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An Improved Process for Isolation of Corn Fiber Gum

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ABSTRACT

Sequential alkaline extraction and alkaline hydrogen peroxide (AHP) bleaching have been used to prepare corn fiber gum in yields ranging from 21 to 40%, depending on the pH of the extraction medium. The pH was adjusted by using different ratios of NaOH and $Ca(OH)_2$. The whitest product was obtained after AHP bleaching of the extract obtained using the lowest pH value. In order for the product gum to give its characteristic clear and low viscosity solutions, it was necessary to remove starch from the corn fiber substrate using α-amylase. The water-insoluble hemicellulose A fraction, a minor component, was removed by neutralizing AHP-treated extracts before ethanol precipitation of the useful hemicellulose B (corn fiber gum) fraction. At ambient temperature, AHP bleaching was near optimal after ≈2 hr under the processing conditions used. High ratios of arabinose (39%) to xylose (50%) were present in the corn fiber gum extracted under various alkaline conditions, and the H_2O_2 processing step did not significantly alter these ratios. The same low levels of galactose (7%) and glucuronic acid (4%) were present regardless of the extraction conditions. Molecular mass of the corn fiber gum preparations ranged from 2.78×10^5 for the material extracted with $Ca(OH)_2$ to 3.94×10^5 for the material extracted with NaOH. Molecular mass was unaffected by the H_2O_2 present in the second processing step. As expected for a carbohydrate polymer with a rather low uronic acid content, solution viscosities were unaffected by the presence of salt.

Corn fiber is a coproduct generated by the wet-milling of corn, and over 4 million tons/year are produced in the United States (USDA 1997). Corn fiber consists primarily of cell-wall material from kernel pericarp. Searches for uses more highly valued than animal feed have focused on the hemicellulose (arabinoxylan) fraction, which accounts for >50% of dry, starch-free fiber (Doner and Hicks 1997). Several processes for producing the arabinoxylan fraction of fiber using various conditions of alkaline extraction have been described in patent literature (Wolf et al 1955, Rutenberg and Herbst 1957, Watson and Williams 1959, Schweiger 1973, Antrim and Harris 1977). Corn fiber arabinoxylan is a hemicellulose and is commonly referred to as corn fiber gum (CFG). No food or industrial applications of CFG have resulted from past efforts, although several useful properties of the material were demonstrated. The opinion was expressed (Rutenberg and Herbst 1957) that the industrial usefulness of CFG would be greatest for products with the least color.

We recently described (Doner and Hicks 1997) a process to produce an off-white CFG in yields up to 42%. Extractions of the arabinoxylan from fiber were conducted in alkaline H_2O_2 solutions adjusted to pH 11.5 with NaOH. The presence of H_2O_2 in the extraction media for unground corn fiber increased hemicellulose yield by about one-third (Doner and Hicks 1977). In addition, more lightly colored CFG was obtained, presumably the result of AHP removal of lignin and protein from intimate associations with the hemicellulosic fiber fraction in the matrix.

In this article, we describe a modified extraction procedure that improves the whiteness of the CFG product in the form of hemicellulose B, the water-soluble and potentially most useful form. Also, H_2O_2 usage was minimized. In this new process, the alkaline hemicellulose extraction and the H_2O_2 treatments were performed sequentially rather than simultaneously as described previously (Doner and Hicks 1997). The process improvements are expected to expand potential applications of CFG.

[1] U.S. Department of Agriculture, Agricultural Research Service, Eastern Regional Research Center, 600 E. Mermaid Lane, Wyndmoor, PA 19038. Names are necessary to report factually on available data; however, the USDA neither guarantees nor warrants the standard of the product, and the use of the name by the USDA implies no approval of the product to the exclusion of others that may also be suitable.

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MATERIALS AND METHODS

Corn Fiber Samples

Fiber samples were kindly provided by American Maize Products Co. (Hammond, IN), Cargill Central Research (Minneapolis, MN), and CPC Corn Products Division (Summit-Argo, IL). Suppliers oven-dried the fiber before shipping. A sample of corn hull hemicellulose was provided by Clinton Corn Processing Co. (Clinton, IA). Fiber samples were ground to a 20-mesh particle size using a Wiley mill, and moisture levels were determined after drying samples to constant weight in a vacuum oven at 70°C.

Starch was removed from 20-mesh fiber with α-amylase treatment (Termamyl, a gift from Novo Nordisk Bioindustrials, Inc. Danbury, CT). Corn fiber (500 g) was stirred at 85–90°C in 4 L of H_2O, and the pH was adjusted to 6.5 by addition of 50% NaOH solution. α-Amylase (20 mL) was added, and the mixture was stirred for 4 hr. The fiber was isolated by centrifugation ($5,000 \times g$ for 5 min) and decantation of the tannish maltodextrin solution. The fiber was washed with water and ethanol, and then dried in a 60°C oven.

Extraction Procedures for CFG

Destarched corn fiber (100 g) was mechanically stirred into water (1 L). NaOH (8 g), $Ca(OH)_2$ (7.4 g), or mixtures of each were added so that 2 meq of alkali/gram of fiber were present in the extraction medium. The mixtures were boiled with mechanical stirring for 1 hr. Residue was removed by centrifugation ($6,000 \times g$ for 10 min) and the hemicellulose-containing supernatant (≈660 mL) was removed by decantation. The remainder of fluid (340 mL) remained associated with residue and contained ≈0.33 of the extracted hemicellulose. Much of this additional material was recovered by adding 800 mL of water to the residue and boiling the mixture for 5 min with stirring. The mixture was then centrifuged, and the supernatant was combined with that of the original extract. The total volume of extracts was ≈1.4 L. Repeated extractions of the residue yielded progressively lower additional quantities of hemicellulose.

To the 1.4-L extract was added 10 g of H_2O_2 (33.3 mL of 30% H_2O_2). After adjusting the pH to 11.5 by addition of ≈20 mL of 50% NaOH, the solution was stirred at ambient temperature for 2 hr.

The H_2O_2-treated alkaline extract was adjusted to pH 4.0–4.5 by addition of concentrated hydrochloric acid (≈37% HCl). After 15–30 min, the hemicellulose A precipitate was removed by vacuum filtration through a Celite filter aid (or by centrifugation at 10,000 × g for 10 min). Two volumes of 95% ethanol was stirred in to the filtrate. After allowing the CFG (hemicellulose B) to settle out as a white flocculent precipitate (≈10 min), the alcohol-water mixture was removed by decantation. The precipitate was stirred in 95%

ethanol for 5 min, isolated by filtration, air-dried in a fume hood, and then dried in a vacuum oven at 50°C for 1 hr. The CFG was then converted to a fine white powder with a conventional chopper-grinder.

The alkaline extract from 10.0 g of corn fiber was treated with 1.0 g (3.33 mL) of 30% H_2O_2. The pH was then adjusted to 11.5 by dropwise addition of 50% NaOH. Aliquots of 1.5 mL were taken periodically, diluted with an equal volume of water, and absorbance values were measured at 450 nm using a recording spectrophotometer (Shimadzu model UV160U).

Properties and Composition of CFG

Color measurements of CFG powders were determined using a color analyzer (Miniscan XE, Hunter Lab, Reston, VA). Viscosities of solutions were determined using a rotary viscometer (Cannon 2000, State College, PA) with a low centipoise adapter equipped for temperature control. Elemental analysis by inductively coupled plasma analysis and ash determinations were performed by Galbraith Laboratories, Inc. (Knoxville, TN).

The neutral sugar composition of CFG samples was determined by gas liquid chromatography (GLC) of alditol acetate derivatives (Albersheim et al 1967) after acid hydrolysis (Saulnier et al 1995) using 1*N* H_2SO_4 at 100°C for 1.5 hr. Corn fiber and residue samples were hydrolyzed under these conditions after preliminary hydrolysis in 12*N* H_2SO_4. For these samples, 5–10 mg of sample was vortexed with 65 µL of 12*N* H_2SO_4 for 45 min at 25°C. This mixture was then diluted to 1*N* H_2SO_4 by addition of 715 µL of water. Capillary GLC was conducted isothermally at 230°C on a 15-m × 0.25-mm SP-2330 column (Supelco, Bellefonte, PA), using a gas chromatograph (Hewlett Packard 5890 Series II). Uronic acid levels were determined by the *m*-phenylphenol method (Blumenkrantz and Asboe-Hansen 1973) using glucuronic acid as standard.

Molecular mass was determined by a high-performance size-exclusion chromatography (HPSEC) system equipped with multi-angle laser light scattering (MALLS) and differential refractive index (DRI) detectors.

Following dialysis and lyophilization of CFG samples, 40 mg was dissolved in 50 m*M* $NaNO_3$ (20 mL) and then centrifuged at 50,000 × *g* for 10 min to remove traces of insoluble material. The solutions were passed through a 0.22-µm sterile Millex-GV filter (Millipore, Corp., Milford, MA) and 100 µL of sample was injected. The mobile phase was 50 m*M* $NaNO_3$ filtered with a 0.4-µm membrane filter (Nucleopore Costar Corp., Cambridge, MA) before degassing. The nominal flow rate was 0.7 mL/min. Columns were thermoregulated at 45°C by immersing them in a water bath.

The chromatography system consisted of a degasser (model KT-35 Shodex, JM Science Inc., Grand Island, NY) connected in series to an autosampler and pump (model 1050, Hewlett-Packard Corp., Rockville, MD), in-line 0.1 µm v/v membrane filter housed in a high-pressure holder (Durapore, Millipore Corp., Bedford MA), 15-ft stainless steel warming coil (0.04 in., i.d.), two GPC 100 cartridge guard columns (10- × 3.2-mm i.d.) and one pre- and one postcolumn set (Synchropak, Synchrom, Inc., Lafayette, IN), three chromatography columns, a MALLS detector fitted with a helium-neon laser (λ = 632.8 nm) (model Dawn F) and a K-5 flow cell (Wyatt Tech., Santa Barbara, CA), and a DRI monitor (model ERC-7510, ERMA Optical Works, Ltd., Tokyo). Two PL-Aquagel OH-60 and one OH-40 chromatography columns (Polymer Labs, Amherst, MA) were serially connected. The exclusion limits for these columns as specified by the manufacturer for polyethylene glycol are 2×10^7, 1×10^5 g/mole, respectively. Each column was 7.5 mm i.d. × 300 mm in length.

The DRI detector signal response factor was measured by injecting a series of known NaCl concentrations directly into the detector cell with a syringe. This response factor was obtained from the slope of the linear plot between NaCl concentration and refractive index response. The factor to correct the Rayleigh ratio at 90° (R_{90}) for instrument geometry was obtained by measuring the scattering intensity of toluene at 90° and tested with pullulan standards (Fishman et al 1996). The responses to scattered light intensity of the photodiodes arrayed around the scattering cell at angles other than 90° were normalized to the diode at 90° with a P-50 pullulan standard. The viscometer was also checked with pullulan standards to ensure that intrinsic viscosities were measured accurately. The concentration of arabinoxylan (CFG) was obtained from the area of its DRI chromatogram. This concentration was calculated using ASTRA software by entering the concentration dependence of the refractive index (dn/dc).

RESULTS AND DISCUSSION

The CFG was prepared according to the scheme shown in Fig. 1. To produce a final product with clear solutions, it was necessary to remove the residual starch from milled corn fiber as the initial processing step (Doner and Hicks 1997). Fiber was milled to 20-mesh particle size to provide greater surface area and more effective extraction. Starch removal was accomplished by its conversion to maltodextrins using α-amylase. A range of conditions can be used for the alkaline extraction step, although mixing by conventional means is difficult at >1:10 ratios of corn fiber to liquid (e.g., 100 g of fiber, db, in 1 L of alkali) because of high viscosities achieved as extraction proceeds.

The AHP treatment of the alkaline extract of corn fiber is best conducted at pH ≈11.5; at that pH level, the oxygen species active in delignification are optimal (Gould 1985). A primary goal in our research was to minimize raw material (alkali and H_2O_2) input to the process. The quantity of H_2O_2 used in our current process was less than one-half of that used previously (Doner and Hicks 1997).

The removal of the water-insoluble hemicellulose A fraction in addition to the starch was essential for obtaining a clear solution, although hemicellulose A generally accounts for <10% of the total hemicellulose in corn fiber extracts (Doner and Hicks 1997). Its removal by acidification of the extract followed by filtration may not be required for applications of CFG not requiring solution clarity.

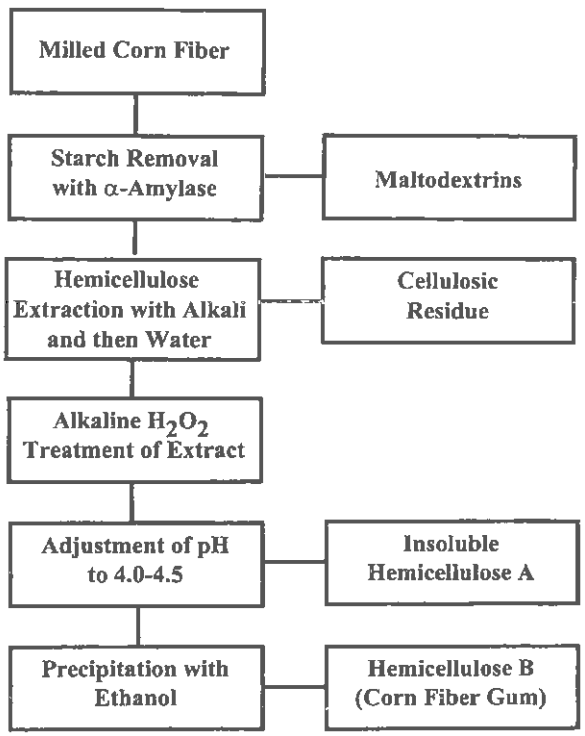

Fig. 1. Flow diagram for production of corn fiber gum (hemicellulose B) from milled corn fiber.

The effect of H_2O_2 addition on the color of the initially very brown NaOH extract of CFG is shown in Fig. 2. Minimal absorbance value was approached in 90 min, and a 2-hr bleaching time at ambient temperature was routinely used.

The analytical results for CFG samples prepared under various alkaline extraction conditions followed by AHP treatment of the extracts are compiled in Table I. Yields of CFG ranged from 21% using $Ca(OH)_2$ to 40% for extraction using NaOH; intermediate yields were obtained with mixtures of the two bases. Yields of 27% CFG were obtained when 1:1 and 1:3 ratios of NaOH to $Ca(OH)_2$ were used, and a 29% yield resulted when a 3:1 ratio was used. In all cases, total alkali to fiber ratio was 2 meq/gram of fiber. Yields correlated with pH of the extraction medium. The $Ca(OH)_2$ extraction was pH 9.8; NaOH extraction was pH 11.1. When equimolar ratios of the two bases were used, the extraction was pH 10.3. The nitrogen levels of the CFG samples were <0.2%, which were significantly lower than that of the initial corn fiber material (1.63%). The Ca and Na levels reflect the alkali type used for the extraction [NaOH or $Ca(OH)_2$].

The neutral sugar and glucuronic acid levels of CFG produced by extraction under various conditions followed by AHP treatment of the extracts are also given in Table I. The high arabinose-xylose ratios attest to the very high degree of branching on the β-(1→4)-D-xylopyranose backbone. Lower levels of galactose and glucuronic acid were present. There appears to be no significant difference in sugar levels between CFG samples extracted under different conditions. Sugar levels were also determined for a CFG sample isolated after extraction with fiber using equimolar NaOH and $Ca(OH)_2$ levels, but with no H_2O_2 added. The levels (arabinose 40.7%, xylose 48.7%, galactose 5.5%, glucuronic acid 5.0%) were very close to those found in the extract that was AHP-treated. It appeared (data not shown) that H_2O_2 had no effect on the monomer composition of the arabinoxylan polysaccharide. The low glucose levels in all samples probably indicates the presence of trace quantities of residual starch in the product. The bulk of residual starch was removed in the insoluble hemicellulose A fraction. The hemicellulose A generated resulting from $Ca(OH)_2$ extraction contained 18.8% glucose.

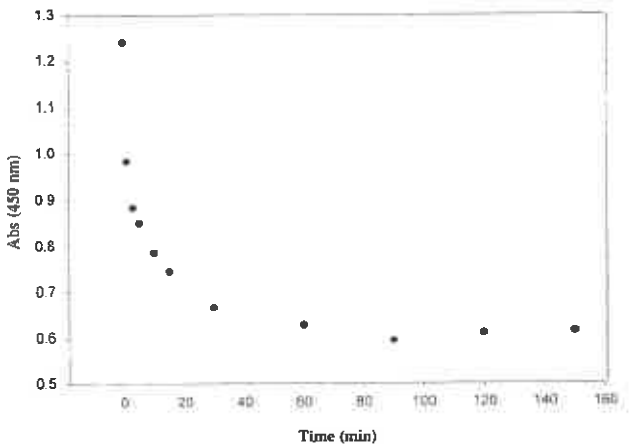

Fig. 2. Rate of hydrogen peroxide bleaching of alkali-extracted corn fiber gum solution at 25°C. Absorbance values measured at 450 nm.

TABLE I
Composition (%) and Properties of Corn Fiber Gum Extracted Under Different Conditions and Treated with H_2O_2

	NaOH	$Ca(OH)_2$	1:1
Yield[a]	40	21	27
Ash	2.15	2.65	2.42
N	0.151	0.135	0.183
Ca	0.30	0.56	0.63
Na	0.52	0.042	0.13
M_r ($\times 10^{-5}$)	3.94 ± 0.04	2.78 ± 0.05	3.03 ± 0.10
Whiteness index[b]	38.9	50.3	49.4
Sugar composition[c]			
Arabinose	39.4	37.7	40.8
Xylose	48.1	49.8	49.5
Galactose	8.4	7.5	5.4
Glucuronic acid	4.2	4.9	4.3
Glucose	0.8	1.0	0.8

[a] Dry weight basis. Starting corn fiber had 5.8% moisture.
[b] Standard = 83.2.
[c] Relative percentages.

The molecular mass (M_r) values of the CFG preparations correlated with the yield and pH level of the extraction medium. When NaOH was used as the extractant, the resulting CFG had an M_r of 3.94×10^5. When $Ca(OH)_2$ was used as extractant, the resulting CFG had an M_r of 2.78×10^5. When an equimolar ratio of NaOH to $Ca(OH)_2$ was used, an intermediate M_r of 3.03×10^5 resulted. It appeared that the more extreme extraction NaOH conditions resulted in liberation of a higher M_r fraction of hemicellulose B molecules. These results are consistent with those reported earlier (Saulnier et al 1995), where corn bran was extracted with 0.5*M* NaOH at 30°C for 2 hr and had an M_r of 2.7×10^5 for hemicellulose. When residual material was extracted with 1.5*M* KOH for 2 hr at 100°C, the resulting hemicellulose had an M_r of 3.7×10^5.

An important characteristic for potential application of CFG is its whiteness. CFG isolated after the milder $Ca(OH)_2$ extraction condition had a higher whiteness index (WI = 50.3) than that isolated by NaOH extraction (WI = 38.9), as shown in Table I. The products extracted with $Ca(OH)_2$ and equimolar ratios of NaOH and $Ca(OH)_2$ appeared very white, while the NaOH-extracted CFG appeared off-white. Products prepared using exhaustive 1.5*M* KOH extraction conditions (Saulnier et al 1995) possessed a grayish hue (WI = 20.6). In studies comparing ethanol and *i*-propanol as precipitants of CFG from aqueous solutions, it was found that addition of two volumes of either alcohol to the AHP-treated and then neutralized extracts was sufficient for quantitative precipitation of CFG. Identical yields were obtained after using both alcohols as precipitants. WI values for *i*-propanol precipitated CFG products were significantly lower than those of ethanol-precipitated products. The ethanol-precipitated CFG with WI = 49.4 (Table I) gave WI = 32.2 when *i*-propanol was used as a precipitant.

There is little apparent effect of 100 m*M* NaCl or 100 m*M* $CaCl_2$ on the viscosity of 5 or 10% CFG solutions (Fig. 3). These

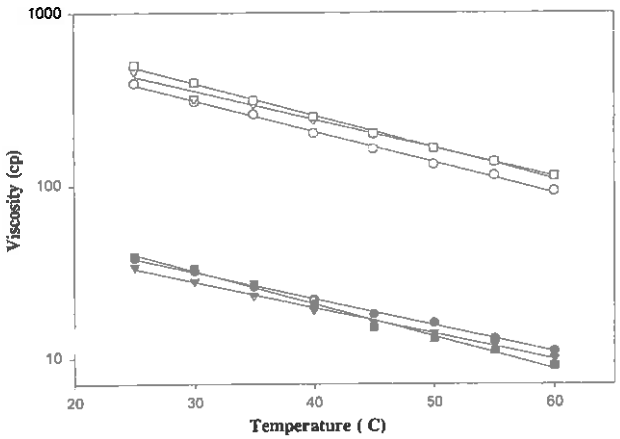

Fig. 3. Viscosities (cP) vs. temperature for 5 and 10% corn fiber gum solutions at pH 5.5 in water (● 5%, ○ 10%), 100 m*M* NaCl (▼ 5%, ▽ 10%), and 100 m*M* $CaCl_2$ (■ 5%, □ 10%).

results are not unexpected for a polysaccharide containing low uronic acid levels. The linear relationship between log viscosity and temperature demonstrates that CFG is stable over the temperature range examined, in either water or salt solution. CFG extracted using equimolar ratios of NaOH and $Ca(OH)_2$ was used in the experiments for Fig. 3. Viscosities of CFG extracted with either NaOH or $Ca(OH)_2$ were not significantly different from those given in Fig. 3.

The process described here for the production of CFG is superior to that reported earlier (Doner and Hicks 1997) in terms of whiteness of product, an important quality characteristic. In addition, some economies with regard to raw material input were accomplished. Options (extraction pH, starch and hemicellulose A removal, time and temperature of AHP treatment) for the process are available which allow preparation of various types of CFG, depending on application. In addition to the CFG generated in the process, there are two additional process streams. These are the cellulosic residue that remains after alkaline extraction of CFG and the ethanol-water supernatant remaining after ethanol precipitation of CFG. Removal of ethanol and water from the supernatant leaves a residue rich in ferulic acid and other phenylpropanoids. Similar levels of CFG, cellulosic residue, and ferulic acid-containing fractions are generated from the process. Current efforts are being directed toward the utilization of the latter fractions.

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