

Starch Retrogradation and Texture of Cooked Milled Rice During Storage

A.A. Perdon, T.J. Siebenmorgen, R.W. Buescher, and E.E. Gbur

ABSTRACT

The effect of storing cooked Bengal and Cypress milled rice at -13 , 3 , 20 , and 36 °C on texture and degree of starch retrogradation was investigated. Cooked rice firmness increased, while stickiness decreased, during storage at -13 and 3 °C. Starch retrogradation, measured with a differential scanning calorimeter, was observed for both cultivars during storage at -13 and 3 °C, but not at 36 °C. At 20 °C, retrogradation occurred in Cypress, but not in Bengal. Starch retrogradation showed positive linear trends with firmness for both cultivars at all storage temperatures ($R^2 = 0.80$) and with stickiness for Bengal stored at -13 and 3 °C and for Cypress stored at 3 and 20 °C ($R^2 = 0.88$).

Key Words: starch retrogradation, cooked rice, texture, storage stability

INTRODUCTION

CHANGES IN STARCH DURING CEREAL processing contribute to product texture, and the most important changes are gelatinization and retrogradation. Gelatinization is the water-mediated disruption of the molecular orders within a starch granule during heating, manifested in granular swelling, native crystallite melting, loss of birefringence, and starch solubilization (Atwell et al., 1988). Starch retrogradation is the reassociation of the molecules of gelatinized starch to form an ordered crystalline structure (Atwell et al., 1988).

The effects of starch gelatinization and retrogradation on texture of baked products are well established (Russell, 1983a, 1983b, 1987; Zeleznak and Hosenev, 1986; Krog et al., 1989; Slade and Levine, 1991). Starch is a partially crystalline, partially amorphous polymer of glucose. Amylose and the branching point of amylopectin contribute to the amorphous region and the outer chains of amylopectin contribute to the crystalline region. Baking results in a completely amorphous starch (Slade and Levine, 1991). When the gelatinized product is cooled, the amylose fraction retrogrades immediately while the amylopectin remains in an amorphous state (Miles et al., 1985a, b; Pomeranz, 1987; Bean and Setser, 1992). During storage, firmness and opacity increase in the baked product. These changes have been correlated with the reassociation and crystal formation of

the amylopectin fraction of gelatinized starch (Miles et al., 1985b; Ring et al., 1987). Keetels et al. (1996a, b) correlated the changes in the mechanical properties of wheat and potato bread with changes in sponge structure and amylopectin recrystallization.

The quality of cooked rice is affected by its starch properties, mainly amylose content (Juliano, 1985). Cooked rice with low amylose is soft and sticky, while rice with high amylose is firm and fluffy. Like bread products, cooked rice texture changes with storage (Lima and Singh, 1993). Firmness of cooked rice gradually increases during storage, and this has been attributed to starch retrogradation. Most studies relating texture or mechanical change to changes in starch properties have focused on gels from rice flour. Biliaderis and Juliano (1993) showed that gel rigidity and starch retrogradation of 22% to 35% rice starch gels increased during storage at 8 °C. They found cultivar differences in rates of increase in gel rigidity and starch retrogradation. Later studies (Perez et al., 1993; Lu et al., 1997; Villareal et al., 1997) also indicated cultivar affected the rate of retrogradation, which may be due to differences in molecular properties of the amylopectin from each cultivar.

Rice is primarily processed and consumed as a whole grain cereal. Lima and Singh (1993) showed that cultivar, storage temperature, and storage duration influenced the texture of cooked milled rice. Understanding the effects of such factors on rice texture is important to food processors to optimize conditions to produce desired texture. The objective of this study was to determine the effects of post-cooking storage temperature and duration on texture and degree of starch retrogradation

of cooked milled rice. Since cultivar differences affected the increase in firmness of cooked milled rice during storage (Antonio et al., 1975; Perez et al., 1993); two cultivars differing in starch properties were studied. Bengal, a medium-grain rice low in amylose, and Cypress, a long-grain rice high in amylose, were used. The relationships between cooked rice texture, firmness, stickiness, and degree of starch retrogradation were also quantified.

MATERIALS & METHODS

Sample collection and preparation

Bengal and Cypress rice were harvested in 1995 from the University of Arkansas Rice Research and Extension Center (Stuttgart, Ark., U.S.A.). The rough rice samples, at $\approx 18\%$ moisture content (MC), were cleaned with a Carter-Day Dockage Tester (Carter-Day Co., Minneapolis, Minn., U.S.A.), placed in double-lined paper bags, and stored at 3 °C for 18 mo prior to analysis. Before dehulling and milling, the rough rice was dried to 12.5% MC in a conditioning chamber set at 37 °C and 54% relative humidity. To produce milled rice, rough rice (150 g) was dehulled with a McGill sample sheller (Rapsco Inc., Brookshire, Texas, U.S.A.) and milled for 45 s in a McGill No. 2 mill (Rapsco Inc., Brookshire, Texas, U.S.A.) set with a 1.5-kg weight positioned on the mill lever arm 15 cm from the center of the milling chamber. Head rice was separated from "brokens" with a Seedburo sizer (Seedburo Equipment Co., Chicago, Ill., U.S.A.). The degree of milling (DOM) was measured with a Satake MM-1B milling meter (Satake USA Inc., Houston, Texas, U.S.A.). Bengal was milled to 92 and Cypress to 95 DOM. The amylose content of the milled rice from each cultivar was measured using the simplified assay procedure described by Juliano (1971).

Rice cooking

Eight batches of head rice from each cultivar were cooked according to the standard method (WRRRC) with modifications as suggested by Mossman et al. (1983). For each batch, 8 g of rice was cooked in a 30-mL beaker with 12 g of deionized water. The beaker was covered with a watch glass and placed on a screen above water boiling in an electric kettle set at 177 °C. After the

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rice steamed for 20 min, the kettle power was turned off. The cooked rice samples were held in the kettle for an additional 10 min. The beakers were removed from the kettle and placed upside down on their cover for 40 min. After cooling, the cooked rice was gently stirred, and samples were taken from each beaker to represent the control (0 h of storage) for each cultivar. Each beaker was sealed with Parafilm prior to storage. Moisture content of the cooked rice from each beaker was measured by drying the samples for 24 h at 130 °C, following the method that Jindal and Siebenmorgen (1987) developed for raw rough rice.

Cooked rice storage

Sample beakers (8) for each cultivar were assigned to 4 storage temperatures by randomly pairing the beakers. Each pair of beakers of cooked rice was sealed in a plastic bag (total 4 bags/cultivar). Each of the 4 bags was stored at a different temperature, -13, 3, 20, and 36 °C. Using a spatula wiped with 95% ethanol, the rice was sampled in duplicate from each beaker in each bag after 24, 48, 72, and 96 h of storage.

Cooked rice texture measurement

The force required to compress 3 grains of cooked rice to 0.1 mm was measured in duplicate with a TA-TX2 Texture Analyzer (Texture Technologies Corp., Scarsdale, N.Y., U.S.A.). The grains were placed 1 cm equidistant from each other. The initial height of the compression probe was set at 14.5 mm. The probe speed during compression was 1 mm/s. During retraction, the probe speed was 2 mm/s. After texture measurement, the rice was immediately collected and sealed in small vials for subsequent analysis of degree of starch retrogradation.

The XT.RA Dimension Software Version 3.2 supplied with the Texture Analyzer was used to analyze each texture profile for firmness and stickiness. The area under the force-time curve generated during compression was designated as the index for firmness with units in Newton-s (N-s). The area under the force-time curve generated during probe retraction was designated as the index for stickiness, also in N-s.

Measurement of starch retrogradation

The degree of starch retrogradation was analyzed with a Perkin-Elmer Pyris 1 differential scanning calorimeter (DSC) equipped with an Intracooler (Perkin-Elmer, Norwalk, Conn., U.S.A.). The DSC was calibrated with indium (melting point = 156.6 °C, $\Delta H_f = 28.6$ J/g). At least 20 to 25 mg of cooked rice from the 3 grains used for texture measurements was placed in pre-weighed aluminum sample pans. The pans were sealed and weighed to determine

the actual sample mass. For all DSC runs, a sealed empty aluminum pan was used as reference. The sample was held isothermally at 20 °C for 5 min before heating from 20 to 90 °C at 10 °C/min. The peak temperature and the enthalpy (ΔH_f , J/g) associated with the retrograded starch melting peak appearing between 45 and 65 °C were calculated. The ΔH_f was used to indicate the degree of starch retrogradation. The DSC analysis was done in duplicate for each of the samples from the texture measurement (total of 8 DSC analyses per cultivar/storage temperature/storage duration combination).

Statistical analysis

The texture and starch retrogradation data were analyzed as a split plot with two replications per treatment combination. The whole plot treatment structure was a completely randomized two-factor factorial with cultivar and storage temperature as the factors. The split plot factor was storage duration. A protected least significant difference (LSD) was used to separate the means. Since there was no measurable starch retrogradation, $\Delta H_f = 0$ J/g, for all

samples stored at 36 °C, this treatment level was not included in the analyses. The data from the control samples (storage duration = 0 h) were used to check cooked rice variability across samples before storage and were not included in subsequent analyses.

Regression analysis of firmness and stickiness on starch retrogradation was performed. Covariance techniques were used to check the dependence of the regression coefficients on cultivar and storage temperature. Single degree of freedom contrast was used to compare individual regression coefficients. All statistical analyses were carried out with SAS Version 6.12 (SAS Institute, Cary, N.C., U.S.A.). Results with p-values (P) < 0.05 were considered significant.

RESULTS & DISCUSSION

TYPICAL TEXTURE PROFILES OF COOKED rice (Fig. 1) showed that, based on classification of food texture profiles (Bourne, 1982), freshly cooked rice from both Bengal and Cypress had a Type A profile (concave downward, typical of soft food). After storage, the profiles changed to Type C (sigmoidal). The change to Type C was

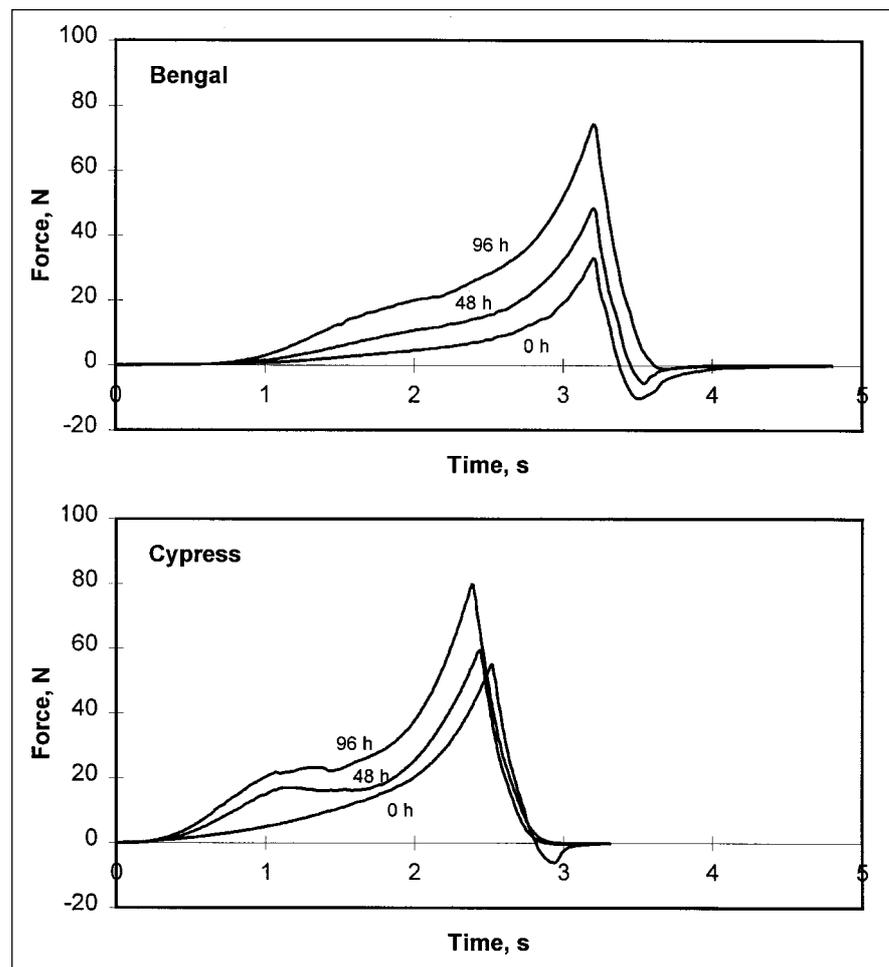


Fig. 1—Texture profiles of Bengal and Cypress cooked milled rice stored at 3 °C for 0, 48, and 96 h.

Starch Retrogradation and Texture of Cooked Rice . . .

Table 1—Analysis of variance for effects of cultivar, storage temperature^a, and storage duration on Bengal and Cypress cooked milled rice firmness, stickiness, and degree of starch retrogradation

Source	dF	Mean square firmness, N-s	P	Mean square stickiness, N-s	P	dF	Mean square starch retrogradation, ΔH_f	P
Cultivar	1	1070.16	0.0001	39.78	0.0001	1	2.17	0.0001
Temperature	3	1509.37	0.0001	11.68	0.0001	2	3.00	0.0001
Cultivar x Temperature	3	381.05	0.0004	4.44	0.0004	2	0.59	0.0025
Whole Plot Error	8	18.55	—	0.22	—	6	0.13	—
Duration	3	1722.28	0.0001	0.64	0.0222	3	3.11	0.0001
Cultivar x Duration	3	100.02	0.0548	0.20	0.3333	3	0.29	0.0204
Temperature x Duration	9	107.74	0.0120	0.22	0.2841	6	0.26	0.0127
Cultivar x Temperature x Duration	9	39.94	0.3599	0.20	0.3400	6	0.15	0.0969
Split Plot Error	24	34.29	—	0.16	—	18	0.07	—

^aData from storage at 36 °C were not included in the statistical analysis for degree of starch retrogradation.

more pronounced for Cypress than Bengal. Keetels et al. (1996a) had reported similar changes in texture profiles of wheat and potato bread after storage.

Analysis of the effects of storage conditions on firmness showed no significant interactions between cultivar, storage temperature, and storage duration (Table 1). However, temperature had significant interactions with cultivar and duration separately ($P = 0.0004$ and 0.0120). Bengal mean firmness values during storage at -13 and 3 °C were different (Fig. 2) from mean firmness values at 20 and 36 °C. Mean

firmness value of Cypress after storage at 3 °C was higher than those at the other storage temperatures. There was difference in firmness values between Cypress cooked rice stored at -13 and 20 °C. The rice stored at 36 °C had the lowest mean firmness. The high mean firmness score for cooked Cypress milled rice was expected because of its high amylose content (25%).

As with firmness, stickiness of cooked rice was not affected by cultivar, storage temperature, and storage duration interactions ($P = 0.3400$) but was affected by cultivar and storage temperature interactions

($P = 0.0004$). Mean stickiness values for Bengal (Fig. 2), averaged across storage durations, decreased at low temperature storage (-13 and 3 °C). The higher mean stickiness value for Bengal was due to its lower amylose content (16%).

Firmness almost doubled from 35.6 N-s to 61.0 N-s (Fig. 3) when cooked rice was stored at -13 °C for 72 h or longer. At 3 °C, firmness increased after storage for 48 h. These results showed that cooked rice firmness increased more during low temperature storage (≤ 3 °C) than higher temperature storage (20 and 36 °C) for both cultivars.

The degree of starch retrogradation, measured by the increase in ΔH_f between 45 and 65 °C, was not affected by cultivar, storage temperature, and storage duration interaction ($P = 0.0969$, Table 1). Storage duration interacted independently with cultivar ($P = 0.0204$, Fig. 4) and storage temperature ($P = 0.0127$, Fig. 5). Increasing storage duration from 24 to 96 h increased the degree of starch retrogradation from 0.27 J/g to 1.30 J/g for Bengal (Fig. 4). For Cypress, ΔH_f increased more rapidly, reaching 1.00 J/g after 48 h storage. This result indicates different retrogradation kinetics for Bengal and Cypress and was expected, since the starch properties of these two cultivars are different. An initial increase in ΔH_f occurred after storage at 3 °C for 48 h (Fig. 5). This result was in agreement with research on kinetics of starch retrogradation where nucleation was the rate-limiting step (Slade and Levine, 1991). The rate of nucleation at 60% moisture content is highest at 4 °C (Slade et al., 1987). The moisture content of all the cooked rice samples tested ranged from 62% to 66% (wb).

Starch retrogradation had a direct linear relationship with firmness (Fig. 6), and the regression coefficients did not depend on cultivar or storage temperature ($P = 0.6229$). Firmness of cooked rice increased by 18.8 N-s for every unit increase in ΔH_f . The relationship between starch retrogradation and stickiness was more complex and was dependent on cultivar and storage temperature ($P = 0.0001$). Linear relationships (Fig. 7) were found between stickiness and

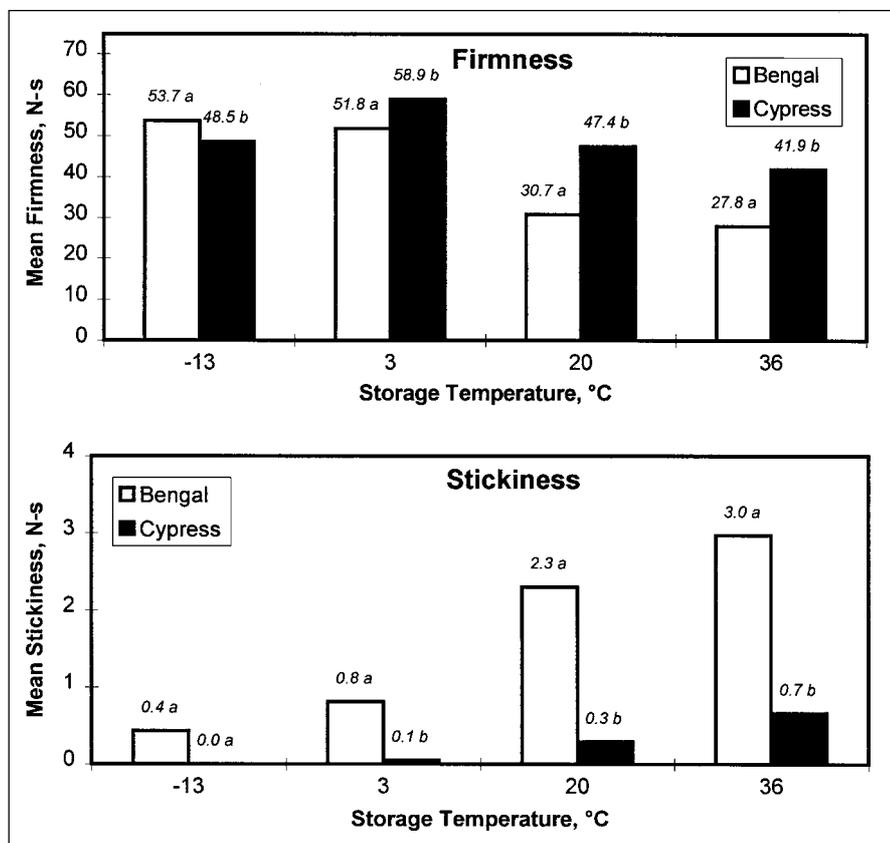


Fig. 2—Effect of storage temperatures on mean firmness^a and stickiness^b (averaged across storage duration) of Bengal and Cypress cooked milled rice.

^{a,b}Using a protected LSD_{0.05}, values followed by the same letter are not significantly different from each other.

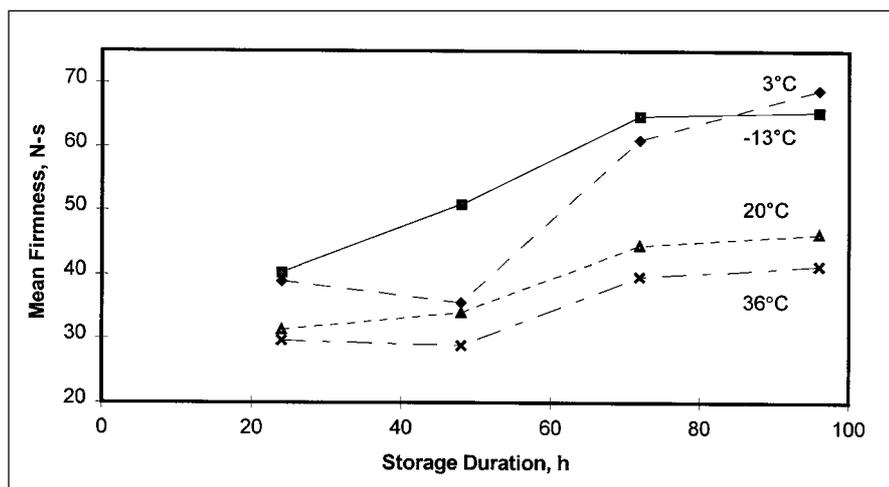


Fig. 3—Effect of storage duration on mean firmness^a (averaged across cultivars) of cooked rice stored at different temperatures.

^aLSD_{0.05} to compare any pair of mean firmness values at the same storage temperature = 8.7 N-s. LSD_{0.05} to compare any pair of mean firmness values at different storage temperatures = 8.0 N-s.

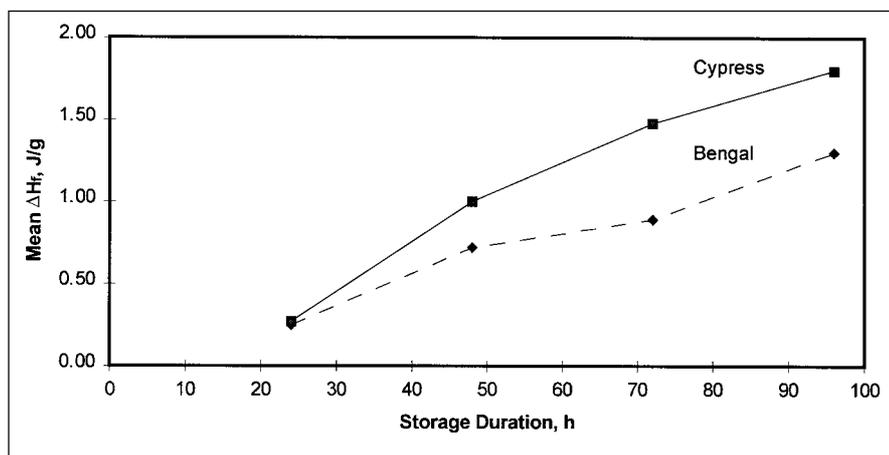


Fig. 4—Effect of storage duration on mean degree of starch retrogradation^a, ΔH_r , (averaged across storage temperatures) in Bengal and Cypress cooked milled rice.

^aLSD_{0.05} to compare any pair of mean ΔH_r s for the same cultivars = 0.39 J/g. LSD_{0.05} to compare any pair of mean ΔH_r s for different cultivars = 0.67 J/g.

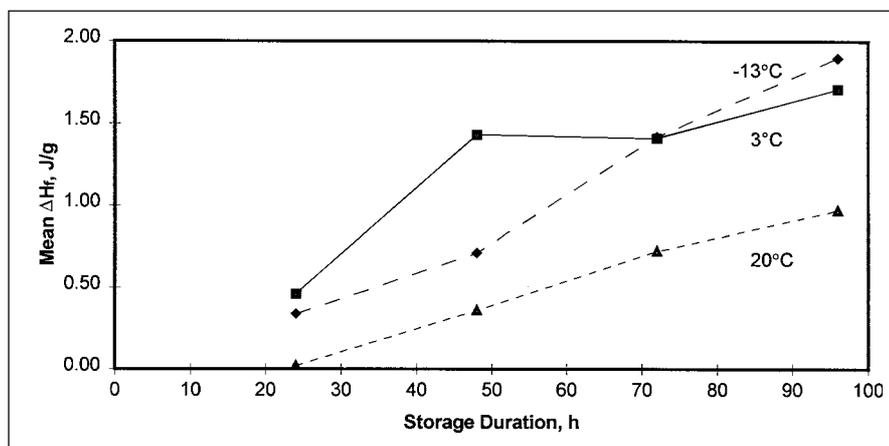


Fig. 5—Effect of storage duration on mean degree of starch retrogradation^a, ΔH_r , (averaged across cultivars) in cooked milled rice stored at different temperatures.

^aLSD_{0.05} to compare any pair of mean ΔH_r s at the same storage temperature = 0.39 J/g. LSD_{0.05} to compare any pair of mean ΔH_r s at different storage temperature = 0.55 J/g.

ΔH_r for Bengal and Cypress cooked milled rice stored at -13, 3, and 20 °C. Regression results for Bengal stored at 20 °C and Cypress stored at -13 °C were not significant. Data for storage at 36 °C for both cultivars were not included because the starch did not retrograde at that temperature (all the ΔH_r s were 0 J/g).

The regression equations of stickiness with the degree of starch retrogradation for Bengal stored at -13 and 3 °C (Fig. 7) were different from each other, with storage at 3 °C showing the strongest correlation. At this condition, stickiness decreased by 1.2 N-s for every unit increase in ΔH_r . At -13 °C, stickiness decreased by 0.5 N-s for every unit increase in ΔH_r . Both regression results were also different from the regression equations obtained for Cypress stored at 3 and 20 °C. In contrast to Bengal, the linear regressions of stickiness with starch retrogradation for Cypress stored at either temperature were not different from each other.

Like other cereal-based food, the degree of starch retrogradation in cooked milled rice affected texture. In general, as the degree of starch retrogradation increased during storage, rice firmness increased and stickiness decreased. These results were similar to those reported from starch gels studies (Perez et al., 1993; Lu et al., 1997; Villareal et al., 1997). As in starch gels, cultivar differences affecting the rate of texture change and starch retrogradation may be explained by differences in the amylose/amylopectin ratios.

CONCLUSIONS

STORAGE TEMPERATURE AND STORAGE duration affected the firmness, stickiness, and degree of starch retrogradation of cooked Bengal and Cypress milled rice. At lower temperatures and longer storage, firmness of the cooked rice increased and stickiness decreased. The degree of starch retrogradation also increased during storage at temperatures below 36 °C. Correlation of the degree of starch retrogradation with firmness was significant for both cultivars at all storage temperatures. With stickiness, significant linear relations between stickiness and starch retrogradation were found for Bengal stored at -13 and 3 °C, and for Cypress stored at 3 and 20 °C. The contribution of starch retrogradation to texture changes during storage of cooked rice appears to be similar to the mechanism involved in staling of baked cereal products during storage. These results may help guide food processors in optimizing conditions to prevent or accelerate starch retrogradation in cooked rice.

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Starch Retrogradation and Texture of Cooked Rice . . .

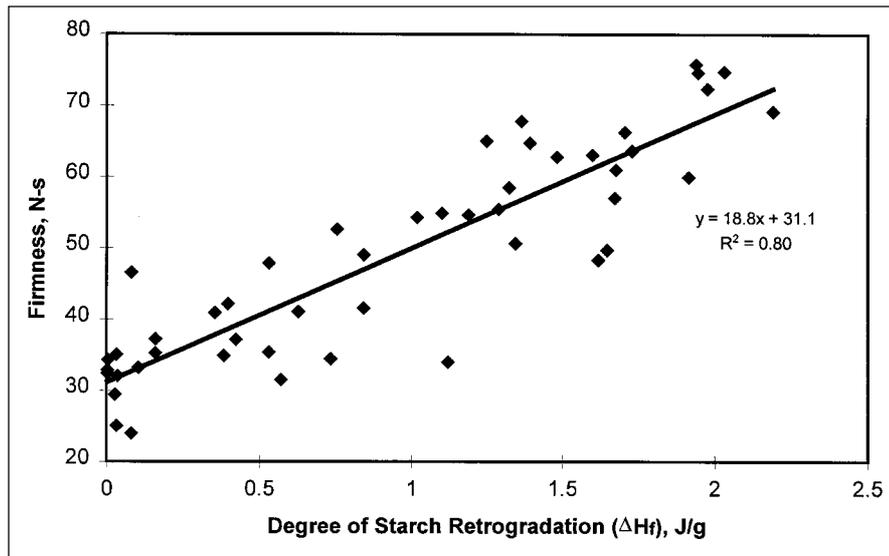


Fig. 6—Regression of measured firmness of cooked milled rice with starch retrogradation (ΔH_r , J/g). Data set includes all cultivars, storage temperatures and durations tested.

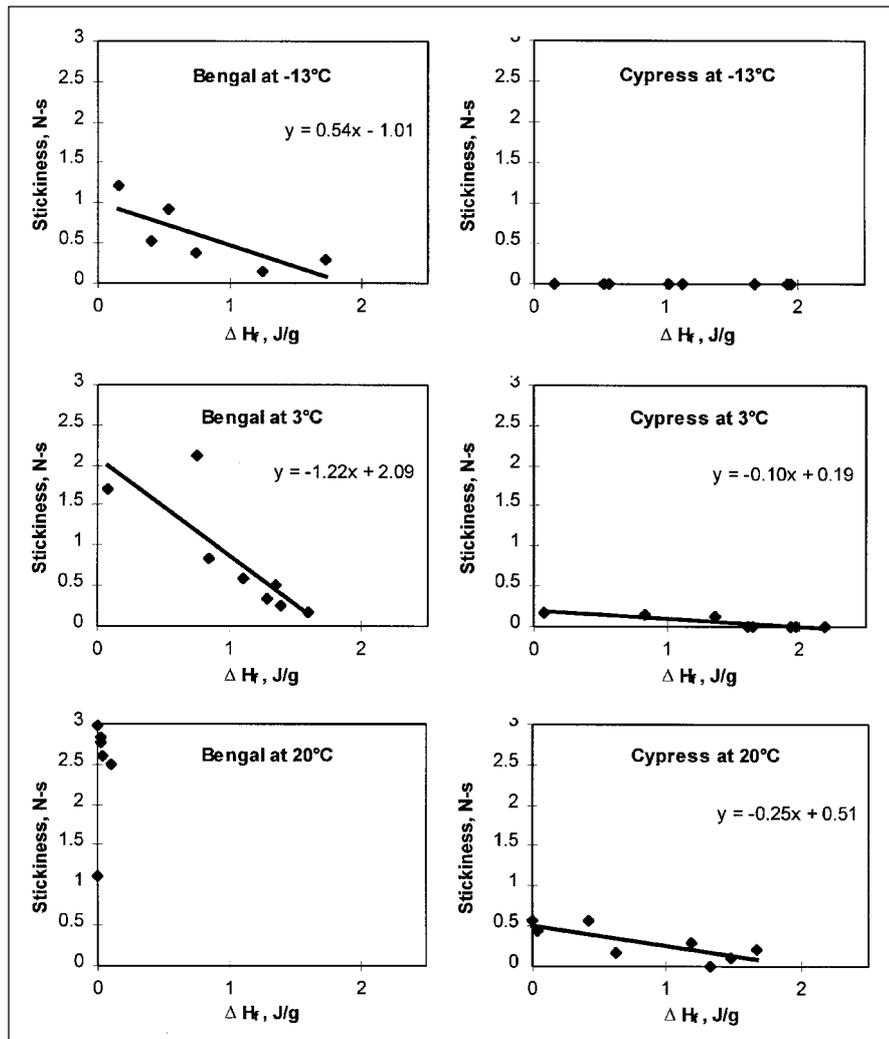


Fig. 7—Regression results of mean stickiness of Bengal and Cypress cooked milled rice stored at -13 , 3 , and 20 °C with starch retrogradation, ΔH_r (test $R^2 = 0.88$).

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