

Contents of Indigestible Fraction, Water Solubility, and Color of Pyrodextrins Made from Waxy Sorghum Starch

Seung-kyu Kwon,¹ Koo Min Chung,^{2,3} Sang Ick Shin,⁴ and Tae Wha Moon⁵

ABSTRACT

Cereal Chem. 82(1):101–104

To investigate the effect of prethinning of starch by acid before pyrolysis on the formation of indigestible fraction (IF) in pyrodextrins, native and prethinned (50°C for 1, 4, and 24 hr) waxy sorghum starches were heated at 120–160°C with 20–60 μL of 9% HCl/g of starch. Pyrodextrin containing 14.6% IF, measured as total dietary fiber by enzymatic-gravimetric method, was produced at 120°C with 20 μL of HCl from native waxy sorghum starch. Prethinning before pyrolysis increased IF content by 0–68%, depending on the conditions for pyrolysis, compared with that of the native starch. Reduction in the molecular size

of starch by prethinning might cause greater mobility during pyroconversion reaction and thus generate higher IF contents. Increasing temperature and acid concentration during pyroconversion also increased IF content of pyrodextrins. Pyrodextrin of 44.9% IF was produced at 160°C with 60 μL of HCl from prethinned starch (50°C for 24 hr). Solubility of pyrodextrins was inversely proportional to IF content ($r = -0.87$) and had a range of 62.7–98.3%. Color of pyrodextrins became brownish with more severe pyroconversion conditions.

Because dietary fiber is an important nutrient, there are attempts to produce it from starchy materials. Resistant starch is a kind of dietary fiber and can be formed in many ways including autoclaving-cooling cycles, hydrothermal treatments, and chemical modification (Eerlingen and Delcour 1995; Thompson 2000; Brumovsky and Thompson 2001).

Pyrodextrins could also be a dietary fiber because they are resistant to α -amylase. Ohkuma et al (1990) reported that 1,2 and 1,3 glucosidic linkages are formed in starch granules during pyroconversion, resulting in amylase resistance, and the pyrodextrins act physiologically as a dietary fiber in the intestine. A pyrodextrin (*Fibersol-2*) made from corn starch commercially is available as a soluble dietary fiber (www.matsutani.com). Woo (1998) reported that pyrodextrins prepared at 140°C from various normal and waxy starches contained indigestible fraction.

Besides transglucosidation, in pyroconversion process, acid-catalyzed breakages of 1,4 and probably 1,6 glucosidic bonds in the starch occurred during the predrying period and initial stages of dextrinization. Three types of pyrodextrins are produced under different conditions. White dextrins are prepared at relatively low temperatures and low pH levels. British gums, on the other hand, are produced at relatively high temperatures and high pH levels, and yellow dextrins are produced at high temperatures and low pH levels. Pyrodextrins have different colors, white to brown, depending on the preparation conditions and relatively good solubility. And their solutions have low viscosity (Wurzburg 1986).

Thompson (2000) reported that partial acid hydrolysis of high-amylose maize starch increased polymer mobility for molecular rearrangement, and improved RS yield with subsequent thermal treatments such as annealing and heat-moisture treatment. If, in the same way, the amorphous regions in waxy starch were partially hydrolyzed, more indigestible fraction would be formed from waxy starch by pyroconversion due to the increased polymer mobility.

The objective of this work was to investigate the effect of thinning of waxy sorghum starch on formation of indigestible fraction during pyroconversion. Waxy sorghum starch was prethinned partially before pyrolysis and indigestible fraction content, water solubility, and whiteness of the pyrodextrins were measured.

MATERIALS AND METHODS

Preparation of Waxy Sorghum Starch

Waxy sorghum starch was isolated using an alkaline steeping method from commercial waxy sorghum purchased at a local market (Chung et al 2000). Its crude protein content (Kjeldahl N \times 6.25) was trace (0.02% on dry basis). Blue value, measured through the iodine absorption method (Gilbert and Spragg 1964), was 0.021, which indicated that the prepared starch contained nearly no amylose. Moisture content of the starch was 9.39%.

Prethinning of Waxy Sorghum Starch with Acid

One part of starch was mixed with four parts of 1N HCl solution. Each slurry was thinned at 50°C for 1, 4, and 24 hr with stirring and neutralized with 1N NaOH solution. Thinned starch products were washed six times with water and dried at 40°C in an air-forced oven. Moisture contents of the starches (prethinned for 1, 4, and 24 hr) were 11.76, 11.73, and 11.59%, respectively.

Pyroconversion

To 20 g of native and prethinned starches, 0.4, 0.8, and 1.2 mL of 9% (w/v) HCl were added and mixed in a blender to disperse HCl evenly. The starch-HCl mixtures were transferred into capped 100-mL pyrex bottles and heated in ovens at 120, 140, and 160°C for 150 min. After cooling to room temperature, 0.4 mL of 30% ammonium bicarbonate solution was added to neutralize the pyroconverted starches, which were then blended as described above and heated at 60°C for 30 min in an oven to remove the ammonia odor. Kjeldahl nitrogen content of some pyrodextrins was 0.04–0.11%. This indicated that even though the odor was removed by heating, nitrogen residue formed by reacting hydrochloric acid and ammonium bicarbonate was present in pyrodextrins.

Average DP_n and Chain Length of Starches

Average degree of polymerization (av. DP_n) was determined by measuring total carbohydrate content through the phenol-sulfuric acid method (Dubois et al 1956) using 0–60 μg of glucose/mL as the standard, and reducing power through the modified Park-Johnson method (Hizukuri et al 1981; Chung and Seib 1991) using 0–6 μg of glucose/mL as the standard. The latter method was

¹ Graduate student, School of Bioresource, College of Natural Science, Andong National University. Current address: Daepyeong Co., Ltd., Sangju, Korea.

² School of Bioresource, College of Natural Science, Andong National University, Andong, Kyungbuk 760-749, Korea.

³ Corresponding author. Phone: 82 54 820 5492. Fax: 82 54 823 1627. E-mail: kmchung@andong.ac.kr

⁴ Graduate student, Department of Food Science and Technology, School of Agricultural Biotechnology, Seoul National University, Korea.

⁵ National Laboratory for Functional Food Carbohydrate, School of Agricultural Biotechnology, and Center for Agricultural Biomaterials, Seoul National University, Korea.

reported to be suitable for reducing power measurements of amylose and amylopectin (Takeda et al 1987).

Average chain length (av. CL) was measured after isoamylolysis. Starch (≈ 40 mg) was dissolved completely by stirring in 1 mL of 1N NaOH solution, neutralized with 1N HCl solution, and diluted to 10 mL with water. To 5 mL of starch solution, 1 mL of 2M acetate buffer (pH 3.5) was added and kept in a 45°C water bath for 10 min. Diluted isoamylase solution (100 μ L [0.01 mL of isoamylase (cat. No 2758, Sigma) + 1 mL of water]) was added and the mixture was incubated for 5 hr with occasional stirring in a water bath. Subsequently, the hydrolyzed solution was heated for 5 min in a boiling water bath to inactivate the enzyme. Chain length was calculated after measuring the total carbohydrate content using the phenolsulfuric acid method and the reducing power method (Robyt and Whelan 1968) with 0–200 μ g of glucose/mL as the standard.

Indigestible Fraction, Water Solubility, Color, and X-Ray Diffractograms

Indigestible fraction (IF) contents of pyrodextrins were determined by assaying the total dietary fiber content (AOAC 1990) with the enzymatic-gravimetric method using a total dietary fiber kit (TDF-100A, Sigma Chemical Co., St. Louis, MO).

Water solubility of pyrodextrins was measured by the Schoch method (1964) with a slight modification. Pyrodextrin solution (10%, w/v) was heated in an 85°C water bath with stirring for 30 min and immediately cooled in an ice water bath. The solution was centrifuged at $5,000 \times g$ for 10 min, and the amount of dried matter in the supernatant was weighed after drying in a 60°C oven overnight and subsequently in a 130°C oven for 1 hr. Solubility (%) was the weight of dried matter in supernatant $\times 100$ /sample weight as dry matter.

Hunter *L* value of pyrodextrins was measured with a color difference meter (JS555, Color Techno System Corp., Tokyo, Japan) after keeping samples for two days in a desiccator for moisture equilibrium.

X-ray diffraction patterns of starches and pyrodextrins were obtained with an X-ray diffractometer (Dip 2030, Mac Science, Japan) operating at 50 kV and 90 mA with CuK radiation of 0.154 nm (nickel filter). The scanning region of the diffraction angle 2θ was 3–29°. Samples for X-ray patterns were exposed to air at room temperature for two days for moisture equilibrium before measurement.

Statistical Analysis

Means of measurements done at least in duplicate were separated by Fisher's least significant differences ($\alpha = 0.05$) using SAS software (8.01e, SAS Institute, Cary, NC).

RESULTS AND DISCUSSION

Average DP_n and CL of Prethinned Starches

The native waxy sorghum starch gave av. DP_n and av. CL of 7,240 and 23, respectively. The DP_n seemed to be small compared with the molecular weight of 8–10 $\times 10^6$ ($\approx 50,000$ – $60,000$ as DP_w) of amylopectin of sorghum starch (Anonymous 1993). The number average DP_n is known to be lower than weight average DP_w due to the wide molecular size distribution in starch (Young 1984). Av. DP_n of waxy sorghum starch was similar to those of amylopectins in other cereal starches. Takeda et al (1987) and Shibamura et al (1994) reported that av. DP_n of rice and wheat amylopectins were 4,700–12,800 and 5,000–9,400, respectively.

When the starch was prethinned at 50°C for 1, 4, and 24 hr, av. DP_n decreased to 870, 240, and 60, respectively. However, av. CL was not affected by prethinning, remaining in the range of 23–24. This implies that α -1,4 linkages in chains were likely protected from acid by being in crystallites during acid-thinning, with only 1,6 linkages in the amorphous regions being affected by acid. Wurzburg (1986) reported that, in acid modification of starch in the granule form, the amorphous regions with α -1,6 linkages are more susceptible to acid penetration and hydrolysis.

TABLE I
Contents (%) of Indigestible Fraction in Pyrodextrins Prepared from Native and Prethinned Waxy Sorghum Starches^a

Pyroconversion Conditions		Prethinning Conditions			
Temp. (°C)	9% HCl (μ L/g of starch)	Native	50°C for 1 hr	50°C for 4 hr	50°C for 24 hr
120	20	14.6	19.2	20.1	24.5
	40	17.0	22.1	22.8	27.7
	60	20.1	22.8	26.3	25.7
140	20	18.1	24.4	22.7	28.2
	40	24.6	26.9	25.9	33.2
	60	25.7	28.4	28.4	36.0
160	20	27.4	30.2	31.0	34.5
	40	28.9	34.1	33.7	42.9
	60	35.0	35.2	37.9	44.9
160	No acid	1.6	2.0	1.5	1.1

^a LSD ($\alpha = 0.05$) for all pyrodextrins except four dextrins with no acid was 2.71.

TABLE II
Water Solubility (%) of Pyrodextrins Prepared from Native and Prethinned Waxy Sorghum Starches^a

Pyroconversion Conditions		Prethinning Conditions			
Temp. (°C)	9% HCl (μ L/g of starch)	Native	50°C for 1 hr	50°C for 4 hr	50°C for 24 hr
120	20	98.3	98.0	98.1	98.2
	40	97.9	97.6	97.1	96.1
	60	97.8	97.1	95.1	92.6
140	20	97.4	96.0	94.6	86.8
	40	96.8	93.7	90.6	78.3
	60	94.4	91.6	89.3	74.0
160	20	96.6	93.7	91.7	77.9
	40	93.3	89.2	86.6	66.7
	60	91.6	86.6	81.1	62.7

^a LSD ($\alpha = 0.05$) for all pyrodextrins was 0.69.

Indigestible Fraction (IF) in Pyrodextrins

When waxy sorghum starch was heated without acid, the content of IF in pyrodextrins was only 1.6%. The IF content of pyrodextrins prepared from the prethinned starches also showed low values of 1.1–2.0% (Table I). However, the contents of IF were much higher when the native and prethinned starches were heated with hydrochloric acid.

The contents of IF in pyrodextrins increased with increasing pyroconversion temperature and the amount of acid added for pyroconversion as well as the degree of prethinning. When waxy sorghum starch was pyroconverted at 120°C with 20 µL of 9% HCl/g of starch, IF content was 14.6% and increased to 17.0 and 20.1% when 40 and 60 µL of HCl were added, respectively. At 160°C, they were 27.4, 28.9, and 35.0%, respectively.

Prethinned starches produced pyrodextrins with higher IF content than that of the native waxy sorghum starch. Moreover, with prolonged thinning, pyrodextrins with higher IF content were produced but showed few exceptions (26.3–25.7% for 4 and 24 hr of thinning, respectively) in 120°C treatment. A pyrodextrin of 44.9% IF was produced when waxy sorghum starch, acid-thinned at 50°C for 24 hr, was treated at 160°C with 60 µL of HCl.

During pyroconversion, starch is hydrolyzed and the cleaved molecules recombine with nearby free hydroxyl groups to produce branched structures (Wurzburg 1986). Ohkuma et al (1990) reported that during pyroconversion the number of 1→6, 1→2, 1→3 linkages increased while 1→4 linkages decreased. By heating, the terminal glucose unit present in reducing ends underwent intramolecular dehydration to form 1,6 dehydroglucose, which subsequently reacted with hydroxyl groups on other chains resulting in new linkages. Also, new bonds could form among cleaved molecules during heating. Consequently, carbohydrate-hydrolyzing enzymes are limited to access their substrate.

Presumably, reduction in the molecular size of starch by prethinning resulted in enhanced mobility during pyroconversion reaction, whereby higher IF content was generated. Brumovsky and Thompson (2001) also produced modified starches containing higher resistant starch content through heat-moisture treatment after partial acid hydrolysis of high-amylose maize starch. They explained that the decrease of molecular weight by partial acid hydrolysis would allow a greater freedom of polymer motion, so more stable structures could be formed on subsequent hydrothermal treatments.

Solubility and *L* Value of Pyrodextrin

Water-solubility is an important factor for the use of pyrodextrins as food ingredients. With increases in the pyroconversion temperature, the amount of added HCl for pyroconversion, and the prethinning period for waxy sorghum starch before pyroconversion, the solubility decreased (Table II). Pyrodextrin prepared at 120°C with 20 µL of HCl/g of starch from native waxy sorghum starch had a solubility of 98.3%. On the contrary, the pyrodextrin prepared under the severest condition, that is, at 160°C with 60 µL of HCl/g of starch from waxy starch prethinned at 50°C for 24 hr,

had a solubility of 62.7%. The solubility showed an opposite trend to the IF content of pyrodextrins, the correlation coefficient between them being –0.87. This might be caused by repolymerization or formation of nonstarchy material such as char during pyroconversion. Wurzburg (1986) reported that repolymerization appeared to take place in the yellow dextrins.

High solubility indicated that the starting materials were broken down to smaller ones during pyroconversion. Ohkuma et al (1990) prepared pyrodextrins with a dextrose equivalent (DE) of 3.8–6.0 after pyroconversion at 180°C from potato starch. Wu (1998) also reported that pyrodextrins showed that 92–100% solubility had DE of 4.8–6.1.

The lightness (*L* value) is another important factor for food use. When the pyrodextrins were prepared with native and prethinned waxy sorghum starch, lightness decreased as more acid was added to the starch and more highly thinned starches were used (Table III). With 20 µL of HCl/g starch, the *L* values were 66.7–91.7, but

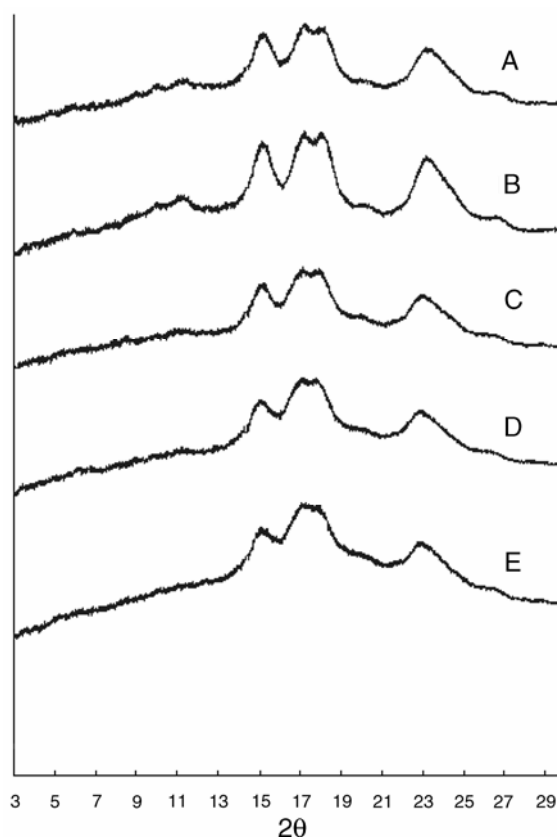


Fig. 1. X-ray diffractograms of starches and pyrodextrins. A, native waxy sorghum starch; B, acid-thinned (50°C for 4 hr) waxy sorghum starch; C–E, pyrodextrins prepared with 40 µL HCl/g at 120, 140, and 160°C, respectively, from B.

TABLE III
Hunter *L* Value of Pyrodextrins Prepared from Native and Prethinned Waxy Sorghum Starches

Pyroconversion Conditions		Prethinning Conditions			
Temp. (°C)	9% HCl (µL/g of starch)	Native	50°C for 1 hr	50°C for 4 hr	50°C for 24 hr
120	20	91.7	83.0	80.7	68.4
	40	78.9	71.9	67.4	51.1
	60	70.5	64.4	59.6	44.1
140	20	89.9	81.1	79.1	67.0
	40	77.3	69.7	67.0	51.1
	60	68.9	64.5	61.0	44.0
160	20	87.0	81.4	77.4	66.6
	40	76.5	69.4	66.0	51.8
	60	68.6	64.2	58.9	44.9

with 40 and 60 μL of HCl/g of starch, they were 51.1–78.9 and 44.0–70.5, respectively. Native starch yielded L values of 68.6–91.7, but the values decreased to 44.0–68.4 with the 24-hr thinned starches. However, the pyroconversion temperature did not cause great differences in L values. The value ranges were 44.1–91.7, 44.0–89.9, and 44.9–87.0 for 120, 140, and 160°C, respectively. This implied that the degree of cleavage of glucosidic linkages by acid largely affected the extent of browning.

Because the pyrodextrins with low L values (<50) showed brown color, it did not seem suitable for light-colored foods. Furthermore, due to the low L values, it was presumed that the pyrodextrins might contain char formed during pyroconversion. To investigate this, the pyrodextrins were hydrolyzed with 2*N* sulfuric acid at boiling temperature. Brown residues were detected only in pyrodextrins ($L < 51.8$) prepared from starches prethinned for 24 hr with 40 and 60 μL of HCl at all temperatures. This indicates dark-colored pyrodextrins may contain nonstarchy materials (char) that could not be hydrolyzed by acid. In pyrodextrins prepared with the 24-hr thinned starch and 60 μL of HCl, 87.0–93.4% of samples were hydrolyzed to glucose.

X-ray Diffraction Pattern

Waxy sorghum starch showed an A-type X-ray diffractogram with strong peaks at $2\theta = 15, 17, 18,$ and 23° similar to other cereal starches (Yoon and Lee 1999) (Fig. 1). Prethinned (50°C for 4 hr) waxy starch also showed the same pattern, but with a sharper peak than the native starch because the amorphous regions of the starch granules disappeared during thinning. Pyrodextrins prepared from the prethinned starch still showed an A-type pattern but with peaks weaker than those of the native and prethinned starches, and the sharpness decreased as the pyroconversion temperature increased, indicating crystallinity decreased during pyroconversion. Woo (1998) also reported that pyrodextrins had the same pattern, but weaker peaks than the native starches.

CONCLUSIONS

By prethinning waxy sorghum starch before pyroconversion, IF level measured as total dietary fiber increased compared with native starch, probably due to the molecular freedom after thinning. The increment was larger when starch was thinned for a longer period. The contents of IF in pyrodextrins also increased with increasing pyrolysis temperature and added acid amount. But, when highly thinned starch was heated under stronger acidic conditions, char was formed, which is not favorable for food use. Refining the process might be required to use the dark brown pyrodextrin as a food additive. Solubility of pyrodextrins was inversely proportional to IF content. Color of pyrodextrins generally became brown as the severity of pyrolysis conditions increased.

ACKNOWLEDGMENTS

This work was supported by Korean Research Foundation Grant (KRF-2000-042-G00022).

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[Received January 12, 2004. Accepted July 19, 2004.]