

Properties of Flours and Starches as Affected by Rough Rice Drying Regime

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ABSTRACT

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Flours and starches from rough rice dried using different treatment combinations of air temperature (T) and relative humidity (RH) were studied to better understand the effect of drying regime on rice functionality. Rough rice from cultivars Bengal and Cypress were dried to a moisture content of $\approx 12\%$ by three drying regimes: low temperature (T 20°C, RH 50%), medium temperature (T 40°C, RH 12%), and high temperature (T 60, RH 17%). Head rice grains were processed into flour and starch and evaluated for pasting characteristics with a Brabender Viscoamylograph, thermal properties with differential scanning calorimetry, starch molecular-size distribution with high-performance size-exclusion chromatography (HPSEC), and amylopectin chain-length distribution with high-performance anion-exchange chroma-

tography with pulsed amperometric detection (HPAEC-PAD). Lower head rice and starch yields were obtained from the batch dried at 60°C which were accompanied by an increase in total soluble solids and total carbohydrates in the pooled alkaline supernatant and wash water used in extracting the starch. Drying regime caused no apparent changes on starch molecular-size distribution and amylopectin chain-length distribution. Starch fine structure differences were due to cultivar. The pasting properties of flour were affected by the drying treatments while those of starch were not, suggesting that the grain components removed in the isolation of starch by alkaline-steeping were important to the observed drying-related changes in rice functionality.

For safe storage and milling, rough rice needs to be dried to a moisture content of $\approx 12\%$ after harvest. Rice is often air-dried at low (35°C) to high (60°C) temperature, with the level of temperature generally dictated by the type of drying equipment. Regardless of the method used in drying rice, the ultimate goal is that the drying operation itself should be efficient without causing deleterious effects on rice end-use quality. To command a premium price, rice kernels should remain intact after milling, thus it is important to avoid drying conditions that promote breakage.

High temperatures can be used in drying rough rice without consequent reduction in head rice yield as long as proper tempering techniques are employed (Cnossen and Siebenmorgen 2000). However, some changes in rice functionality associated with the temperature and time used in drying have been reported (Iwasaki and Tani 1966; Sato et al 1971; Saito et al 1974a; Champagne et al 1998; Meullenet et al 1999; Inprasit and Noomhorn 2001; Wiset et al 2001). Iwasaki and Tani (1966) reported that heating exerted an effect similar to aging on rice texture based on some cooking quality tests. Heat-dried rice produced a lower quantity of crackers compared with room temperature-dried rice (Saito et al 1974a). Champagne et al (1998) found that a commercial drying temperature of 60°C resulted in cooked rice with higher cohesiveness based on texture profile analysis with a texture analyzer. Meullenet et al (1999) observed that a high drying temperature (54.3°C) resulted in less firm cooked rice kernels but with higher cohesiveness of mass based on sensory evaluation by a trained panel. Water absorption and stickiness-to-hardness ratio decreased while *b*-value and hardness of cooked rice increased with drying temperature, exposure and drying duration, longer tempering time, and rate of water removal (Inprasit and Noomhorn 2001). Inprasit and Noomhorn (2001) added that rice cooking and eating qualities were changed by single and multistage commercial drying. Wiset et al (2001) noted that head rice yield, amylose content, gel consistency, water absorption, and volume expansion were affected by the method or temperature used in drying rough rice.

The mechanisms governing the changes in rice functionality associated with the conditions used in drying rough rice are not fully understood. Shcherbakov et al (1977) noticed that drying rice at $>50^\circ\text{C}$ resulted in a temperature-dependent decrease in soluble proteins, particularly albumins, globulins, and prolamins, and increases in free

amino acids and insoluble proteins. Federova et al (1977) used a drying temperature range of 35–120°C and found that high drying temperatures modified rice protein composition, reduced soluble proteins, and increased nonprotein nitrogen compounds. Increasing drying temperature brought about a decrease in free lipids and an increase in bound lipids (Shcherbakov et al 1977). Increasing drying temperature also increased enzymatic activity up to a certain limit, after which it decreased (Federova et al 1977). Saito et al (1974b) observed higher catalase and protease activities in heat-dried grains (30–50°C) than those dried at room temperature but no marked difference was detected in other physical and chemical properties.

It is well known that changes in starch properties during cereal processing affect product quality, especially texture, because starch is a main component in cereals. Starch owes much of its functionality to two major components, amylose and amylopectin, as well as to the physical organization of these macromolecules into the granule structure. Literatures on rice starch changes associated with drying are inadequate. A more thorough study of the fine structures and other physicochemical properties of starch may provide a deeper insight about the effect of drying regime on milled rice end-use quality. Hence, this work assessed the structures and physicochemical properties of starches isolated from rough rice dried using different combinations of air temperature and relative humidity. A comparison between the physicochemical properties of flour and starch samples was also made to account for the importance of other grain components that are present in flour but are removed during starch extraction.

MATERIALS AND METHODS

Materials

Rough rice samples from cultivars Bengal (medium-grain) and Cypress (long-grain) were obtained from the 2001 crop of the University of Arkansas Rice Research and Extension Center in Stuttgart, AR. The harvest moisture content (MC) of the samples was 22.0 and 20.5% for Bengal and Cypress, respectively.

Drying of Rough Rice

Rough rice samples were dried by thin-layer drying as described by Cnossen and Siebenmorgen (2000). One batch was dried with air at 60°C and 17.0% relative humidity (RH), corresponding to an equilibrium moisture content (EMC) of 5.5%, for 40 min. Another batch was dried at 40°C and 12% RH, corresponding to an EMC of 5.8%, for 90 min. Immediately after drying, the samples were tempered in sealed plastic bags for 3 hr at the temperature of the drying air. The samples were then taken out of the sealed bag, spread evenly on meshed trays, and then gently cooled and dried in a chamber

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at 20°C and 50% RH until the target MC of 12.5% was reached. A batch that served as a control was entirely dried on meshed trays in the chamber at 20°C and 50% RH to a MC of 12.5%.

Milling of Samples

A dehusker (THU-35, Satake, Hiroshima, Japan) was used to dehull duplicate 150-g rough rice samples. The brown rice recovered was weighed and then milled for 30 sec in a McGill No. 2 mill (Rapsco, Brookshire, TX). Head rice was separated from the broken kernels through a double-tray sizing device (GrainMan Machinery Mfg., Miami, FL). Flour samples were obtained by grinding with a cyclone sample mill (Udy, Fort Collins, CO) fitted with a 100-mesh sieve. Total milled rice and head rice yields were calculated as percentages by weight of rough rice. Translucency and whiteness were measured on head rice samples with a Satake milling meter (model MM-1B).

Isolation of Starch

Starch samples were prepared based on the alkaline-steeping method of Yang et al (1984) with slight modifications. Head rice sample (10 g, db) was soaked in 40 mL of 0.1% sodium hydroxide (NaOH) for 24 hr. The soaked sample was then wet-milled in an Osterizer blender for 4 min at speed 6, filtered through a U.S. standard test sieve #230, and centrifuged for 15 min at 1,500 × g. The supernatant was transferred into a 250-mL volumetric flask while the top yellow, curd-like layer of the residue was discarded by carefully scraping it off with a spatula. The remaining starch residue was again extracted with 0.1% NaOH, centrifuged using the same speed, and the supernatant collected into the same 250-mL volumetric flask. The residue was then adjusted to pH 6.5 with 0.2M HCl and washed with 40 mL of deionized water three times. For each washing, the supernatant was also transferred into the same 250-mL volumetric flask. The starch residue was then dried at 40°C for 24 hr. Starch yield was calculated on a dry weight basis.

Analysis of Supernatant

The pooled supernatant from starch extraction was diluted to 250 mL, shaken well, and its total carbohydrate was determined by the phenol-sulfuric acid method (Dubois et al 1956) using a 1.0-mL aliquot. Another 5 mL of supernatant was transferred into a pre-weighed aluminum moisture dish and dried to a constant weight at 105°C for 24 hr. The residue was allowed to cool in a dessicator and then weighed to calculate total soluble solids. Duplicate samples were

used for each analysis. Total carbohydrates and total soluble solids were expressed as percentages by weight (db) of the head rice used in starch extraction.

Pasting and Thermal Properties

Flour and starch pasting properties were measured according to Approved Method 61-01 (AACC 2000) with a Viskograph-E (C.W. Brabender Instruments, South Hackensack, NJ). Thermal properties were assessed by differential scanning calorimetry (Pyris-1, Perkin-Elmer, Norwalk, CT) following the method of Wang et al (1992).

Characterization of Starch Structures

The relative amount of amylose, amylopectin, and intermediate material in the starch samples were analyzed by high-performance size-exclusion chromatography (HPSEC) following the method of Kasemsuwan et al (1995) as modified by Wang and Wang (2000). The HPSEC system (Waters, Milford, MA) consisted of a 515 HPLC pump with an injector of 100 µL sample loop, an in-line degasser, a 2410 refractive index detector maintained at 40°C, and a series of Shodex OHpak columns (KB-802 and KB-804) maintained at 55°C. Amylopectin, intermediate material, and amylose content were calculated automatically from the area of their corresponding peaks.

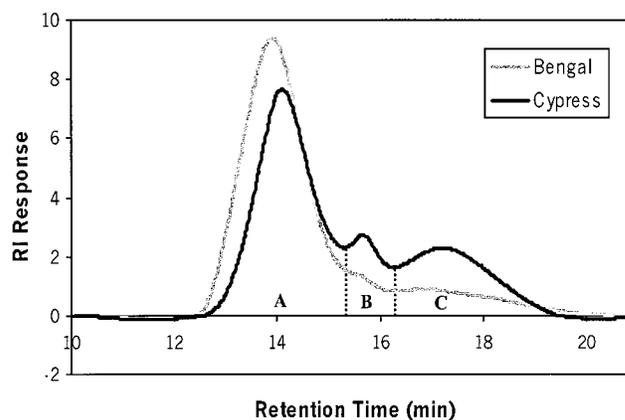


Fig. 1. High-performance size exclusion chromatograph of native starch solutions from rice cultivars Bengal and Cypress. A: amylopectin, B: intermediate materials, and C: amylose.

TABLE I
Milling Characteristics and Physical Attributes of Head Rice as Affected by Rough Rice Drying Regimes

Rice Cultivar	T/RH ^a	Total Milled Rice Yield (%)	Head Rice Yield (%)	Grain Translucency (%)	Grain Whiteness (%)
Bengal	20/50	71.8ab ^b	61.1bc	4.0ab	36.6a
	40/12	72.6b	57.2b	3.7a	36.4a
	60/17	72.5b	52.5a	3.5a	37.8ab
Cypress	20/50	69.1a	63.6c	4.5b	38.3b
	40/12	68.4a	63.5c	4.3b	38.5b
	60/17	69.0a	61.9bc	4.0ab	39.3b

^a T, drying temperature (°C); RH, relative humidity (%).

^b Values followed by the same letter in the same column are not significantly different ($P < 0.05$).

TABLE II
Starch Recovery and Total Carbohydrates and Total Soluble Solids in Pooled Supernatant as Affected by Rough Rice Drying Regimes

Rice Cultivar	T/RH ^a	Starch Recovery (% db)	Total Carbohydrates in Supernatant (% db)	Total Soluble Solids in Supernatant (% db)
Bengal	20/50	60.5b ^b	1.18b	6.82a
	40/12	60.0b	1.26bc	7.60bc
	60/17	57.5a	1.52d	7.95c
Cypress	20/50	62.1c	1.04a	6.62a
	40/12	61.2bc	1.18b	7.48b
	60/17	58.3ab	1.38c	7.32b

^a T, drying temperature (°C); RH, relative humidity (%).

^b Values followed by the same letter in the same column are not significantly different ($P < 0.05$).

TABLE III
Differences in Distribution (%) of Starch Molecular Sizes and Amylopectin Chains Between Bengal and Cypress Rice Cultivars

Structural Feature	Bengal	Cypress
Starch molecular sizes		
Amylopectin	77.37 ± 0.64	58.33 ± 0.51
Amylose	16.07 ± 0.42	26.20 ± 0.33
Intermediate material	6.57 ± 0.31	15.47 ± 0.62
Amylopectin Chains		
DP 6–12 (A chain)	24.30 ± 0.20	19.30 ± 0.40
DP 13–24 (B1 chain)	50.77 ± 0.09	51.03 ± 0.11
DP 25–36 (B2 chain)	14.03 ± 0.04	15.17 ± 0.29
DP 37–60 (B3+longer chains)	10.90 ± 0.13	14.47 ± 0.22
Average chain length (DP)	20.47 ± 0.09	22.50 ± 0.07

The chain-length distribution of amylopectin was determined by high-performance anion-exchange chromatography with pulsed amperometric detection (HPAEC-PAD) according to the method of Kasemsuwan et al (1995) with modifications (Wang and Wang 2000). The HPAEC system (Dionex DX500 Sunnyvale, CA) components were GP50 gradient pump, LC20-1 chromatography organizer, ED40 electrochemical detector, 4x50 CarboPac PA1 guard column, 4x250-mm CarboPac PA1 analytical column, and AS40 automated sampler.

Statistical Analysis

The experimental data were analyzed with SAS for Windows, v. 8.1 (SAS Institute, Cary, NC). Analysis of variance was done to detect any significant contribution of drying regime and cultivar on the different physicochemical properties examined. Significantly different means were identified by Duncan's multiple range test at $P < 0.05$.

RESULTS AND DISCUSSION

Milling and Starch Yield

The data on milling yield (total milled rice and head rice), grain translucency, and grain whiteness are shown in Table I. High-temperature drying resulted in a lower head rice yield for the medium-grain Bengal but not for the long-grain Cypress. The drying regimes did not cause significant effects on total milled rice yield, grains translucency, and grain whiteness. Table II shows the data on starch extraction yield as well as the total carbohydrates and total soluble solids in the pooled supernatant and wash water used in extracting the starch. Drying at 60°C resulted in a significantly lower starch yield for both cultivars. The decrease in starch yield was accompanied by an increase in the amount of total carbohydrates and total soluble solids. However, based on the numbers presented in Table II, the amount of starch recovered plus the amount of soluble solids and total carbohydrates in the pooled supernatant could not fully account the total starch content of the rice grain which is ≈90% (db) (Juliano 1998). This implies that the yellow curd that is normally discarded in the routine alkaline-steeping method of extracting starch still contains some starchy materials aside from protein. The yellow curd may contain some initial products of nonenzymatic browning and carbohydrate-protein complex. It is inferred that the high-temperature drying altered some of the starch granules in the rice grains, which in turn, contributed to the observed decrease in head rice and starch yields, and the change in solubility-extractability behavior of the rice grains in dilute alkaline (NaOH) solution.

Distributions in Starch Molecular Size and Amylopectin Chain

Figure 1 shows the molecular size distribution of Bengal and Cypress starches and their percentages based on the areas of the peaks are summarized in Table I. Starch fractions were categorized into amylopectin (A), intermediate material (B), and amylose (C) based on the retention time because of their differences in molecular size. Bengal was higher in percentage amylopectin but lower in intermediate material and amylose content compared with

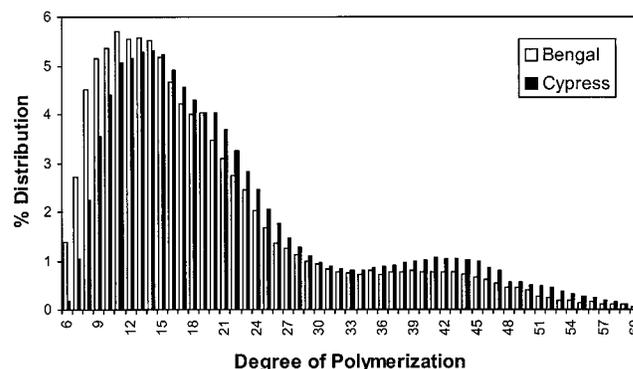


Fig. 2. Chain-length distribution of isoamylase-debranched amylopectin from rice cultivars Bengal and Cypress as determined by high-performance anion exchange chromatography with pulsed amperometric detection.

Cypress. Figure 2 presents the chain-length distribution of isoamylase-debranched amylopectin from Bengal and Cypress as resolved by HPAEC-PAD. Bengal had more short chains (DP 6–12) and lesser long chains (DP 37–60) compared with Cypress (Table III). The chains corresponding to DP 13–36 were comparable for both cultivars. Cypress was higher with respect to the average length of the amylopectin branch chains than Bengal (Table III). No significant differences in apparent molecular size distribution of starch and amylopectin chain-length distribution were observed as a result of drying regime for either cultivar (data not shown). This suggests that the composition and purity of the starches isolated by the alkaline-steeping procedure were fairly uniform within cultivar and across drying treatments. Although it was earlier inferred that some starch granules were altered by high-temperature drying, the altered granules may either get dispersed into the solvents used to extract and wash starch or become incorporated with protein in the yellow curd that was discarded in the extraction process.

Pasting Properties of Rice Flour and Starch

The pasting property data obtained with a Brabender Viscoamylograph are shown in Table IV (for flour) and Table V (for starch). Bengal rough rice dried at 40 and 60°C resulted in higher flour peak, final, and breakdown viscosities, and paste consistency compared with the batch dried at 20°C. These differences, however, were not observed in the Cypress flour samples regardless of the drying temperature. In a related study, Champagne et al (1998) observed that a commercial drying temperature of 60°C affected the cooked rice cohesiveness of Bengal but not the other cultivars. Similarly, high-temperature drying affected the head rice yield of Bengal and not of Cypress (Table I). Hence, there is a cultivar disparity in terms of sensitivity or response to air temperature and relative humidity treatments. Aside from the differences in starch fine structures between Bengal and Cypress (Figs. 1 and 2, and Table III), another possible reason for the disparity is the difference in protein content and composition between the cultivars. Chung et al (2000) found that Cypress was higher in total extractable protein content and 60 kDa protein fraction compared with Bengal. Proteins with disulfide bonds affect amylograph viscosity by its ability to restrict starch granule swelling during gelatinization (Hamaker and Griffin 1993). Hamaker and Griffin (1993) inferred that when disulfide bonds were disrupted, rice granules could swell to a larger size, thereby increasing viscosity. A high drying temperature possibly induced disruption of protein disulfide bonds as the flours from Bengal rough rice dried at 40 and 60°C had higher amylograph viscosities compared with the sample dried at 20°C.

Although cultivar variation was evident, drying regime had no apparent effect on the pasting properties of the isolated starches (Table V). This indicates that the isolated starches were fairly uniform in purity and composition regardless of the drying regime used. The

TABLE IV
Pasting Properties of Flours (10% slurry, db) as Affected by Rough Rice Drying Regimes

RiceCultivar	T/RH ^a	Paste Viscosity Parameter (BU)					
		Pasting Temp. (°C)	Peak	Final	Breakdown	Setback	Consistency
Bengal	20/50	70.5a ^b	525a	503a	222a	23b	200a
	40/12	71.0a	618b	588b	310b	30b	280b
	60/17	71.0a	643b	593b	328b	50b	278b
Cypress	20/50	76.0b	738c	870c	323b	-137a	460c
	40/12	76.0b	730c	875c	320b	-145a	465c
	60/17	76.0b	730c	882c	307b	-153a	460c

^a T, drying temperature (°C); RH, relative humidity (%).

^b Values followed by the same letter in the same column are not significantly different ($P < 0.05$).

TABLE V
Pasting Properties of Starches (10% slurry, db) as Affected by Rough Rice Drying Regimes

RiceCultivar	T/RH ^a	Paste Viscosity Parameter (BU)					
		PastingTemp. (°C)	Peak	Final	Breakdown	Setback	Consistency
Bengal	20/50	70.0a ^b	1,258b	918a	633b	340b	293a
	40/12	69.5a	1,240b	933a	610b	307b	303a
	60/17	70.0a	1,273b	983a	648b	290b	358b
Cypress	20/50	76.3b	1,143a	1,120b	525a	23a	503c
	40/12	76.0b	1,183a	1,150b	533a	33a	500c
	60/17	76.0b	1,170a	1,160b	515a	10a	545c

^a T, drying temperature (°C); RH, relative humidity (%).

^b Values followed by the same letter in the same column are not significantly different ($P < 0.05$).

TABLE VI
Thermal Properties of Rice Flours and Starches as Affected by Rough Rice Drying Regimes

Rice Cultivar	T/RH ^a	Flour			Starch		
		Onset Temp. (°C)	Peak Temp. (°C)	Enthalpy (J/g)	Onset Temp. (°C)	Peak Temp. (°C)	Enthalpy (J/g)
Bengal	20/50	66.5a ^b	73.0a	9.0a	66.7a	72.6a	12.5a
	40/12	67.0a	73.1a	8.9a	67.8a	73.0a	12.7a
	60/17	66.7a	73.1a	9.2a	65.8a	71.7a	12.7a
Cypress	20/50	74.2b	79.1b	9.4a	73.8b	78.3b	15.0b
	40/12	74.4b	79.4b	8.9a	73.6b	78.3b	14.9b
	60/17	74.9b	79.7b	9.2a	73.9b	78.6b	15.1b

^a T, drying temperature (°C); RH, relative humidity (%).

^b Values followed by the same letter in the same column are not significantly different ($P < 0.05$).

amylograph viscosities were higher for starches compared with those of the flour counterparts because protein and other alkali-soluble components did not contribute to as much viscosity as starch did.

Thermal Properties

The thermal properties of the flours and starches assessed by differential scanning calorimetry are presented in Table VI. The thermal properties of both flours and starches were apparently unaffected by the conditions used in drying rough rice. Cultivar effect was noticeable, with Bengal being lower in onset temperature, peak temperature, and enthalpy of gelatinization compared with Cypress. Enthalpy of gelatinization was higher for the starch samples compared with the flour counterparts. These findings are consistent with those of Russel (1987) and Fan et al (1999), suggesting that rice flour had a lower gelatinization enthalpy than pure starch due to the enthalpy-lowering effects of the nonstarch components in flour.

CONCLUSIONS

The starches isolated from rough rice samples dried using different combinations of air temperature and relative humidity differed mainly in extraction yield but not in fine structures (molecular size distribution and amylopectin chain-length distribution), pasting characteristics, and thermal properties. The decrease in starch and milling yields, the changes in flour pasting properties, as well as the increase in total soluble solids and total carbohydrates in the pooled supernatant used in isolating starch are indications that some starch granules of the rice grains were altered by high-temperature drying. The effects of high-

temperature drying on rice functionality (particularly, head rice yield, starch yield, and flour pasting properties) were more apparent in the medium-grain Bengal than in the long-grain Cypress. Hence, attention should be observed in drying rough rice because optimum drying conditions are likely to differ from one cultivar to another.

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