Modification of Corn Fiber Through Chemical Treatments in Combination with Twin-Screw Extrusion

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ABSTRACT

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Corn fiber modification was achieved through acid, alkaline, and consecutive acid-alkaline treatments in combination with simultaneous thermal treatment. Twin-screw extrusion of the modified corn fiber was conducted to achieve additional fiber solubilization. A comparative study was performed on the functional properties of native and chemically modified corn fiber with and without extrusion. Soluble fiber content increased after chemical treatments alone or in combination with twin-screw extrusion. Consecutive acid-alkaline treatment most effectively increased the solubility of corn fiber. X-ray diffraction and scanning electron microscopy revealed altered fiber crystallinity and intermolecular structure after chemical and extrusion treatments.

Soluble fiber has been reported to reduce elevated blood cholesterol, triglyceride, and glucose levels (Anderson, 1986). Peas, beans, fruits, and vegetables are good sources of soluble fiber, whereas most grain-based foods are not. In food, soluble dietary fiber can affect texture, gelling, thickening, and emulsifying properties. Insoluble fiber functions as a water-holding-capacity agent, which can reduce intestinal transit time when present in adequate amounts in food. A wide variety of fiber-enriched foods has been introduced in the past few years, including high-fiber bread, cakes, ready-to-eat breakfast cereals, and expanded snack foods. Although corn bran is a low-cost, food-grade cereal fiber source, its use as an ingredient in foods has been relatively unsatisfactory due to its poor functionality. Therefore, the need for the modification of the functional characteristics of cereal brans before their incorporation into foods is evident.

Extrusion cooking has been considered an alternate approach by which to modify the functionality of dietary fiber. Björck et al (1984) reported that a significant increase in soluble fiber content could be achieved during extrusion of wheat flour. Fulger and Bradbury (1985) pointed out that the functional properties of corn bran were improved by applying high temperature and high shear during extrusion. Artz et al (1990) investigated the effect of extrusion processing on the functional properties of various corn fiber and corn starch formulations. Maximum interaction between corn fiber and corn starch was observed at a 50% fiber concentration, while high temperature, intermediate shear, and intermediate residence time were maintained. However, no significant changes in the ratio of soluble to insoluble fiber were found upon extrusion. Moreover, there was no evidence that the inclusion of starch enhanced the modification of corn fiber. Although extrusion was done at severe processing conditions, the residence time of the corn fiber as it passed through the extruder was apparently not long enough to allow severe chemical changes, particularly considering that corn fiber is a material very resistant to modification.

Chemical hydrolysis is another approach for dietary fiber modification. Sulfuric acid and trifluoroacetic acid have been used to hydrolyze hemicellulose (Englyst and Cummings, 1984). Olson et al (1988) reported that acid hydrolysis of cereal brans produced a series of monosaccharides, which resulted in increased nutritional availability and fermentability of the dietary fiber due to increased fiber solubility. In general, more significant modification of the corn fiber may be obtained by using chemical pretreatments in combination with twin-screw extrusion.

MATERIALS AND METHODS

Materials

A dry-milled corn bran isolate containing 4.5% moisture, 8.5% protein, 4.1% free sugar, 10.4% starch, 16.6% cellulose, 55.7% hemicellulose, and a total of 0.2% lignin and ash was donated by the Lauhoff Grain Company (Danville, IL). Reagent grade HCl and NaOH were used to prepare acid and alkaline solutions.

Chemical Treatments

A mixture of corn fiber and water, at a ratio of 1:5 was adjusted to specific acidic pH values (pH 2.0–4.0) with 6.0*N* HCl (acid treatment) and to specific alkaline pH values (pH 9.0–11.0) with 6.0*N* NaOH (alkaline treatment). The mixtures were then heated at 90°C for different periods of time ranging from 1 to 4 hr. At the end of each treatment, the supernatant was removed, neutralized, and then centrifuged at 700 × *g* for 10 min. Pentose and hexose contents were measured for the acid treatment using high-performance liquid chromatography according to the procedure of Folkes and Taylor (1982). Total sugar content was determined for the alkaline treatment according to the method described by Dubois et al (1956). The precipitate was washed with water and dried using an air drier (Proctor Schwartz, Philadelphia, PA) at 75°C for 2 hr, followed by grinding and screening through a 2-mm sieve. The acid-alkaline treatment involved consecutive acid and alkaline treatments, according to the aforementioned procedures. For the acidic treatment, the mixture was adjusted to pH 2.0 with 6.0*N* HCl, while for the alkaline treatment, the mixture was adjusted to pH 11.0 with 6.0*N* NaOH.

Extrusion of Native and Chemically Modified Corn Fiber

Native, and acid- and alkaline-treated corn fibers were extruded using a ZSK-30 twin-screw extruder (Werner & Pfleiderer Corp., Ramsey, NJ). Conditions for extrusion were selected according to preliminary work to ensure conditions suitable for bran modification. The barrel temperatures of the first two sections were maintained at 40 and 90°C, and the remaining three sections were held at 120°C. Extrusion was carried out at 50% moisture and a dry feed rate of 200 g/min. The screw speed used was 350 rpm, with a screw configuration as shown in Figure 1. A

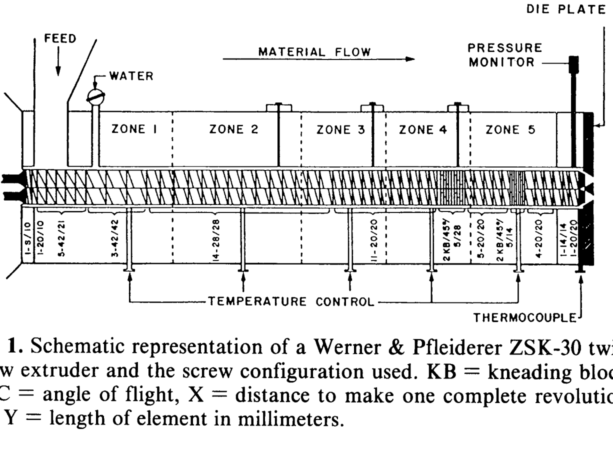

Fig. 1. Schematic representation of a Werner & Pfleiderer ZSK-30 twin-screw extruder and the screw configuration used. KB = kneading block, 45°C = angle of flight, X = distance to make one complete revolution, and Y = length of element in millimeters.

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dual-orifice die (3 mm in diameter) was used. The extrudate was gently dried in an air drier at room temperature for 24 hr, then ground and sieved.

Water-Holding Capacity

Water-holding capacity (WHC) was determined by mixing 2 g of sample with 25 ml of distilled water, agitating the mixture for 30 min at room temperature, and then centrifuging the sample at 10,000 × *g* for 30 min at 20°C. The liquid retained by the insoluble solids was determined and reported as WHC in milliliters of water retained per gram of extrudate.

Fiber Analysis

Soluble and insoluble fiber contents were determined for each sample by the procedure described by Asp et al (1983). The method of analysis involves the enzymatic removal of starch and protein.

Scanning Electron Microscopy

Dried, ground extrudate samples were mounted on a pin stub, coated with gold-palladium, and examined on the lower stage of an ISI-DS-130 scanning electron microscope with an accelerating voltage of 10 kV.

X-Ray Crystallography

X-ray crystallography of representative samples was done using a Rigaku/D MAX unit (Rigaku Denki Co., Ltd., Tokyo, Japan). Ground extrudates were mounted on glass slides using double-sided sticky tape. Conditions used for X-ray crystallography were 40 kV, 20 mA, 4 scanning speed, 7° start angle, 30° stop angle, and 0.02 step sampling.

RESULTS AND DISCUSSION

Scanning Electron Microscopy

The surface morphology of the native corn fiber was observed to be smooth and compact (Fig. 2a), whereas simply extruded corn fiber showed limited changes in surface structure and particle size as compared with the raw material (Fig. 2b). The acid-treated and alkaline-treated corn fibers appeared to have more open structures with a high degree of porosity (Fig. 2c and d, respectively). Extrusion of the modified corn fiber resulted in further disruption of the fiber structure, as indicated by an additional increase in surface porosity as well as a reduction in particle size (Fig. 3a and b). An extremely high degree of porosity in surface morphology and significantly reduced particle size were observed in the acid-alkaline treated corn fiber (Fig. 3c).

Water-Holding Capacity

A significant increase in WHC was observed for the acid-treated corn fiber as compared with the original raw fiber ($P = 0.05$) (Table I). A positive correlation existed between the WHC of acid-treated corn fiber and the pentose and hexose concentrations in the supernatant for each treatment. In addition, increasing the heating temperature and heating time and decreasing the pH in the medium all increased WHC and pentose and hexose concentrations (Table II). The modification of WHC by acid may be due mainly to the solubilization of the major components of corn fiber by hydrolysis. Cellulose and hemicellulose are the major components of the cell wall. Xylose (pentose) and arabinose (hexose) are the predominant monomeric residues that constitute hemicellulose in corn fiber (Asp and Johansson, 1984). The molecules of cellulose, a linear polymer with β-1,4-linked glucose units, are closely packed through hydrogen bonding, forming a highly ordered structure (Asp and Johansson, 1984). In the structure of corn fiber, hemicellulose and cellulose are associated with each other, forming a series of strong microfibrils. Olson et al (1988) reported that hydrolysis of hemicellulose in cereal brans with trifluoroacetic acid produced a series of pentoses and hexoses, such as glucose, rhamnose, arabinose, xylose, mannose, and galactose. Nikitin (1966) pointed out that most hemicelluloses

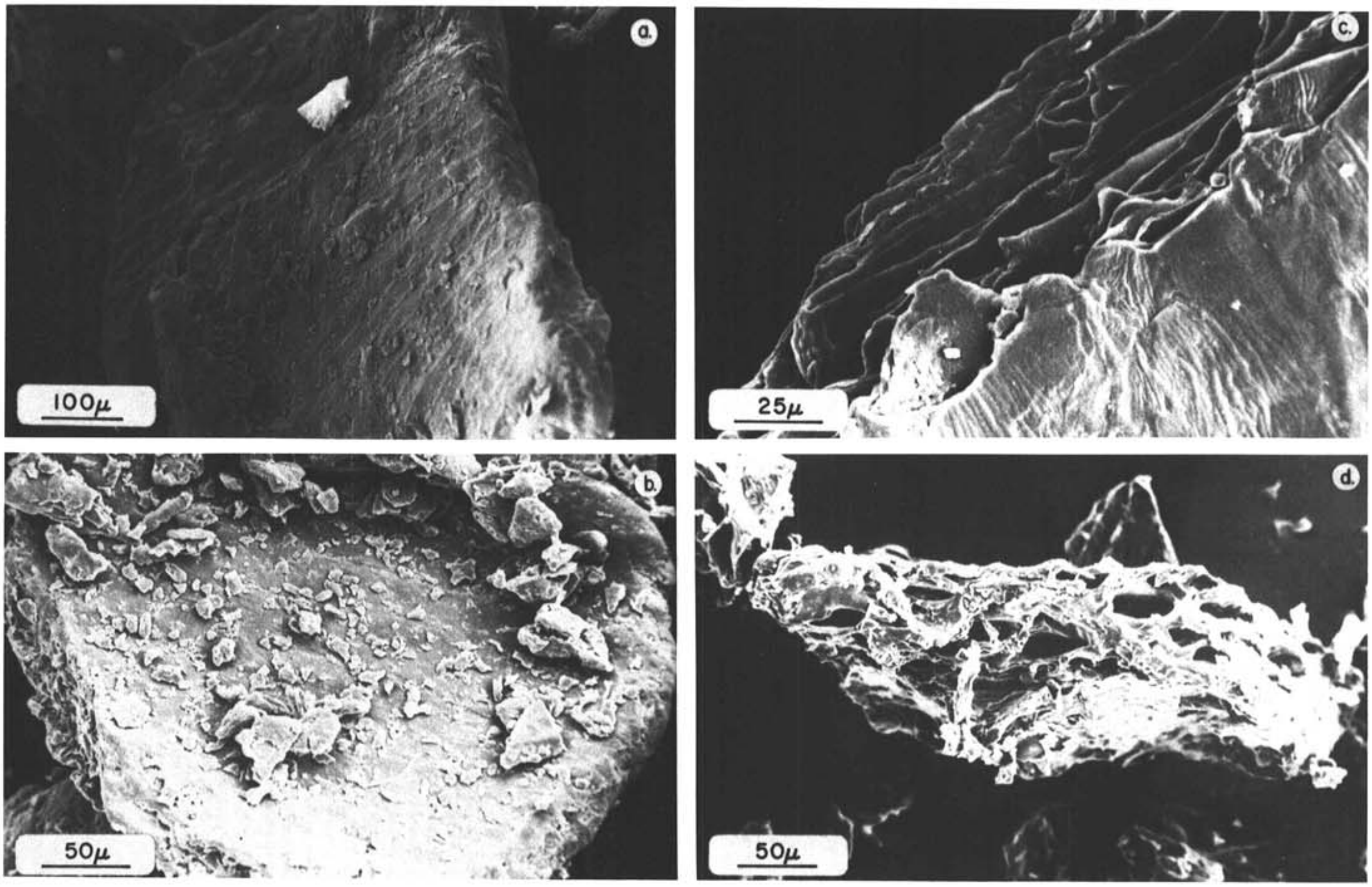

Fig. 2. Scanning electron micrographs of corn fiber. **a,** native; **b,** extruded; **c,** acid-treated; **d,** alkaline-treated.

in plant tissues were easily transformed to a partly hydrolyzed, water-soluble product through treatment with dilute acids at 100° C, whereas cellulose was only insignificantly affected under these conditions. Thus, the hydrolysis of cellulose requires more drastic conditions (high temperatures and/or acid concentrations). The tendency of hemicellulose to become easily hydrolyzed is explained by either its looser (amorphous) structure, or the low stability of the glucosidic bonds between pentose and hexose units. Therefore, under the conditions used in our study, pentoses and hexoses, as detected in the supernatant, are expected to originate primarily from the hydrolysis of hemicellulose. As a result, modification of the WHC of corn fiber by acid may be mainly due to the alteration of the hemicellulose fraction. The increased surface porosity may facilitate the penetration and absorption of water inside the fiber matrix. Since the rate of acid hydrolysis of hemicellulose and cellulose depends on heating temperature and acid concentration, any desired rate of hydrolysis may be easily attained. A rapid increase in the rate of acid hydrolysis of hemicellulose and cellulose was observed with increased temperature and acid concentration (Nikitin, 1966). Similar results were obtained in our study; the highest degree of hydrolysis occurred at the highest processing temperature (90° C), processing time (4 hr), and acid concentration (pH 2.0).

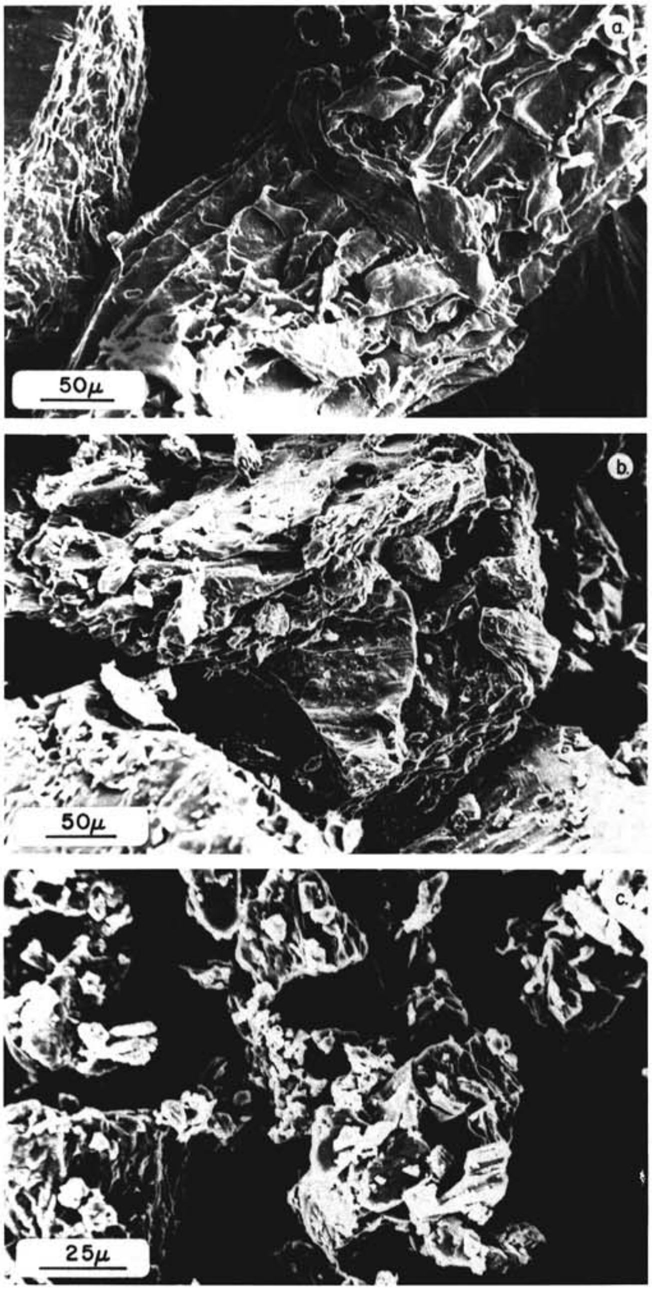

Fig. 3. Scanning electron micrographs of corn fiber. **a,** acid-treated and extruded; **b,** alkaline-treated and extruded; **c,** acid-alkaline-treated.

A significant increase in WHC was observed after alkaline treatment ($P = 0.05$) (Table I), although less dramatic than after acid treatment. A positive correlation existed between WHC and total sugar concentration in the supernatant. They both increased with an increase in heating temperature, heating time, and pH value of the medium (Table III). The modification of WHC may be partly due to the swelling of the physical structure of corn fiber by alkali, which leads to the formation of a more open structure. Nikitin (1966) stated that alkali swelling of cellulosic materials was associated with changes in the chain molecular flexibility and intermolecular interactions. The important factors influencing the degree of swelling are the absorption of alkali, the concentration, temperature, fiber structure, and the medium in which the swelling takes place. On the other hand, alkali catalyzes the interaction between plant tissue and water and facilitates the solubilization of hemicelluloses at elevated temperature. In our study, the optimum alkaline modification of corn fiber occurred at a temperature of 90° C, a heating time of 4 hr, and a pH value of 11.0 in the medium. The altered

TABLE I
Effect of Different Treatments on Water-Holding Capacity (WHC), Soluble Fiber Content, and Insoluble Fiber Content

Corn Fiber	WHC (g water/g)	Soluble fiber (%)	Insoluble Fiber (%)
Native	2.94	1.38	81.27
Extruded	2.56	1.39	74.22
Acid-treated	4.62	1.70	90.57
Acid-treated extruded	4.34	2.13	84.31
Alkaline-treated	3.64	3.36	77.02
Alkaline-treated-extruded	3.45	3.64	73.37
Alkaline-acid-treated	2.78	2.81	75.78
Acid-alkaline-treated	2.15	12.00	38.45
LSD ($\alpha = 0.05$)	0.51	0.30	2.27

TABLE II
Effect of Heating Temperature, Heating Time, and Acidic pH Value of the Medium on Water-Holding Capacity (WHC) and Pentose and Hexose Concentrations in the Supernatant

Temperature (°C)	pH	Heating Time (hr)	WHC (g water/g)	Pentose (mg/ml)	Hexose (mg/ml)
80	2	1	3.17	4.12	3.35
		2	3.41	8.30	3.76
		3	3.62	10.80	4.36
		4	3.70	10.90	4.60
	3	1	2.93	1.05	1.34
		2	2.97	1.60	1.69
		3	2.99	2.36	1.82
		4	3.02	2.66	1.83
	4	1	2.72	1.15	1.32
		2	2.74	1.24	1.52
		3	2.75	1.26	1.97
		4	2.75	1.32	2.00
90	2	1	3.71	6.05	4.61
		2	4.11	11.16	6.15
		3	4.32	15.17	6.22
		4	4.62	16.50	6.47
	3	1	3.05	1.13	1.43
		2	3.15	2.03	1.85
		3	3.17	2.57	1.79
		4	3.19	3.42	1.92
	4	1	2.93	1.11	1.61
		2	2.91	1.33	1.81
		3	3.03	1.37	1.96
		4	3.06	1.42	2.21
LSD ($\alpha = 0.05$)	···	···	0.46	1.78	1.45

structure of alkaline-treated corn fiber, as characterized by an open structure with increased porosity, may facilitate the penetration and absorption of water by the fiber matrix and thus improve its WHC.

A slight decrease in WHC was observed after extrusion of raw, acid-treated, and alkaline-treated corn fiber as compared with their unextruded counterparts (Table I). However, the changes were not significant ($P = 0.05$). Significantly lower WHC was found for acid-alkaline-treated corn fiber as compared with the native corn fiber ($P = 0.05$) (Table I). Cadden (1987) pointed out that the WHC of cereal brans is affected by the particle size and physical structure of the fiber matrix. Reducing the particle size of AACC wheat bran decreased WHC, due, in part, to the collapse of its fibrous matrix. In our study, the decreases in WHC after extrusion may come from the collapse of the fiber matrix as a result of the high pressure and high shear applied during extrusion. A reduction in particle size and the enhanced solubility of acid-alkaline-treated corn fiber may be the main reasons for its decreased WHC.

X-Ray Crystallography

The crystalline structure of cellulose fibers, as described in detail by Jones et al (1971), consists of submicroscopic elongated units called crystallites. Nikitin (1966) described the physical heterogeneity of fiber materials as being composed of highly ordered crystalline cellulose regions, amorphous cellulose, and hemicellulose regions. The highly ordered cellulose regions are the major contributors to fiber crystallinity. In our study, samples given alkaline treatment appeared to have a lower degree of crystallinity as compared with the native corn fiber. The decreased peak height, as observed from the X-ray diffraction spectra of most alkaline-treated corn fibers (including alkaline-treated, alkaline-treated-extruded, acid-alkaline-treated, and alkaline-acid-treated corn fibers), is an indication of decreased crystallinity (Fig. 4). No significant changes in the X-ray diffraction pattern were observed for corn fibers after acid treatment and extrusion alone. The swelling of the corn fiber matrix, in particular, and the disruption of highly ordered crystalline cellulose regions as a result of alkaline swelling in combination with extensive heating may be the main reasons for the reduction in fiber crystallinity.

TABLE III
Effect of Heating Temperature, Heating Time, and Alkaline pH Value of the Medium on Water-Holding Capacity (WHC) and Total Sugar in the Supernatant

Temperature (°C)	pH	Heating Time (hr)	WHC (g water/g)	Total Sugar (mg/ml)
80	9	1	2.88	7.24
		2	2.83	7.53
		3	2.91	7.58
		4	2.94	8.68
	10	1	2.97	7.49
		2	3.05	7.51
		3	3.11	8.77
		4	3.14	9.96
	11	1	2.99	7.97
		2	3.20	9.26
		3	3.27	9.90
		4	3.34	10.46
90	9	1	2.93	8.65
		2	2.99	8.97
		3	3.18	9.34
		4	3.24	9.56
	10	1	2.88	9.20
		2	3.14	9.34
		3	3.25	9.64
		4	3.47	9.96
	11	1	2.89	9.84
		2	3.07	10.11
		3	3.31	10.34
		4	3.64	12.06
LSD ($\alpha = 0.05$)	···	···	0.31	1.24

Soluble and Insoluble Fiber Content

The soluble and insoluble fiber contents of the native and all the chemically modified corn brans were measured (Table I). Extrusion processing resulted in a slight increase in soluble fiber content for both native and chemically modified corn fibers as compared with their unextruded counterparts. However, the increases were not significant ($P = 0.05$). Significantly increased soluble fiber contents, however, were observed after acid and alkaline treatments ($P = 0.05$). Acid-alkaline-treated corn fiber had the highest soluble fiber content and the corresponding lowest insoluble fiber content as compared with any other sample ($P = 0.05$). Chemical hydrolysis resulted in partial breaking of the polysaccharide chains of the major fiber components, weakening the interactions among various polysaccharide chains and subsequently reducing the chain size. Hence, the mobility of the polysaccharide molecules was greatly increased, facilitating their interaction with water molecules and their associated solubility. The extremely high soluble fiber content and the low insoluble fiber content observed after consecutive acid-alkaline treatments may be due to the fact that acid treatment can open the structure and increase the surface porosity of the fiber particle, making it easier for the hydroxyl groups to penetrate inside and perform hydrolysis during the subsequent alkaline treatment.

CONCLUSION

Modification of the crystalline structure of corn bran can be successfully achieved through the use of acid, alkaline, or acid-

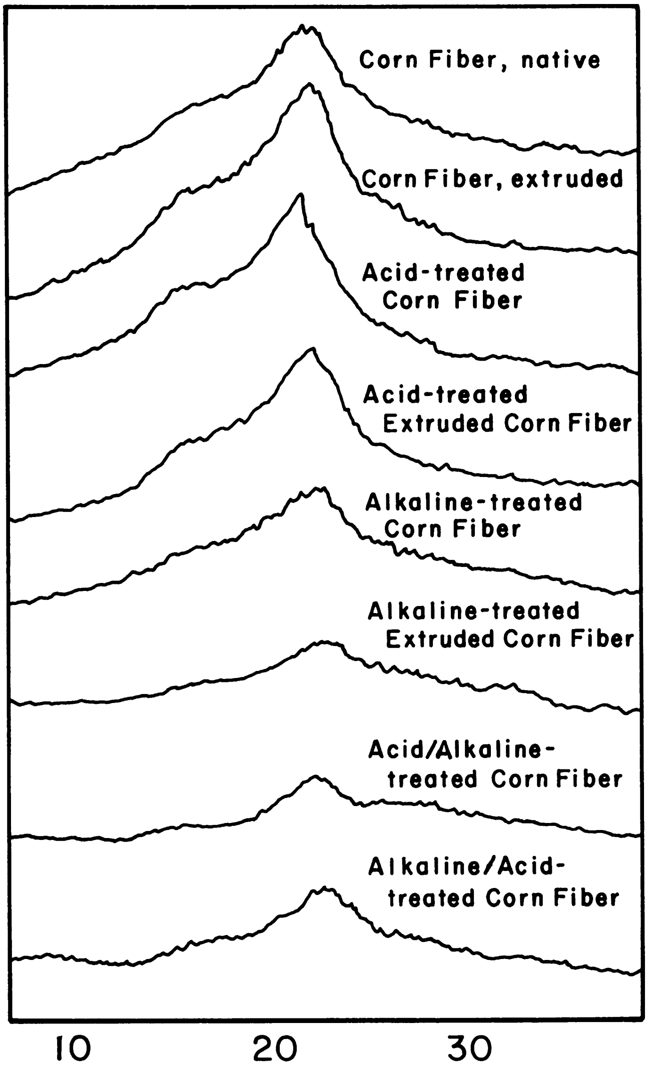

Fig. 4. X-ray diffraction patterns of native and modified corn fiber.

alkaline pretreatments. Perhaps because of the short residence time of the material in the unit, extrusion did not appear to introduce any significant additional modification in the bran. Thus, based on the needs for certain solubility, WHC, and overall organoleptic properties, pretreatments can be given to the corn bran to improve its performance or to increase its level of incorporation in food products.

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