	435 b
4	69.50 c	640 a	95 a (3.0)	630 b	425 b
5	68.75 d	470 c–e	95 a (3.0)	605 c	230 e
6	69.00 cd	450 de	95 a (3.0)	565 d	255 d
7	69.00 cd	535 bc	95 a (3.0)	675 a	275 d
8	69.50 c	415 e	95 a (1.5)	425 g	335 c

^aEach value represents the mean of two replicates. Mean comparisons followed by the same letter are not significantly different ($P < 0.05$) within the same column.

^bTemperature at which the initial rise in curve reached 10 BU; LSD = 0.66.

^cViscosity at the peak; LSD = 66.

^dAfter temperature first reached 95°C. Values in parentheses indicate time (in minutes) that sample maintained peak temperature.

^ePeak height after holding 15 min at 95°C; LSD = 16.

^fDifference in BU between 15-min height and height after cooling to 50°C; LSD = 25.

a normal pattern and was comparable to literature profiles (Medcalf and Gilles 1966, Tipples 1980). The viscosity of commercial starch decreased upon holding at 95°C because of the breakdown of gelatinized starch granules and dispersion of amylose, which is called shear-thinning (Rasper 1980). Some alkali starches (Fig. 2, starches 5–7) showed less shear-thinning than commercial starch. Instead, the viscosity of alkali starch paste continued to increase after the holding and cooling cycles. The presence of sodium and/or hydroxyl ions in the alkali starch may have helped to strengthen the bonding forces within the granules. This may have prevented physical breakdown of granules, which results in increased viscosity of starch even after 30 min of holding at 95°C. The increased viscosity at a higher temperature and the occurrence of a short broad peak in the holding cycle for alkali starches could be due to the presence of absorbed sodium hydroxide in the starch granules that causes granule swelling (Lancaster and Conway 1968). It was speculated in an earlier study (Mangels and Bailey 1933) that increased viscosity of starches in alkali suspensions is because of jostling of granules.

The effect of sodium hydroxide on amylograph characteristics of corn starch was similar to the effect caused by various salts of Na⁺ and K⁺ ions on corn starch amylograms (Medcalf and Gilles 1966). Ganz (1965), in a study on the effect of sodium chloride on the pasting of wheat starch, found that salt increases and regulates the swelling of starch granules. The increase was believed to be due to an enhanced maintenance of granule integrity. That is, the granule swells to a greater extent or remains intact for a longer time before fragmentation occurs.

Starches extracted at low alkali concentration (Fig. 1, starches 1–4) showed higher viscosity at 95°C than those extracted at a higher alkali concentration (Fig. 2, starches 5–8). Similar differences in viscosity also were observed during the cooling cycle. Although starch suspensions were prepared in a buffer solution

at pH 5.30–5.35 before amylogram determinations, the increase in viscosity of alkali starches at a higher heating temperature could be due to the absorbed alkali and not to the pH. Also, increased swelling and, thus, increased viscosity of alkali starches could be because of the anions (OH⁻) associated at the specific sites in the starch, where anions create a larger hydration sphere (Medcalf and Gilles 1966).

The amylogram pattern of the alkali starches obtained here was very similar to amylograms of some cross-bonded starches found earlier by Medcalf and Gilles (1966). Cross bonding of starch reduces significantly the ability of the starch to swell and consequently prevents the decrease in viscosity because of the breakdown of highly swollen granules (Leach et al 1959). This enhances the stability of the paste at increased viscosity at the peak, as found when wheat starch was suspended in an alkali solution.

Endotherms

The DSC data (Table IV) obtained by the analysis of the endotherms indicated that the peak temperature of the low alkali-extracted starches was similar to that of the commercial starch. The peak temperatures for high alkali-extracted starches were significantly higher than those of commercial starch. The gelatinization temperature increased with increasing alkali concentration. Starches extracted at the lower temperature (starches 1 and 2, Table IV) had lower onset temperatures than those of high-temperature extracted starches (starches 3 and 4). This supports the granule integrity and stabilizes and regulates the swelling during amylogram determination. The heat of gelatinization of all of the alkali starches was not significantly different from that of the commercial starch (Table IV).

The endotherm of the commercial starch (Fig. 3C) corresponded closely with those found in literature (Stevens and Elton 1971). The gelatinization peaks of the alkali starches 1 and 2 (Fig. 3) were similar to the flour peak but slightly shorter and broader than the peak of commercial starch (Fig. 3), indicating that gelatinization occurred over a broader temperature range. Wootton and Bamunuarachchi (1978) found that substituted starches caused broadening of the shape of the gelatinization endotherm. It is possible that the alkali extraction process and sorption of alkali by the starch, particularly those extracted at low concentration and temperature (starches 1 and 2), may have caused changes similar to those in substituted starches. This correlates well with the amylograph results.

Starches 3 and 4 (Fig. 3) showed shape and curve patterns similar to those of commercial starch. The noticeable difference was in the gelatinization peak of the starches extracted at the high temperature (starches 3 and 4), which was sharper than that

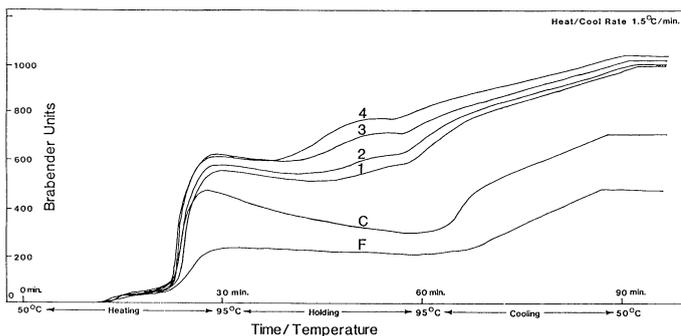


Fig. 1. Amylogram of flour (F), commercial starch (C), and alkali starches (1–4) obtained using a complete cycle of heating, holding, and cooling. The alkali starches were extracted at low alkali concentration. A duplicate extraction had the same curve profile.

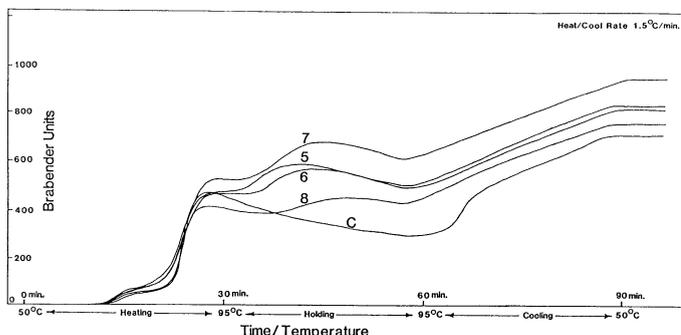


Fig. 2. Amylogram of commercial starch (C) and alkali starches (5–8) obtained using a complete cycle of heating, holding, and cooling. The alkali starches were extracted at high alkali concentration. A duplicate extraction had the same curve profile.

TABLE IV
Differential Scanning Calorimeter Data^a of Corn Flour, Commercial Starch, and Alkali-Extracted Starches

Sample Identification	Peak Temperature ^b (°C)	Onset of Gelatinization ^c (°C)	Endothermic Heat to Gelatinize Starch ^d (Cal/g)
Flour	72.37	69.07	2.57
Commercial starch	72.89 b	68.90 b	3.26 a
Starch 1	72.40 b	64.82 d	2.88 a
2	72.33 b	65.10 d	3.14 a
3	72.41 b	68.17 c	3.14 a
4	72.79 b	68.98 b	3.09 a
5	74.99 a	69.14 b	2.65 a
6	74.55 a	68.86 b	2.72 a
7	74.86 a	71.47 a	3.06 a
8	74.72 a	71.72 a	3.54 a

^a Each value represents the mean of two replicates. Mean comparisons followed by the same letter are not significantly different ($P < 0.05$) within the same column.

^b LSD = 0.77.

^c LSD = 0.64.

^d LSD = 0.93.

extracted at low temperature (starches 1 and 2). Starch heated above 50°C in excess water causes annealing, which results in an increase in onset temperature, a narrowing of the gelatinization range, and a tendency toward increased gelatinization enthalpy (Krueger et al 1987). The endotherm changes observed for high-temperature extracted starches are due more to annealing at 55°C than to any effect of sodium hydroxide.

The endotherms of the starches extracted at high alkali concentrations (Fig. 3, starches 5–8) were unusual and unexpected. An exothermic peak was observed between temperatures of 100–145°C. This indicated that heat was released during the heating of the starch beyond the gelatinization temperature. It is difficult to suggest any concise and reasonable explanation for this behavior, but on the basis of the information found in this study it is suspected that the release of sodium ions from the granules and/or the oxidation of starch fragments may play a role. Earlier studies have suggested that the absorption of sodium hydroxide by starch is an exothermic process (DeWillingen and DeGroot 1971). This implies that at higher temperatures less sodium hydroxide is absorbed. This agrees with the results in Table I that the sodium contents of starches extracted using high alkali concentration and high temperature (starches 7 and 8) were lower than those extracted using high alkali concentration and low temperatures (starches 5 and 6). It was beyond the scope of the present investigation to rationalize the exothermic peak.

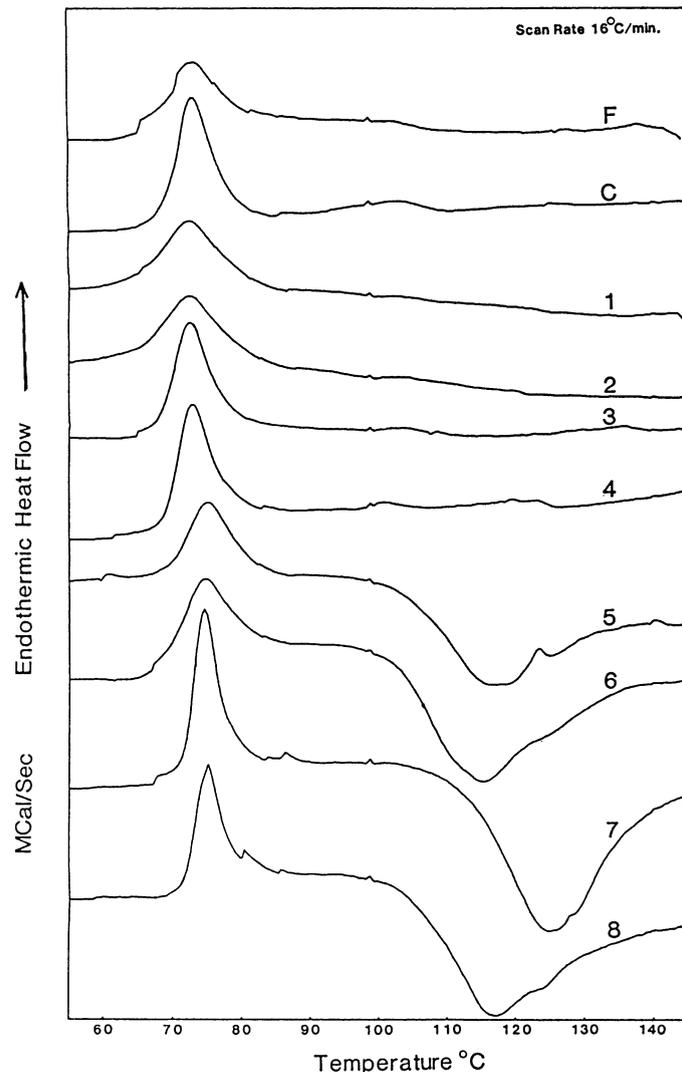


Fig. 3. Endotherm of flour (F), commercial starch (C), and alkali starches (1–8) obtained in a differential scanning calorimeter using 1:2 starch-water suspension for a temperature range of 55–145°C. The replicate endotherm had the same curve profile.

The gelatinization peak of starches 5–8 was correspondingly similar to that of alkali starches 1–4, but the peaks were sharper for starches 7 and 8. Extraction time (30 or 90 min) had no significant effect on the endotherm characteristics of alkali starches.

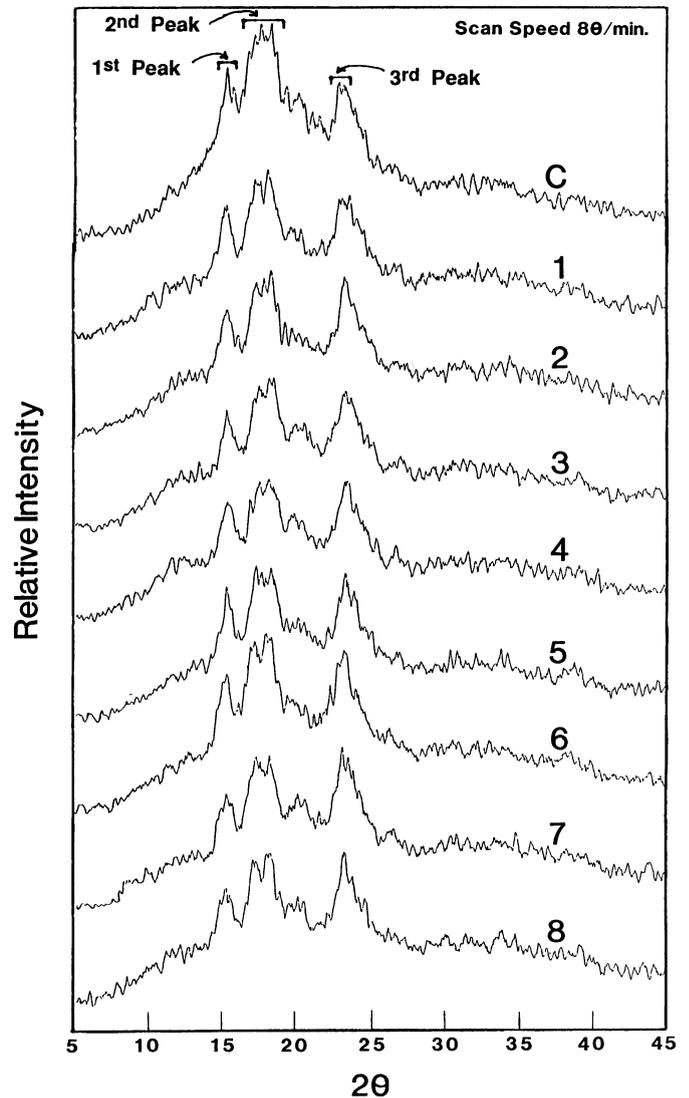


Fig. 4. The X-ray diffraction pattern of commercial starch (C) and alkali starches (1–8) with relative intensities. The duplicate samples had the same X-ray patterns.

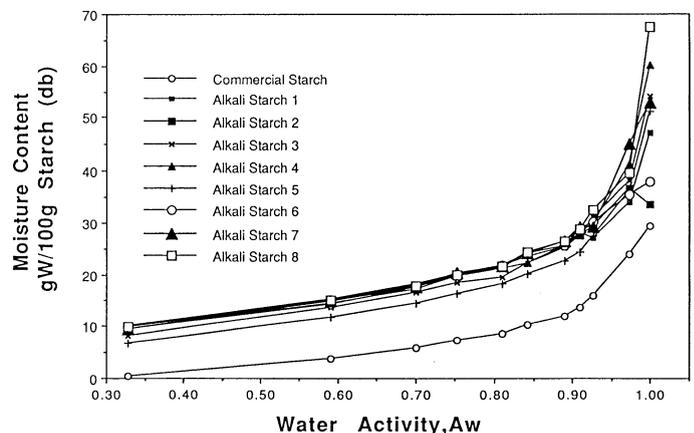


Fig. 5. Vapor sorption isotherms of commercial starch and alkali starches obtained using salt solutions at 25°C.

X-Ray Diffraction Patterns

The X-ray diffraction pattern of the commercial starch (Fig. 4C) was similar to that found in the literature (Hoseney 1986). The typical A-type pattern indicated that the starch was in its native state and was of cereal origin. The distinct peaks demonstrated the crystalline nature of the starch granules. The X-ray pattern of alkali starches (Fig. 4, 1-8) showed a similar A-type pattern with distinct peaks, indicating that the alkali extraction process did not alter the characteristic A-type pattern and that the starch granules still possessed the crystalline nature similar to that of commercial starch. There was some minor but noticeable difference in the peaks of the starches extracted at high alkali concentrations (starches 5-8). The third peak was taller than the peaks of commercial starch and alkali starches 1-4. The second peak was shorter for starches 5-8. This indicated a slight superimposition of a V-type pattern over the A type. An earlier study (Montgomery and Senti 1958) showed that granular starches, when heated in an aqueous solution of polar organic solvents, showed the V-type pattern superimposed on either A- or B-type patterns. The extraction time and temperature had no noticeable effect on the diffraction pattern of alkali starches.

Birefringence

All alkali starches showed characteristic polarization (maltese) crosses under polarized light similar to those observed for the native commercial starch. This suggested that the alkali extraction process and/or absorption of sodium ion did not gelatinize the starch granule. Extraction of starch at higher alkali concentrations and/or higher temperature has been found to gelatinize the starch granules (Dimler et al 1944). However, the level of alkali concentration (0.1 and 0.4%) and the temperature (25 and 55°C) used in this study to extract starch from corn flour did not gelatinize the starch. This was evident by the presence of birefringence and of X-ray peaks on the alkali starches.

Vapor Sorption Isotherms

The isotherms of all of the alkali starches (Fig. 5) were similar in curve characteristics to those of commercial starch and to those found in literature for native starches. However, the isotherms of all alkali starches were above the isotherm of commercial starch. There was no significant difference among the isotherms of the alkali starches. The alkali starches showed increased vapor sorption at a given water activity and room temperature. This finding corresponded with the results from the amylograph: alkali increases swelling and hydration of starch granules. This increase in hygroscopic properties appears to be due to the formation of a complex between starch and sodium ions. Sorption studies on freeze-dried mixtures of sodium chloride and starch (Chinachoti and Steinberg 1985) indicated that sodium chloride interacts with the starch and that the resulting complex absorbs

more moisture than starch or sodium chloride alone. Sodium content level did not influence the vapor sorption behavior of the alkali starches.

The increased vapor sorption by alkali starches could have tremendous beneficial implications on food product and process development and on the characteristics and stability of a product. The results obtained in this study implied that at a given water activity level, alkali starch had a higher moisture content than that of the commercial starch. Conversely, at a given moisture content, alkali starch exhibited lower water activity than the commercial starch. For example, at 10% moisture content, low alkali-extracted starches had water activity of approximately 0.33, whereas the commercial starch at the same moisture content had water activity of 0.81 (Fig. 5). Alkali-extracted starch can be a potential ingredient in combination with other ingredients in a product formulation to help lower the water activity. Low water activity of a food system increases the shelf life and product stability.

Scanning Electron Microphotographs

The microphotograph of corn flour showed (Fig. 6) starch granules with protein attached to the surface of the granules. Spherical small bright entities are the zein protein bodies. The glutelin, which is the structural protein, encloses the starch granules into a matrix arrangement (Watson 1987). In the case of flour, this matrix is partially disintegrated because of the mechanical shear during milling. However, some matrix arrangement along with granules was seen in the upper left corner

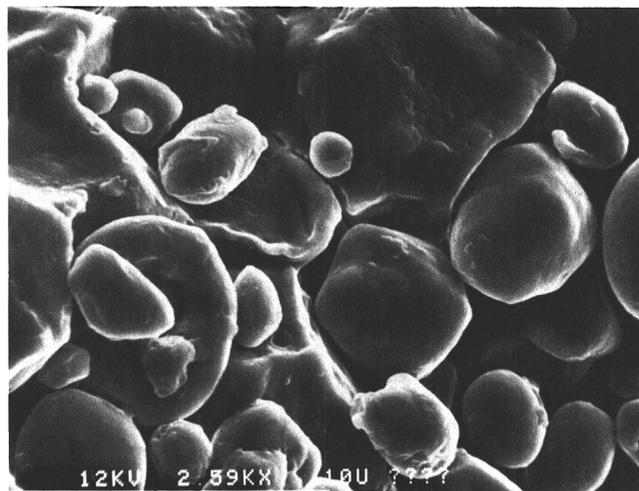


Fig. 6. Scanning electron microphotograph of corn flour.

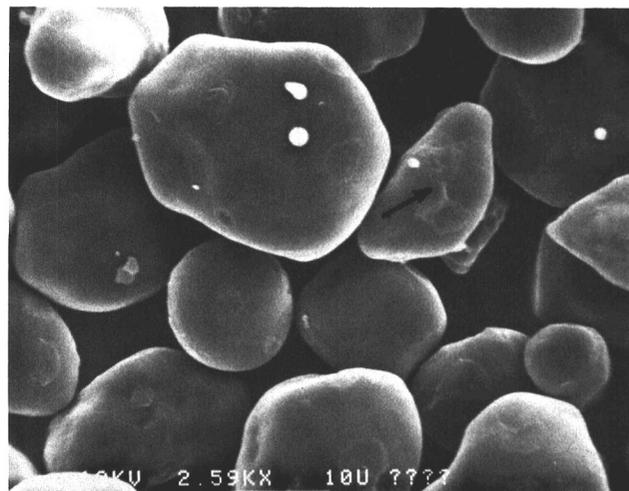


Fig. 7. Scanning electron microphotograph of commercial starch.

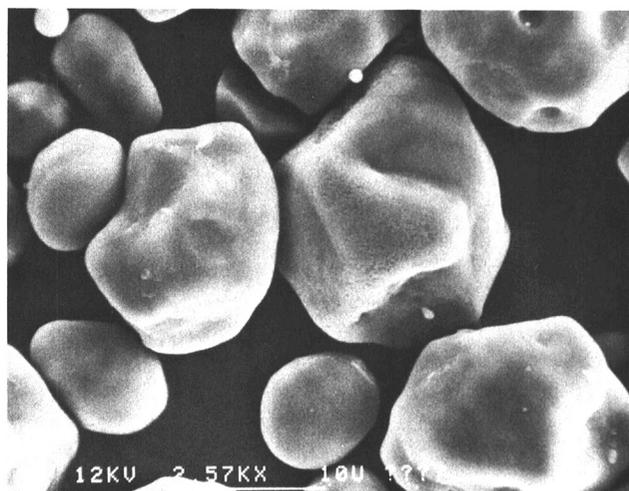


Fig. 8. Scanning electron microphotograph of alkali starch 4.

of the photograph (Fig. 6). Some free granules also were seen in the lower right corner of the photograph.

The commercial starch (Fig. 7) showed isolated starch granules free of adhering protein structures. Because the commercial starch had 0.35% protein content, some protein that was adhered to the granule was seen in the form of white patches on the surface of the starch granule (arrow in Fig. 7) in this particular scan of the sample.

The microphotograph of the alkali starch 4 (Fig. 8) showed similar distinct isolated granules as found in the commercial sample. The granules were free of any attached protein matrix. Starches 1 and 8 showed some protein attached to the surface of the granule because of the higher protein content (0.74 and 0.55%, respectively) of those starches than of the commercial starch and alkali starch 4. This was due to the difficulties in the separation of starch from viscous flour slurry obtained at a high alkali concentration, high temperature, and longer steep time. The shape and surface characteristics of the alkali starch granules looked very similar to those of the commercial starch granules. Thus the alkali extraction process and the absorbed sodium did not change the shape and surface characteristics of the starch granules, and starch granules free of any adhering protein substances were able to be obtained.

Enzymatic Hydrolysis

The concentration of maltose produced from alkali starch (Fig. 9) was significantly lower than that of commercial starch. However, the production pattern of glucose (Fig. 10) indicated no significant difference in the concentrations of glucose throughout the hydrolysis process for both commercial and alkali starches, except at 48 hr of saccharification, when the alkali starch produced significantly more glucose than the commercial starch. Thus, even though the initial concentration of maltose was low for alkali

starch compared with commercial starch, the production of glucose was not affected. This indicates either that the activity of glucoamylase was enhanced in the case of alkali starch or that the maltose produced from alkali starch was converted into glucose at a faster rate than that from commercial starch.

CONCLUSIONS

The protein content of most of the alkali-extracted starches was significantly different from that of commercially purified corn starch. The starches extracted at low alkali concentrations and high temperature had the lowest protein contents. At high alkali concentrations, temperature and time had no significant effect on the protein content of the starches. However, the sodium content was much higher than that of the commercial starch. Low alkali-extracted starches had almost twice the sodium content and high alkali-extracted starches had about four to six times the sodium content of commercial starch. All alkali starches had low initial pasting temperature, high peak viscosity, and little shear-thinning, indicating higher starch swelling and maintenance of granular integrity for a longer time before fragmentation occurs. Low alkali-extracted starches had higher setback viscosity than that of commercial starch, indicating high stability of the cooled starch pastes. Extraction time, in general, had no significant effect on the amylograph properties of the alkali starches. The DSC data indicated that the higher the absorbed sodium, the higher the gelatinization temperature. The endothermic heat required to gelatinize starch was similar for all the starches. The X-ray diffraction patterns of all alkali starches were similar in shape and characteristics to those of commercial starch. The DSC and X-ray profiles of starches extracted at higher alkali concentrations showed similarities with substituted and/or cross-linked starches. All of the alkali starches absorbed higher moisture than the commercial starch at a given water activity. The isotherm results supported the amylograph data, i.e., higher swelling and hydration by alkali starches. The microphotographs and enzymatic hydrolysis characteristics of alkali starch 4 were similar to those of the commercial starch. Thus, the alkali extraction process used to extract starch from corn flour can result in starch with a low protein content, high viscosity, high hydration capacity, and more heat and shear stability than the commercial corn starch. The alkali-extracted starch also can have X-ray, birefringence, morphology, and enzymatic hydrolysis characteristics similar to those of commercial starch.

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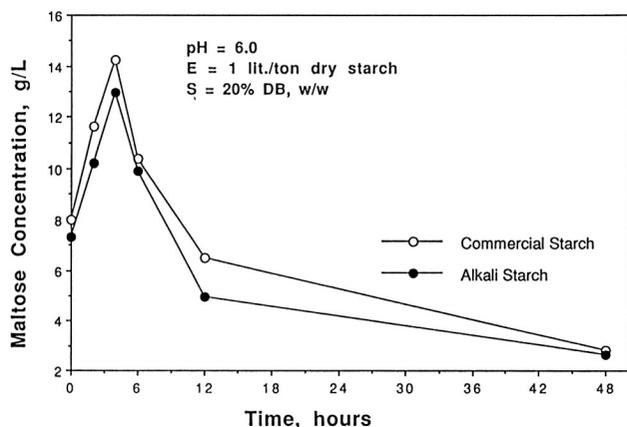


Fig. 9. Concentration of maltose of liquified commercial starch and alkali starch 4 at each time interval until 48 hr of saccharification.

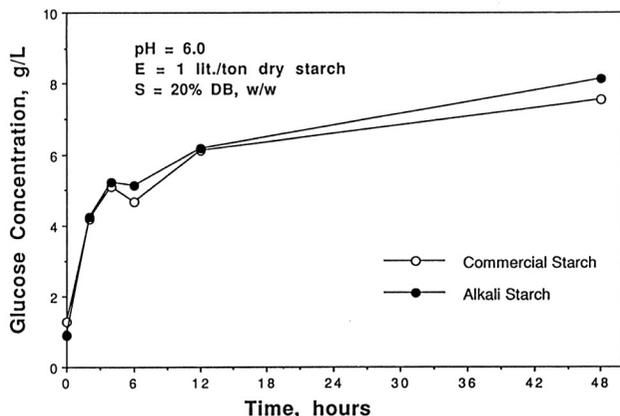


Fig. 10. Concentration of glucose of liquified commercial starch and alkali starch 4 at each time interval until 48 hr of saccharification.

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