

# Effects of Rough Rice Storage Conditions on Gelatinization and Retrogradation Properties of Rice Flours<sup>1</sup>

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## ABSTRACT

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Changes in gelatinization and retrogradation properties of two rice cultivars, Bengal and Kaybonnet, during rough rice storage were studied using differential scanning calorimetry (DSC). The storage variables included two storage moisture contents (12 and 14%), three storage temperatures (4, 21, and 38°C), and four storage durations (0, 3, 9, and 16 weeks). Rough rice cultivar, storage temperature, moisture content, and duration affected ( $P < 0.05$ ) the enthalpies and temperatures of gelatin-

ization and retrogradation of rice flour. Bengal had a higher gelatinization enthalpy ( $P < 0.005$ ) but lower gelatinization temperatures ( $P < 0.0001$ ) than the long-grain Kaybonnet. Rice stored at 38°C exhibited higher gelatinization enthalpy and temperatures ( $P < 0.05$ ) than those stored at 4 or 21°C. Storage duration affected the gelatinization and retrogradation properties through a higher order, rather than a linear, relationship.

Rice undergoes a series of chemical and physicochemical changes during storage, particularly in the first few months of storage after the harvest. These changes significantly affect milling quality, cooking properties, and flour functionality. Rice exhibits a higher hardness index and head rice yield after several months of storage (Villareal et al 1976). There is a significant change in texture and sensory properties of cooked rice after the milled rice is stored for a period of time (Perez and Juliano 1981). Water uptake and volume expansion of cooked rice increases, whereas solubility of amylose, stickiness, and solids loss upon cooking decrease as storage time increases (Indudhara Swamy et al 1978, Chrastil 1990). Amylograph peak viscosity also increases after freshly harvested rice is stored for a certain period of time (Perez and Juliano 1981, Perdon et al 1997). Storage changes in rice properties tend to occur at a faster pace in high-amylose rather than in low-amylose cultivars (Indudhara Swamy et al 1978).

Although previous studies documented observed changes, limited information is available concerning quantitative relationships between storage parameters and changes in rice quality and functionality. Gras et al (1989) provided an expression relating the rate of yellowing of milled rice to temperature, water activity, and oxygen concentration in stored rice and reported that the major factors affecting the rate of yellowing of rice were storage temperature and water activity. In a recent study of long-grain rice storage, Daniels et al (1998) reported that cooking properties and amylographic peak viscosity were related to rough rice storage temperature and duration through nonlinear rather than linear relationships and that there were significant interaction effects among the postharvest parameters on rice properties.

Starch is the predominant component in rice; therefore, gelatinization and retrogradation of starch significantly influence the properties of cooked rice and the use of rice flour as a food ingredient (Juliano 1990, Perez et al 1993). Typical U.S. short- and medium-grain cultivars have relatively low gelatinization temperatures, whereas long-grain cultivars have intermediate gelatinization temperatures (Webb 1985). Marshall (1992) showed that gelatinization temperatures of whole rice grain decreased, but the associated gelatinization enthalpy increased, as the degree of milling

increased. In a recent study of thermal properties of Cypress rice using differential scanning calorimetry (DSC), Fan et al (1999) found that predrying, drying, and storage treatments had significant effects on gelatinization and retrogradation characteristics of rice flour. However, no information is available in the literature relating starch gelatinization and retrogradation behaviors of rice flour to rough rice storage history.

The objective of this work, therefore, was to quantify the effects of rough rice storage temperature, moisture content, and duration on the subsequent gelatinization and retrogradation behaviors of Bengal and Kaybonnet rice flours.

## MATERIALS AND METHODS

### Experimental Design

Two rice cultivars were used in this study: Bengal, a medium-grain cultivar, and Kaybonnet, a long-grain cultivar. For each cultivar, storage treatments consisted of two storage moisture contents (12 and 14% wb), three storage temperatures (4, 21, and 38°C), and four storage durations (0, 3, 9, and 16 weeks), for a total of 48 different sample treatments in the study.

### Rice Harvest

Both cultivars were harvested using a plot combine in the Fall of 1996. The Bengal was harvested from the University of Arkansas (UofA) Rice Research and Extension Center (Stuttgart, AR) with a moisture content (mc) of 18.0% wb, and the Kaybonnet was harvested from the UofA Northeast Research Extension Center (Keiser, AR) with 18.3% mc, wb.

### Drying and Storage

The rough rice was immediately transported to the UofA Rice Processing Laboratory on the day of harvest and cleaned in a Carter-Day dockage tester (Seedboro Equipment Co., Chicago, IL). Top and middle screen sizes were no. 28 and no. 25, respectively, while the bottom screen size for the long- and medium-grain cultivars was no. 22 and no. 4, respectively.

The rough rice was subjected to a 20-min drying treatment in a thin-layer (<2 cm) dryer with air supplied by a commercial relative humidity and temperature control unit (Climate-Lab-AA, Parameter Generation and Control, Inc., Black Mountain, NC). The drying air was controlled at 60.0°C and 16.9% rh, which corresponded to an equilibrium of 5.8% mc, as calculated by the Chung equation (ASAE 1995). Upon removal from the drier, the samples were immediately transferred to a conditioning chamber controlled at 21°C and 50% rh and equilibrated until reaching the target moisture contents of 12.0 or 14.0% (<1 week). Subsequently, each lot of equilibrated rice was divided through a Boerner divider (Seedboro) into 1,400-g samples that were placed in individual per-

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forated plastic bags. Four bags for each cultivar-moisture content-temperature combination were placed into an air-tight polyethylene bucket and stored in one of three storage chambers maintained at 4, 21, or 38°C. One sample was then removed from each bucket at 0, 3, 9, and 16 weeks.

### Flour Preparations

After each prescribed storage period, three 150-g subsamples were randomly separated from each original sample and equilibrated for 6–8 hr at room temperature in sealed plastic bags. Each 150-g subsample was dehulled in a McGill laboratory hulling machine (Seedboro). The resulting brown rice was milled in a McGill #2 laboratory mill for 26–76 sec, yielding a  $90 \pm 3$  degree of milling on a MM-1B milling meter (Satake, Hiroshima, Japan). The head rice was collected using a double-tray shaker table (Seedboro) where both trays had 4.76- and 3.97-mm indentations for the Kaybonnet and Bengal rice samples, respectively. Head rice (60 g) was then ground to flour in a laboratory cyclone mill equipped with a 0.5-mm screen (Udy Corp., Fort Collins, CO).

### Gelatinization and Retrogradation Measurements

Gelatinization and retrogradation of rice flour were evaluated using DSC (Pyris 1, Perkin-Elmer Co. Norwalk, CT). Rice flour (3.5–4.5 mg) was weighed into an aluminum DSC sample pan, and distilled water was added through a microsyringe to give a water-to-flour (dry solid) ratio of 2.5:1 (w/w) after determining the flour moisture content (AOAC 1990). Immediately thereafter, the sealed sample pans were first heated from 20 to 110°C, with a heating rate of 10°C/min, to determine the gelatinization enthalpy and temperature. The gelatinized samples were then held at 4°C for seven days (in the sample pans) and subsequently rescanned from 20 to 90°C at 10°C/min to determine the retrogradation temperature and enthalpy. A pan containing 15  $\mu$ L of distilled water was used as a reference during scanning. The DSC instrument was calibrated using indium.

The temperatures and enthalpies for gelatinization and retrogradation were extracted from the DSC thermograms with Pyris data analysis software (Perkin-Elmer). The enthalpy ( $\Delta H$ , J/g of rice flour, dwb) required to melt starch crystallites was measured

from the area of endothermic peaks in the thermograms. Onset temperature ( $T_o$ ), peak temperature ( $T_p$ ), and conclusion temperature ( $T_c$ ) of thermal transitions were determined as in Russell (1987). Three replicate measurements were conducted for each sample. The standard deviations among replicates for all samples was  $<0.6$  J/g for enthalpy and  $<0.5^\circ\text{C}$  for temperature.

### Statistical Analysis

An analysis of variance (ANOVA) was first performed to determine the significant postharvest factors and interactions affecting the gelatinization and retrogradation properties of rice flour. A full polynomial model was then constructed, including all significant terms and interactions, with higher order terms as allowed by the degrees of freedom for each variable (Daniels et al 1998). The significant polynomial terms were used to assess the relationships between the rough rice storage conditions and the rice flour properties. Duncan's multiple range tests were also conducted on the main effect means. Significance of all tests was established at  $\alpha = 0.05$  unless otherwise indicated. All statistical analyses were conducted with SAS statistical analysis software (SAS Insitute, Cary, NC).

## RESULTS AND DISCUSSION

### Data Trends

In general, the gelatinization enthalpy increased as the rough rice storage duration increased (Tables I and II). For example, after 16 weeks of rough rice storage at 38°C and 12% mc, the gelatinization enthalpy of Bengal rice flour increased from 9.7 to 10.9 J/g. The gelatinization temperatures varied with storage duration as well. The change in the conclusion temperatures of gelatinization appeared to be greater than that in the onset and peak temperatures at a given storage duration. Compared to the medium-grain Bengal, long-grain Kaybonnet rice flour gelatinized at a higher temperature.

The transitions for retrogradation of gelatinized Bengal or Kaybonnet rice flour took place at relatively low temperatures, typically from 45 to 63°C (Tables I and II). Both rice cultivars exhibited similar retrogradation peak temperatures of  $\approx 55^\circ\text{C}$ . Kaybonnet

TABLE I  
Gelatinization and Retrogradation Properties of Flour from Bengal Rice with Different Storage Durations and Temperatures

Moisture Content (%)	Storage Duration (weeks)	Storage Temp. (°C)	Gelatinization <sup>a</sup>				Retrogradation <sup>a</sup>			
			$\Delta H$ (J/g)	$T_o$ (°C)	$T_p$ (°C)	$T_c$ (°C)	$\Delta H$ (J/g)	$T_o$ (°C)	$T_p$ (°C)	$T_c$ (°C)
		No storage	9.7	64.8	70.5	77.0	1.1	45.6	54.3	60.9
12	3	4	8.2	64.5	70.7	77.4	1.0	45.6	56.3	62.0
		21	8.9	63.7	69.9	77.3	1.8	45.7	55.9	61.6
		38	9.4	64.1	70.1	76.8	1.3	45.9	56.3	60.9
	9	4	9.2	64.2	70.7	78.0	0.6	44.7	55.8	62.6
		21	9.1	64.5	70.6	77.8	1.1	46.3	56.0	62.1
		38	9.5	64.6	71.2	78.4	0.3	47.1	56.5	62.6
	16	4	9.6	65.7	71.8	78.5	1.7	46.7	55.8	62.7
		21	9.9	66.3	72.1	79.2	2.0	44.1	55.5	63.8
		38	10.9	66.7	72.8	79.3	1.9	45.4	55.2	62.5
14	3	4	8.8	64.3	70.4	77.3	1.2	47.2	56.5	62.0
		21	8.4	63.0	69.3	75.8	0.5	47.2	55.5	61.0
		38	8.5	63.5	69.7	76.9	1.3	45.8	55.5	61.1
	9	4	8.5	64.2	70.5	77.9	0.8	46.9	56.5	62.6
		21	8.6	64.3	70.5	77.8	0.6	47.5	56.0	62.4
		38	8.6	65.2	71.0	78.7	0.9	46.1	55.6	62.8
	16	4	10.4	64.7	71.3	79.3	1.8	46.0	56.5	62.9
		21	10.2	65.1	71.6	80.9	2.4	46.3	56.3	63.8
		38	11.6	65.9	72.9	81.5	2.2	45.5	55.7	63.6

<sup>a</sup>  $T_o$ ,  $T_p$ , and  $T_c$  (°C) = onset, peak, and conclusion temperatures, respectively. Means of triplicate measurements.

**TABLE II**  
**Gelatinization and Retrogradation Properties of Flour from Kaybonnet Rice with Different Storage Durations and Temperatures**

Moisture Content (%)	Storage Duration (weeks)	Storage Temp.(°C)	Gelatinization <sup>a</sup>				Retrogradation <sup>a</sup>			
			$\Delta H$ (J/g)	$T_o$ (°C)	$T_p$ (°C)	$T_c$ (°C)	$\Delta H$ (J/g)	$T_o$ (°C)	$T_p$ (°C)	$T_c$ (°C)
		No storage	8.2	70.5	75.1	80.6	5.8	45.3	55.1	63.7
12	3	4	7.4	70.6	75.2	80.7	5.9	44.1	55.2	63.0
		21	7.9	70.4	75.0	81.0	6.1	44.2	55.6	62.5
		38	7.8	70.7	75.2	80.9	6.2	43.8	55.5	62.2
	9	4	8.7	69.8	75.5	80.8	5.3	45.6	56.4	64.9
		21	10.0	70.8	75.7	81.4	5.1	46.0	56.7	65.2
		38	9.8	70.9	76.1	82.4	5.5	46.4	56.7	65.4
	16	4	9.4	69.5	75.0	79.5	6.1	44.8	54.8	64.0
		21	9.5	69.8	75.2	80.2	7.2	44.3	54.4	63.7
		38	9.8	70.0	76.3	81.2	6.2	45.0	55.1	63.3
14	3	4	7.5	70.2	74.9	81.1	6.2	44.6	55.5	62.5
		21	7.7	70.6	75.4	81.1	5.9	44.8	55.5	65.7
		38	7.1	71.1	76.0	82.0	6.0	45.1	55.5	62.2
	9	4	9.4	70.1	75.6	81.6	5.0	45.4	55.7	65.3
		21	9.7	70.7	75.6	81.7	4.9	46.0	56.4	65.7
		38	9.8	70.8	76.1	82.4	4.9	46.6	56.3	64.2
	16	4	9.4	69.4	75.3	80.1	6.7	43.4	54.8	64.1
		21	9.3	69.7	75.6	80.2	6.1	44.0	55.4	65.7
		38	9.5	70.1	76.7	81.7	5.8	46.1	55.8	64.2

<sup>a</sup>  $T_o$ ,  $T_p$ , and  $T_c$  (°C) = onset, peak, and conclusion temperatures, respectively. Means of triplicate measurements.

rice flour (no storage) had a retrogradation enthalpy of 5.8 J/g (4°C, seven days), whereas the retrogradation enthalpy for Bengal rice was only 1.1 J/g at the same retrogradation conditions. The greater degree of retrogradation with Kaybonnet was largely due to its higher amylose content (Fan and Marks 1998). Although the gelatinization temperatures were markedly different, Kaybonnet exhibited retrogradation temperatures close to those of Bengal.

### Statistical Analyses

The ANOVA showed that cultivar had a significant effect on the enthalpy and temperatures of gelatinization and retrogradation of rice flours from previously stored rice (Table III). Bengal had a higher ( $P < 0.005$ ) gelatinization enthalpy and lower ( $P < 0.0001$ ) onset, peak, and conclusion temperatures than Kaybonnet. Kaybonnet flour had higher ( $P < 0.0001$ ) retrogradation enthalpies than Bengal flour. Additionally, Kaybonnet showed significantly lower onset and peak temperatures of retrogradation ( $P < 0.05$ ) but a significantly higher conclusion temperature ( $P < 0.001$ ) than Bengal.

Storage moisture contents (12 and 14%) did not significantly affect the enthalpies or peak temperatures of gelatinization and retrogradation of Kaybonnet and Bengal rice flours (Table III). However, rice stored at 14% mc exhibited a higher ( $P < 0.05$ ) conclusion temperature of gelatinization and onset temperature of retrogradation than the other samples.

Storage temperature significantly affected gelatinization properties of flour from previously stored rice (Table III). Rice stored at 38°C showed significantly higher gelatinization enthalpy and temperatures ( $P < 0.05$ ) than did rice stored at 4 or 21°C. These results were consistent with what was previously reported for long-grain Cypress rice stored for 20 weeks after different predrying and drying treatments (Fan et al 1999). There was also a significant interactive effect of storage temperature and storage duration on gelatinization peak temperature ( $P < 0.05$ ). Additionally, rough rice storage temperature had an interactive effect with cultivar and moisture content ( $P < 0.05$ ) on retrogradation onset and peak temperatures, but it did not affect retrogradation enthalpy.

Rough rice storage duration had a significant effect on both gelatinization and retrogradation of rice flour (Table III). The

mean gelatinization enthalpy after 16 weeks of storage was higher ( $P < 0.05$ ) than those after three or nine weeks. The mean peak temperatures of gelatinization did not significantly change during the first three weeks of storage. However, the rice stored for 9 or 16 weeks showed a higher ( $P < 0.05$ ) gelatinization peak temperature than that stored for 0 or 3 weeks.

In a study of age-induced changes for long-grain rice, Daniels et al (1998) demonstrated that head rice yield, water absorption, and volume expansion upon cooking, and amylographic peak viscosity were nonlinearly related to postharvest factors. To similarly quantify the effects of storage conditions on gelatinization and retrogradation properties, we developed a full polynomial model for such properties that contained all the significant storage terms (Table III). The effects of storage conditions on the gelatinization and retrogradation properties of rice flour were expressed in terms of polynomial models with  $R^2 \geq 0.87$  (Table IV). Rough rice storage temperature had a significant effect on the enthalpy of gelatinization through a linear relationship and on the associated peak temperature through a second-order relationship. Rough rice storage duration significantly affected the gelatinization and retrogradation properties through higher order (second or third order) relationships. Additionally, significant interactions between storage duration and cultivar or moisture content indicate that grain type and moisture content affect the rate of change for gelatinization and retrogradation properties.

### CONCLUSIONS

Rough rice cultivar, storage temperature, moisture content, and duration had significant effects on gelatinization and retrogradation properties of stored rice. Gelatinization and retrogradation properties of rice flour were not related to storage variables by simple linear relationships. Rough rice storage temperature and duration, in particular, affected flour properties by second- or third-order relationships.

The measured rice flour properties are important parameters for value-added processing. Gelatinization enthalpy of starch affects the energy required for cooking rice products. Likewise, gelatinization temperatures are directly related to rice cooking times (Juliano and

**TABLE III**  
Significance (*P* values) of Storage Variables on Gelatinization and Retrogradation Properties of Rice Flour

Source of Variation <sup>a</sup>	Degrees of Freedom	Gelatinization <sup>b</sup>				Retrogradation <sup>b</sup>			
		$\Delta H$ (J/g)	$T_o$ (°C)	$T_p$ (°C)	$T_c$ (°C)	$\Delta H$ (J/g)	$T_o$ (°C)	$T_p$ (°C)	$T_c$ (°C)
CULT	1	0.0011	0.0001	0.0001	0.0001	0.0001	0.0012	0.0176	0.0006
MC	1	...	...	...	0.0116	...	0.0238	...	
DUR	3	0.0004	0.0407	0.0009	0.0031	0.0102	0.0093	0.0005	0.0058
TEMP	2	0.0463	0.0307	0.0081	0.0145	...	...	...	...
CULT*MC	1	...	...	0.0405	...	...	...	...	...
CULT*DUR	3	0.0031	0.0012	0.0041	0.0010	...	0.0200	0.0031	...
CULT*TEMP	2	...	...	...	...	...	...	0.0105	...
MC*TEMP	2	...	...	...	...	...	...	...	...
DUR*TEMP	4	...	...	0.0403	...	...	...	...	...
CULT*MC*TEMP	2	...	...	...	...	...	0.0260	0.0415	...
CULT*MC*DUR	6	...	...	...	...	...	...	0.0310	...
CULT*DUR*TEMP	4	...	...	...	...	...	...	...	...
MC*DUR*TEMP	4	...	...	...	...	...	...	...	...

<sup>a</sup> CULT = cultivar; MC = moisture content; DUR = storage duration; TEMP = storage temperature.

<sup>b</sup>  $T_o$ ,  $T_p$ , and  $T_c$  (°C) = onset, peak, and conclusion temperatures, respectively.

<sup>c</sup> Not significant.

**TABLE IV**  
Highest Order Significant (*P* < 0.05) Terms in the Polynomial Models for Gelatinization and Retrogradation Properties as Functions of Storage Conditions (*n* = 40)

Parameters	Highest Order Significant Terms <sup>a</sup>	<i>R</i> <sup>2</sup>
Gelatinization		
Enthalpy	TEMP, CULT*DUR <sup>3</sup>	0.87
Peak temperature	TEMP <sup>2</sup> , CULT*MC, DUR <sup>3</sup>	0.99
Retrogradation		
Enthalpy	CULT, DUR <sup>2</sup>	0.98
Peak temperature	TEMP*CULT, CULT*DUR <sup>3</sup> , CULT*MC*DUR <sup>2</sup>	0.88

<sup>a</sup> CULT = cultivar; MC = moisture content; DUR = storage duration; TEMP = storage temperature. Superscripts 2 and 3 indicate second and third order relationships.

Perez 1983). Retrogradation results in the staling of cooked rice and starch gels (Perez et al 1993) and therefore affects the quality of the further processed products.

The results of this study indicate that all rough rice storage conditions (i.e., temperature, moisture content, and duration) significantly affect these flour properties. Thus, it is important to understand the relationship between postharvest handling and end-use quality of rice products. Furthermore, it may be possible to control rough rice storage conditions to produce desired changes in the functional attributes of the rice.

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