Effect of Degree of Milling of Brown Rice and Particle Size of Milled Rice on Starch Gelatinization[1]

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ABSTRACT

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Unmilled and milled Lemont long-grain rice samples were evaluated by differential scanning calorimetry to determine the effect of abrasive milling or disruption of kernel integrity on starch gelatinization. Kernel integrity was disrupted by pulverizing kernels to different particle sizes, and starch gelatinization was measured for the various fractions. Unmilled (brown) rice kernels had higher gelatinization onset (T_o), peak (T_p), and conclusion (T_c) temperatures than any milled sample. Partial removal of the bran layer resulted in a sharp decrease in these temperatures. Continued abrasive milling further decreased T_p and T_c until the degree of milling reached about 20%. Further milling to 66% had little effect on the gelatinization temperatures. Gelatinization enthalpies (ΔH) increased until a 20–25% degree of milling was attained, but no additional change was observed upon further milling. In contrast, reduction in particle size caused a large decrease in T_p, T_c, and ΔH but only a modest decrease in T_o. These results indicate that starch gelatinization can be altered through abrasive milling or changes in particle size.

The study of starch gelatinization in whole-kernel milled rice has only recently been addressed (Normand and Marshall 1989). This initial study prompted further investigation on the effect on starch gelatinization of limited milling and lipid removal in brown rice (Champagne et al 1990) and the effect of lipid and protein removal in milled rice (Marshall et al 1990). Treatment of milled rice with lipid solvents or a proteolytic enzyme resulted in a substantial decrease in gelatinization temperatures (Marshall et al 1990). However, the removal of lipid or protein, per se, had little effect on starch gelatinization. Gelatinization temperatures were reduced by greater exposure of the starch granules to water through the introduction of pits and fissures in the kernel caused by the treatments. Normand and Marshall (1989), Marshall et al (1990), and Champagne et al (1990) observed complex gelatinization endotherms for the kernel as compared with those for rice flour. Normand and Marshall (1989) postulated that this complexity was because of differences in water accessibility to starch granules, which caused gelatinization to occur at different temperatures. Marshall et al (1990) further postulated that water accessibility may be controlled by differences in composition of cellular material within specific layers of the kernel. These structures would delay starch gelatinization by acting as a barrier to water movement into the starch granules, and gelatinization would occur at higher temperatures. Champagne et al (1990) found gelatinization temperatures significantly reduced upon removal of the outer layers of the kernel. The high wax content of these layers was implicated as a barrier to water absorption and, thus, resulted in higher gelatinization temperatures. Consecutive milling of the kernel or exposure of the interior kernel surface by destruction of kernel integrity could locate further barriers to water movement and their effect on starch gelatinization.

The objectives of this study were to determine the effect on starch gelatinization of degree of milling and of controlled modification of kernel integrity by sectioning or pulverizing kernels to various particle sizes.

MATERIALS AND METHODS

Materials

Lemont (long grain) rough rice was obtained from the Louisiana State University Rice Experiment Station, Crowley, and dehulled in a McGill sheller (H. T. McGill Co., Houston, TX).

Preparation of Milled Rice

Brown rice was milled in a bench model Satake grain testing mill (model TM-05, Satake Engineering Co., Tokyo, Japan) for specific time intervals to produce different degrees of milling. For the time intervals used, the milling process generated little heat. Bran or polish was separated from the kernels using a 20-

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mesh screen. The degree of milling was determined using the following equation:

$$1 - (\text{wt of milled rice/wt of brown rice}) \times 100.$$

Kernels could not be conveniently milled to more than 66% degree of milling, i.e., 66% of the original kernel weight removed by abrasive milling, as the kernels were too small for any further milling to occur.

Particle Size Preparation and Measurement

Milled kernels were cut crosswise into one-half, one-quarter, and one-eighth sections using a sharp scalpel. The mean length of each section was determined by randomly selecting 30 kernel pieces from each group and measuring the section length of each piece using a Cambridge Instruments model 970 image analyzer (Cambridge Instruments, Ltd., Cambridge, England) equipped with a macroviewer stage. The image analyzer was operated with a Newvicon video camera (Cambridge Instruments) equipped with a Tamron 35- to 80-mm F2.8 macro/zoom lens (Tamron Co., Tokyo, Japan). Lighting was supplied by four separately adjustable incandescent lamps using automatically controlled lighting intensity. For the sectioned rice kernels, the image analyzer was calibrated so that each picture point (pixel) had a linear dimension of 0.073 mm.

Pulverized kernels were prepared by placing milled kernels in a porcelain mortar and hand grinding with a porcelain pestle. Pulverizing was done at a slow rate so that no perceptible heat was generated. The pulverized sample contained a broad range of particle sizes. The particles were passed through a series of 10 sieves with mesh sizes from 53 to 14,000 μm. The particles were collected on the wire mesh surface of the sieves and brushed into containers.

Milled rice kernels were passed through a Udy cyclone mill equipped with a 1-mm screen (Udy Corp., Fort Collins, CO). The milled flour was passed through the 10 sieves. The material collected on each sieve was weighed, and a percentage of the total weight was calculated for each particle size range.

Differential Scanning Calorimetry Analysis

Differential scanning calorimetry (DSC) was conducted using a Hart Scientific calorimeter (model 7708, Hart Scientific, Pleasant Grove, UT). The calorimeter was periodically calibrated by either electrical calibration with internal heaters or by determining the heat of fusion (ΔH_{fus}) of water and comparing the calorimeter value with the literature value. The experimental ΔH_{fus} agreed to within ±5% of the literature value.

About 0.2 g of sample was used and sufficient water was added to the sample ampoule to obtain approximately 70% final moisture content in the whole kernels or kernel fractions after heating in the differential scanning calorimeter. Water was used in the reference ampoule. All milled kernels and kernel fractions were soaked at least 1 hr in the sample ampoule to reach an equilibrium moisture content of 39–40% at room temperature (Hogan and Planck 1958) before heating in the calorimeter. Brown rice was soaked for 5 hr in the sample ampoule to equilibrate the moisture in the kernels, as the presence of the bran layer required a longer soaking time (Normand and Marshall 1989).

All samples were subjected to two programmed, consecutive heating and cooling cycles in the calorimeter. Samples were heated from 20 to 110°C at a heating rate of 1.0°C/min, held at 110°C for 5 min, and then cooled from 110 to 20°C at a cooling rate of 1.0°C/min. The cycle was then repeated. The second heating established a baseline for each run because no starch gelatinization endotherm was observed during the second heating. Baseline subtractions were made on all thermal curves, and only corrected curves are shown. At a minimum, duplicate determinations were made on every sample, but only representative thermal curves are shown in the figures.

Calculation of the thermal parameters for starch gelatinization were described previously (Normand and Marshall 1989).

Starch Analysis

Starch was determined by AACC method 76-11 (AACC 1983). Brown rice had the lowest starch content (81%, dwb). Starch content increased in the milled samples to 90% (dwb). Because starch content varied among unmilled and milled rice, gelatinization enthalpies were calculated on a per gram starch basis rather than a per gram solids basis to more effectively compare enthalpy values in the milling study.

Moisture Content

Moisture contents were determined by oven drying at 105°C for 24 hr.

RESULTS

Effect of Milling on Starch Gelatinization

A series of thermal curves was generated for rice kernels milled to different degrees. Representative curves of five such samples are shown in Figure 1. They depict unmilled (brown) rice, 6% milled rice with most of the bran removed, 10% milled rice with bran and polish layers removed, and deep milled rice at 31 and 66% degrees of milling with different amounts of starchy endosperm removed. Milling shifted the gelatinization endotherm to lower temperatures (Fig. 1, compare curves A and B). In addition, partial removal of the bran layer resulted in the appearance of a low temperature shoulder (LTS) observed previously (Champagne et al 1990), which remained upon further milling (Fig. 1, curves C–E). The magnitude of the LTS appeared to

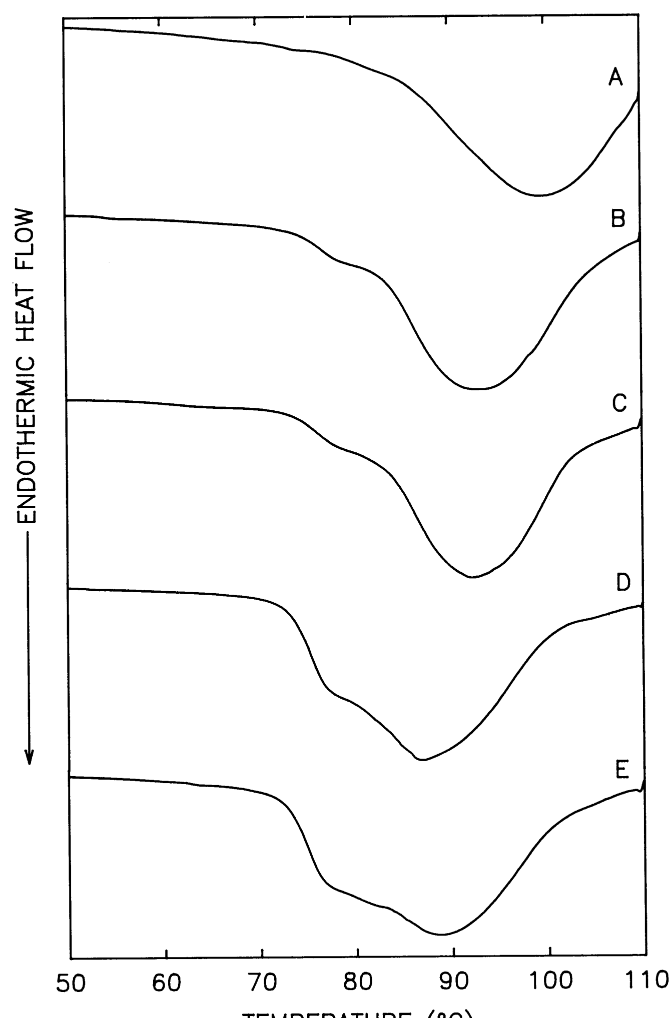

Fig. 1. Differential scanning calorimetric thermal curves of Lemont rice kernels milled to different degrees: unmilled (brown) (A), 6% (B), 10% (C), 31% (D), and 66% (E). The heating rate of the calorimeter was 1.0°C/min, and the water content of all samples was 70% (w/w).

increase in relation to the total endotherm as the degree of milling increased (Fig. 1, compare curves C–E).

A more comprehensive picture of the effect of degree of milling on starch gelatinization can be seen in Figures 2 and 3. T_o decreased until about 10% of the kernel had been removed. This degree of milling removes the bran and polish layers from the kernel. Removal of subsequent layers (starchy endosperm) had no further effect on T_o, as only slight variation in the values was observed (Fig. 2). The total decrease in T_o over the entire milling range was about 3°C. T_p showed the same general trend as T_o (Fig. 2). T_c could not be directly determined for brown rice because of the absence of a concluding baseline (Fig. 1, curve A). Instrument limitations would not allow scanning beyond 110°C. Therefore, the T_c for brown rice was >110°C. T_p and T_c steadily declined until about 20% degree of milling was reached. Further milling had little effect on either value. At 20% degree of milling, T_p had decreased about 10–11°C compared with T_p for brown rice.

Because of the absence of a concluding baseline, ΔH for the unmilled kernels could not be calculated. However, the results in Figure 3 show that ΔH for milled rice increased until the degree of milling reached 20–25%, after which degree of milling had no apparent further effect on this parameter.

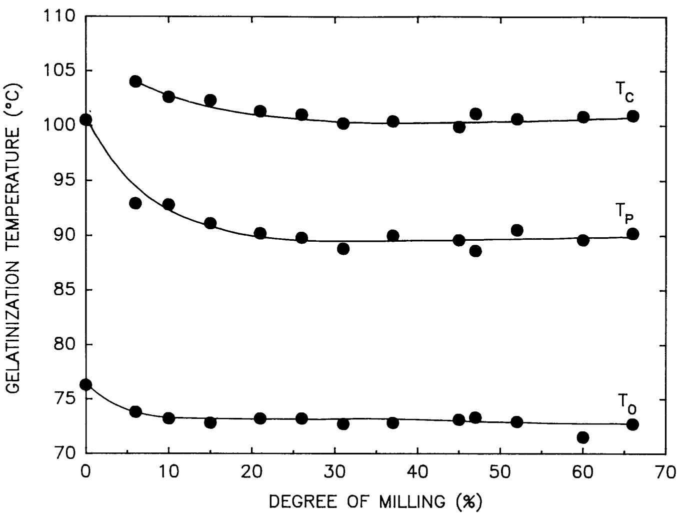

Fig. 2. The effect of degree of milling on the starch gelatinization temperatures for Lemont unmilled and milled rice. Onset (T_o), peak (T_p), and conclusion (T_c) temperatures were obtained from thermal curves at the degree of milling shown and represent the mean of duplicate determinations. The conclusion temperature of brown rice (0% milled) could not be determined because of the absence of a concluding baseline on the thermal curve.

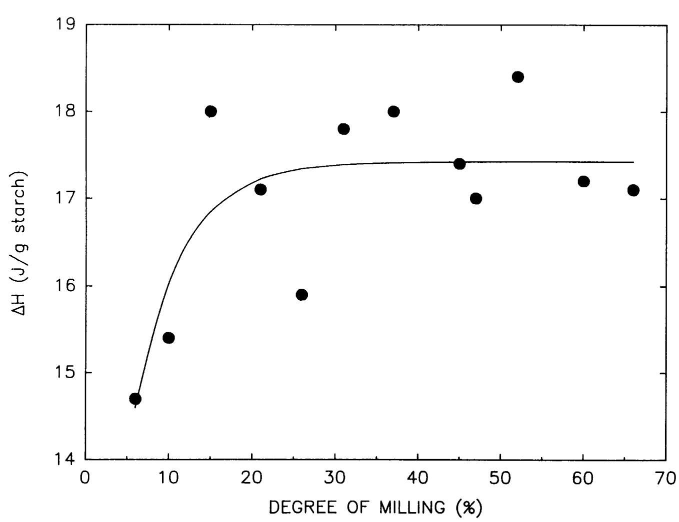

Fig. 3. The effect of degree of milling on gelatinization enthalpy (ΔH) for Lemont rice. ΔH at 0% degree of milling could not be determined because of the absence of a concluding baseline on the thermal curve. ΔH was calculated from gelatinization endotherms at the degrees of milling shown and represents the means of duplicate determinations.

Effect of Particle Size on Starch Gelatinization

Milling reduced kernel size, but the integrity of the intact kernel was not affected. To evaluate the effect of different particle sizes on starch gelatinization, whole kernels were either sectioned with

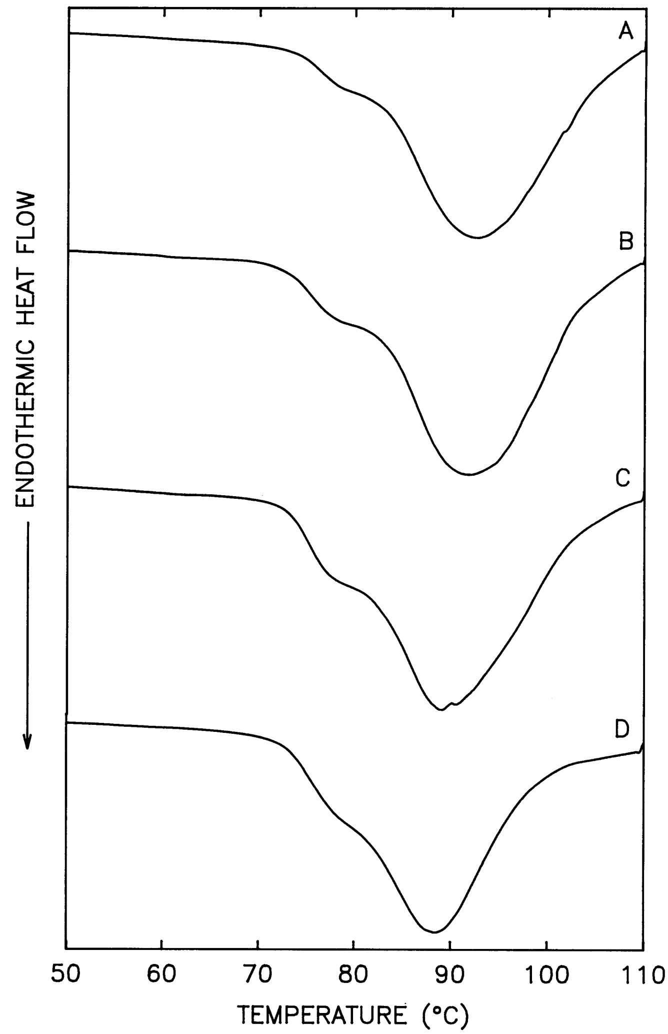

Fig. 4. Differential scanning calorimetric thermal curves for Lemont whole kernel milled rice and kernel sections. A, unsectioned (whole) kernels; B, one-half kernels; C, one-quarter kernels; D, one-eighth kernels. The heating rate of the calorimeter was 1.0°C/min, and the water content of all samples was 70% (w/w).

TABLE I
Thermal Parameters[a] of Milled Lemont Rice[b] Sectioned to Pieces of Equivalent Size

Number of Sections (length in μm[c])	Gelatinization Temperatures,[d] °C T_o	T_p	T_c	ΔH (J/g of solids)
0 (6,770 ± 37)	73.3 ± 0.2	93.4 ± 0.7	103.7 ± 0.4	14.1 ± 1.4
2 (3,680 ± 36)	72.8 ± 0.2	92.1 ± 0.0	103.2 ± 0.5	14.8 ± 0.4
4 (1,840 ± 29)	73.4 ± 0.5	89.9 ± 0.1	102.0 ± 0.0	14.4 ± 0.4
8 (1,300 ± 25)	72.8 ± 0.4	88.8 ± 0.2	98.2 ± 0.1	15.1 ± 0.1

[a] Values are means ± standard errors of the means for duplicate determinations.
[b] Moisture content of calorimeter samples was 70%.
[c] Mean length ± standard errors of the means of 30 sectioned kernels selected at random. Section lengths determined by image analysis.
[d] T_o, T_p, and T_c = Onset, peak, and conclusion temperatures, respectively.

a scalpel or pulverized with a mortar and pestle, and the effect on starch gelatinization was monitored.

Figure 4 shows the thermal curves that result from sectioning milled rice kernels. As the kernel fractions became smaller, the LTS became more prominent. The thermal parameters generated from these curves are given in Table I. Comparing one-eighth kernel with whole kernel samples, decreases of 4–5 and 5–6°C were observed for T_p and T_c, respectively. T_o and ΔH values showed little change as a result of sectioning.

Crushing and grinding kernels caused extensive changes in starch gelatinization when the kernel fragments were separated into different particle size ranges and evaluated by DSC (Fig. 5). The curves show a progressive increase in the presence of what was once the LTS and a progressive decrease and eventual disappearance (Fig. 5, curve E) of what was once the major endotherm seen in whole kernel rice (Fig. 4, curve A).

The effect of particle size on starch gelatinization parameters can be seen in Table II. At the smallest particle size range (53–64 μm), a decrease of 1°C was observed for T_o, but decreases of 16 and 20°C for T_p and T_c, respectively, were seen when compared with gelatinization temperatures for intact milled rice (Table I). Particle sizes smaller than 250 μm yielded no additional changes in T_o and T_p, but the particle size had to be reduced to less than 125 μm before no further change in T_c was noted.

No appreciable change in ΔH was observed until the kernels were pulverized rather than sectioned (compare Tables I and II). For the pulverized kernels, ΔH appeared to depend on particle size, and reducing the particle size below 500 μm steadily reduced the values for ΔH. We speculate that gelatinization enthalpies for particles below 250 μm may be unusually low because of an increase in damaged starch granules in these samples. Damaged starch has been shown to lower ΔH in rice flour (Nishita and Bean 1982).

A rice sample, prepared in a Udy cyclone mill, had a particle size range of 53–710 μm (Table II). However, 79% of the sample was in the particle size range of 125–355 μm and 43% of the sample was found between 180–250 μm. Because more of the flour particles appeared in the range of 180–250 μm than at any other particle size, thermal parameters for this sample were compared with thermal parameters for the 180- to 250-μm sample prepared with a mortar and pestle and found to be similar. These data (Table II) provide an opportunity to compare starch gelatinization of samples of comparable particle size but prepared by two different methods. The fact that the thermal data are similar indicates that the method of sample preparation is less important than the particle size, at least for this particle size range.

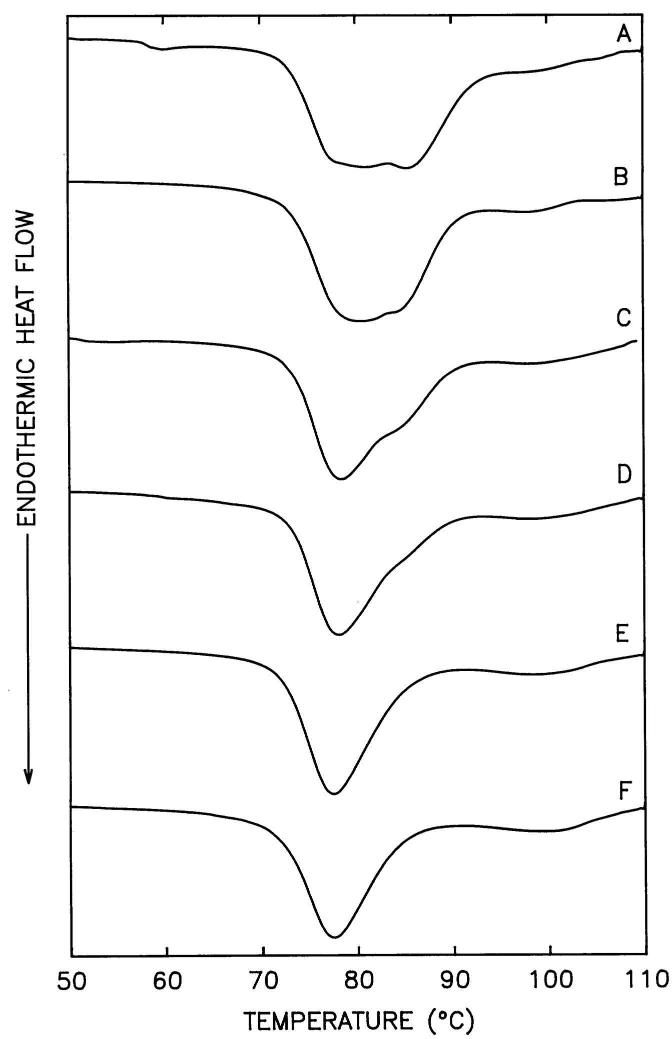

Fig. 5. Differential scanning calorimetric thermal curves for Lemont rice kernels reduced by mortar and pestle to particle sizes of 710–1400 (A), 500–710 (B), 355–500 (C), 250–355 (D), 180–250 (E), and 125–180 (F) μm. The heating rate of the calorimeter was 1.0°C/min, and the water content of all samples was 70% (w/w).

DISCUSSION

Two different methods of modifying whole kernels were used to investigate the effect of the modification on starch gelatinization. In one series of experiments, brown rice was used as starting material, kernels were milled to increased degrees of milling, and starch gelatinization was measured by DSC. Successive milling resulted in a steady decrease in most gelatinization temperatures of the residual kernel until about 20% degree of milling was achieved (Fig. 2). Therefore, the components of the kernel that can delay gelatinization by retarding water movement were removed. Layers of kernel removed at this degree of milling include the caryopsis coat, aleurone and subaleurone layers, and a part of the starchy endosperm (Juliano and Bechtel 1985). The caryopsis coat consists of the pericarp and seed coat, which have high wax contents (Bechtel and Pomeranz 1977). Champagne et al (1990) concluded that these waxy layers may be acting as a diffusion barrier for water and retarding its penetration to the starch granules, thereby delaying the gelatinization process. Removal of the waxy layers would eliminate the barrier and allow gelatinization to occur at a lower temperature.

In addition to the waxy barrier, differences in the characteristics of the starch granules located in the starchy endosperm also may influence gelatinization. He and Suzuki (1989) compared the physicochemical properties of starch granules from the outer layer and central core of rice endosperm. They obtained outer layer starch from the 8–25% milling fraction and central core starch

TABLE II
Thermal Parameters[a] of Milled Lemont Rice[b] Reduced to Different Particle Size Ranges

Particle Size Range (μm)	Gelatinization Temperatures,[c] °C			ΔH (J/g of solids)
	T_o	T_p	T_c	
710–1,400	73.1 ± 0.1	82.0 ± 1.1	92.0 ± 0.1	11.8 ± 0.5
500–710	73.5 ± 0.1	80.8 ± 0.2	90.2 ± 0.1	11.8 ± 0.3
355–500	73.4 ± 0.1	77.8 ± 0.1	89.8 ± 0.1	11.4 ± 0.2
250–355	73.3 ± 0.1	77.7 ± 0.1	89.4 ± 0.1	10.6 ± 0.2
180–250	72.4 ± 0.1	77.2 ± 0.0	85.8 ± 0.0	9.5 ± 0.3
125–180	72.4 ± 0.1	77.2 ± 0.2	85.1 ± 0.1	9.3 ± 0.3
90–125	72.3 ± 0.3	77.0 ± 0.0	83.9 ± 0.1	8.2 ± 0.6
64–90	72.5 ± 0.3	77.2 ± 0.1	84.2 ± 0.1	6.4 ± 0.5
53–64	72.4 ± 0.1	77.2 ± 0.1	83.4 ± 0.0	6.4 ± 0.3
Sample prepared in Udy cyclone mill				
53–710[d]	72.8 ± 0.0	77.4 ± 0.1	86.0 ± 0.2	10.0 ± 0.2

[a] Values are means ± standard errors of the means for duplicate determinations.
[b] Moisture content of calorimeter samples was 70%.
[c] T_o, T_p, and T_c = Onset, peak, and conclusion temperatures, respectively.
[d] Seventy-nine percent of the sample was collected in the particle size range 125–355 μm, with 43% in the 180–250 μm range.

from the remainder of the kernel. They noted a lower T_p and a slightly higher ΔH in central core starch compared with the outer layer starch values. They observed other differences in the two starch fractions and found that the outer layer and central core starches differed in their chemical composition as well as in their granule structure. The authors concluded that these differences were dependent on a physiological gradient formed during development of the rice grain.

In connection with the observations of He and Suzuki (1989), we determined that 70–75% of the total lipid resided in the outer 20% of the kernel (data not shown), and Hogan et al (1964) had demonstrated 40–45% of the total protein was removed after 20% degree of milling of long-grain rice. With relatively high levels of lipid and protein in those layers, lipid and protein may interact with starch during cooking and affect starch gelatinization. Removal of most of the total protein and lipid in milled rice resulted in only a small decrease in starch gelatinization (Marshall et al 1990). Therefore, the presence of lipid and protein, although concentrated in the outer layers of the kernel, may play only a minor role in influencing gelatinization.

Because the steepest decline in T_o and T_p occurred before 5% degree of milling (Fig. 2), the components in the outer bran layer probably have the greatest impact on retarding water penetration to the starch granules.

Milling allows starch gelatinization to be monitored by removing layers of rice kernel in which the layers differ in chemical composition and granule structure (He and Suzuki 1989). However, the kernel remains intact using this method. A simple method of modifying kernel integrity is to section the kernel into roughly equal parts. Sectioning the kernel in this manner would be a controlled method of exposing starch granules along the face of the cut, setting up a situation analogous to the numerous fissures produced by water soaking or by exposing the kernels to lipid solvents (Marshall et al 1990). Indeed, kernels divided into one-eighth sections (Fig. 4, curve D) showed a thermal curve comparable to thermal curves generated by exposing kernels to water or lipid solvents (Marshall et al 1990). In that study, Marshall et al (1990) demonstrated that the presence of the fissures was the major contributor to changes in the thermal curves.

The influence of kernel integrity on starch gelatinization was even more pronounced when rice kernels were pulverized and separated into various particle size ranges (Fig. 5). The sequence of curves clearly shows the pronounced influence of particle size on starch gelatinization and depicts the transformation of the gelatinization endotherm from a broad, complex transition to a narrow, simple thermal curve. The extent to which gelatinization is affected may depend on the degree of exposure of the starch granules. The degree of exposure dictates the ratio of granules easily accessible to water to granules less easily accessible. Controlling the number of granules directly exposed to water during cooking appears to be an effective method for altering starch gelatinization.

Our results show that starch gelatinization may be decreased by either milling or fractionation of the kernel into different particle sizes. Lower gelatinization temperatures would be desirable to rice processors because starch gelatinization temperatures and rice cooking times appear to be directly related (Juliano and Perez 1983). Partial removal of the bran layer would decrease the cooking time from that for brown rice, and some nutritional benefit could still be derived from the remaining bran. Desikachar et al (1965) showed that milling brown rice to only 2–3% degree of milling considerably improved water absorption and decreased cooking time. If further reduction in gelatinization temperatures (cooking time) is desirable, the kernels can be incrementally milled to about 20% degree of milling. Alternatively, use of other long-grain varieties with lower gelatinization temperatures than Lemont can be considered, because Lemont has an intermediate starch gelatinization temperature among long-grain rices.

To create a rice product with substantially lower gelatinization temperatures (cooking times), kernel structure must be modified. Two earlier patents (Alexander 1954, Bardet and Giesse 1961) described commercial processes where brown rice was exposed to hot, dry air, which produced fissures in the kernel surface but did not gelatinize the starch. The extensive fissuring reduced cooking time by allowing rapid water penetration to the starch granules. Our results provide an explanation for these observations and indicate that under these conditions, gelatinization temperatures are lowered with a concomitant reduction in cooking time. Surprisingly, gelatinization enthalpies remain largely unchanged and appear to be a factor only under conditions where the kernel is reduced to smaller particles.

Finally, if retention of kernel structure is not a requirement, such as in products where rice may be added as grits, gelatinization temperatures, gelatinization enthalpies, and cooking times can be considerably reduced by controlling the particle size of the broken kernel.

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