

# Modeling Starch Gelatinization Kinetics of Milled Rice Flour

Carlos A. Ojeda,<sup>1</sup> Marcela P. Tolaba,<sup>1</sup> and Constantino Suárez<sup>1</sup>

## ABSTRACT

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Milled long-grain rice samples were evaluated by differential scanning calorimetry (DSC) to determine the kinetics of starch gelatinization. The experiments were conducted with milled rice flour with a 10.6% degree of milling. DSC thermograms were obtained from 35 to 110°C using heating rates between 1°C/min and 15°C/min. The rate constants were evaluated, and two activation energies were found for different tempera-

ture ranges. At <70.1°C gelatinization was not completed. It was assumed that at <70.1°C gelatinization would only affect the amorphous regions. During the subsequent phase the crystalline regions destabilized by the amorphous component begin to gelatinize. For moisture content of 70%, wet basis, and a heating rate of 12°C/min, the enthalpy of gelatinization reaches a constant value of 7.3 J/g.

Starch constitutes the major component of rice. Consequently, gelatinization appears to be an adequate parameter of the cooking process. The course of starch gelatinization may be followed by different methods. Using the technique of differential scanning calorimetry (DSC), Wirakartakusumah (1981) determined the degree of gelatinization and gelatinization temperatures of starch isolated from parboiled rice. Based on the experimental fact that incomplete parboiling results in partial or surface starch gelatinization, Marshall et al (1993) developed an alternative method that measures the percentage of translucent kernels in a given sample of parboiled rice.

Many studies have been reported on the gelatinization kinetics of starch-water systems in excess water (>70%, w/w) (Slade and Levine 1991, Zanoni et al 1995, among others). However, very little has been done on gelatinization kinetics of starch in rough rice. Lund and Wirakartakusumah (1984) studied rice starch gelatinization kinetics by DSC and found that the process follows first-order kinetics only beyond a certain degree of gelatinization. According to the authors, during the initial phase of gelatinization only the amorphous regions of the starch would be affected by the heating process and would not follow first-order kinetics.

Normand and Marshall (1989) measured the gelatinization of rough rice by DSC and found significant differences in gelatinization parameters of whole kernels and those of rice flour. Enthalpies of whole kernels were systematically larger than those of rice flour. Marshall (1992) has also reported that the particle size of rice flour influences the enthalpy of gelatinization, as well as the onset and conclusion temperatures of gelatinization.

The present work is an attempt to evaluate the changes that rice starch undergoes during the heating of mixtures of water and milled rice flour in excess water. For this purpose, the kinetic constants of milled rice flour gelatinization will be estimated following the dynamic method developed by Ozawa (1970).

**Theory.** Ozawa (1970) demonstrated that differential thermal analysis can be employed for the determination of rate constants and activation energies. The method is based on the assumption that the temperature of maximum deflection (peak temperature,  $T_p$ ) in differential thermal analysis is also the temperature of the maximum reaction rate. For reactions of the type solid (A) → solid (B), the rate of reaction can be described as:

$$\frac{dx}{dt} = Z e^{-E_a/RT} (1-x)^n \quad (1)$$

where  $x$  = fraction reacted,  $Z$  = preexponential factor,  $n$  = reaction order,  $E_a$  = activation energy,  $T$  = absolute temperature, and  $R$  = universal gas constant.

If the temperature rises during the reaction, the reaction rate will rise to a maximum value then return to zero as the reactant is exhausted. At maximum reaction rate:

$$(T = T_p), \quad \frac{d}{dt} \left( \frac{dx}{dt} \right) = 0,$$

then:

$$Z e^{-E_a/RT_p} \left[ (1-x)^n \left( \frac{\beta E_a}{RT_p^2} \right) - n(1-x)^{n-1} \left( \frac{dx}{dt} \right)_{max} \right] = 0 \quad (2)$$

where it was assumed that the heating temperature varies linearly with time, with  $\beta$  = the constant rate of temperature rise. To satisfy the above condition at  $T = T_p$ , the term in brackets from Eq. 2 should be zero, so:

$$\left( \frac{dx}{dt} \right)_{max} = \frac{\beta E_a (1-x)}{n R T_p^2} \quad (3)$$

On the other hand, when  $T$  reaches  $T_p$ , it can be written from Eq. 1 that:

$$\left( \frac{dx}{dt} \right)_{max} = Z e^{-E_a/RT_p} (1-x)^n \quad (4)$$

Combining and rearranging Eq. 3 and 4, and assuming that  $n = 1$ :

$$\frac{\beta}{T_p^2} = \frac{Z R}{E_a} e^{-E_a/RT_p} \quad (5)$$

Taking the natural logarithm of both sides yields,

$$\ln \frac{\beta}{T_p^2} = \ln \left( \frac{Z R}{E_a} \right) - \frac{E_a}{R T_p} \quad (6)$$

So, for a first-order reaction, the logarithm of the heating rate divided by the square of absolute  $T_p$  versus the reciprocal absolute  $T_p$  is a linear relationship. Equation 6 makes possible the determination of  $E_a$  and  $Z$  for a first-order reaction by making differential thermal analysis patterns at a number of heating rates.

## MATERIALS AND METHODS

Rough rice samples of Irga long-grain rice were obtained from the Province of Entre Ríos, Argentina (crop 1997). For a better characterization, the starch content of rice was determined polarimetrically (Egan et al 1987). The amylose content was determined following the modified method of Pérez and Juliano (1978). The resulting values were 61.9 and 26.0%, dry basis, for starch and amylose contents, respectively.

<sup>1</sup> Departamento de Industrias, Facultad de Ciencias Exactas y Naturales, Ciudad Universitaria, (1428) Buenos Aires, Argentina

Samples of whole grain rice were dehulled in a bench model grain testing mill (MT-95, Suzuki Co., San Pablo, Brazil) and milled for a specific time interval (2 min) to produce a 10% degree of milling. The degree of milling (DOM) was determined as:

$$\text{DOM} = \left( 1 - \frac{\text{weight of milled rice}}{\text{weight of brown rice}} \right) \times 100$$

To prepare the flour, samples of milled rice were ground to fine particles in a laboratory mill. After that, the particles were finely pulverized in a porcelain mortar and hand-ground with a porcelain pestle. This process of pulverizing was carefully done at a slow rate to minimize heat generation. As the pulverized sample contained a broad range of particle sizes, these were passed through a series of sieves with mesh sizes from 74 to 250  $\mu\text{m}$ . The fraction retained (177–74  $\mu\text{m}$ ) was used for the experiments.

Moisture content of rice flour, determined by vacuum oven drying at 70°C in presence of  $\text{P}_2\text{O}_5$  to constant weight, was 13%, dry basis.

### Differential Scanning Calorimetry

A PL-DSC calorimeter (Polymer Laboratories LTD, Surrey, UK) comprising the modulus and thermal controller was used. Heat flow and temperature calibrations were periodically performed using pure indium with a heat of fusion of 28.41 J/g and a melting temperature of 156.66°C. Experimental values agreed to within  $\pm 3\%$  of the literature value.

Rice flour ( $\approx 6$  mg) of known moisture content, weighed to an accuracy of  $\pm 0.01$  mg, was added to the aluminum pan. Distilled water was added to the pan by a micropipette, and the pan was then hermetically sealed. A water-to-flour ratio of 2:1 was used in all DSC runs. High-pressure DSC pans were used to prevent moisture evaporation loss. The water-flour mixture was maintained at least 1 hr in the pan before heating in the calorimeter.

Thermograms were obtained by scanning the sample from 35 to 110°C at various heating rates. An empty aluminum reference pan with a lid was used to balance the heat capacity of the sample pan. The heating rate was varied between 1 and 15°C/min. During the runs, the space surrounding the sample cell was flushed with dry nitrogen to avoid condensation on the outside of the cells. All samples were subjected to two programmed, consecutive heating and cooling cycles in the calorimeter. From the second heating, a

baseline was established for each run given that no starch gelatinization endotherm was observed during the second heating. For each thermogram, onset ( $T_o$ ), peak ( $T_p$ ), and conclusion ( $T_c$ ) temperatures and enthalpy of gelatinization ( $\Delta H$ , J/g) were evaluated using DSC software (Rheometric Scientific Plus V, version 5.40). A minimum of triplicate determinations of thermograms was made.

The  $\Delta H$  was also calculated by drawing a straight line between  $T_o$  and  $T_c$  and calculating the area underneath the curve. This was expressed in joules per gram, dry weight of rice flour.

## RESULTS AND DISCUSSION

The effect of the heating rate on the thermal characteristics is listed in Table I for some values of the heating rates investigated. The increase of the heating rate caused an increase of  $\Delta H$  value. For the highest heating rate investigated, the  $\Delta H$  values seem to approach a constant value of  $\approx 7.3$  J/g. This value is somewhat higher than that reported by Normand and Marshall (1989) for rice flour for a similar water-to-flour ratio.

In Table I, the  $T_o$  and  $T_c$  of gelatinization increased with the heating rate until a heating rate of  $\approx 12^\circ\text{C}/\text{min}$  was reached. This effect becomes particularly marked for  $T_c$  with consequent increase of gelatinization temperature ranges. A similar tendency of the variation of  $T_c$  with the particle size was reported by Marshall (1992), even though the differences ( $T_c - T_o$ ) were much lower than those found here. In Table I, the largest difference between  $T_o$  and  $T_c$  was  $\approx 20^\circ\text{C}$ , which is probably due to the variable crystallite structure in starch granules. Granules that contain the least stable crystallites melted first. For water-to-flour ratios of  $\geq 2:1$ , the  $\Delta H$  of phase transitions equaled 7.3 J/g.

Table II gives the average  $T_p$ , the inverse  $1/T_p$ , and the corresponding and  $\beta/T_p^2$  values for the different heating rates. To correlate the variables  $\beta$  and  $T_p$  according to Eq. 6, the inverse  $1/T_p$  and  $\ln(\beta/T_p^2)$  were calculated. The variable  $\ln(\beta/T_p^2)$  was selected as the independent variable by statistical analysis ( $F$ -test). As the dependent variable, standard deviation, was not constant (Table II), a weighted least square regression was applied. The assigned weights were inversely proportional to the respective standard deviations.

To fit experimental data to Eq. 6, two procedures were followed. The first consisted of fitting the data to obtain a single straight line. In this case, the goodness of fit was very poor. In the second case, two straight lines were used to fit the experimental data, which resulted in a better fit (the analysis of variances was significant with  $P < 0.01$ ). The best fit of the data, using two straight lines, is shown in Fig. 1. The activation energy dropped from

TABLE I  
Enthalpy Values ( $\Delta H$ ), Onset ( $T_o$ ), Peak ( $T_p$ ), and Conclusion ( $T_c$ )  
Temperatures of Rice Milled Flour at Different Heating Rates<sup>a</sup>

Heating Rate (°C/min)	$\Delta H$ (J/g)	$T_o$ (°C)	$T_p$ (°C)	$T_c$ (°C)
1	1.9 $\pm$ 0.2	59.5 $\pm$ 2.3	58.6 $\pm$ 0.5	62.0 $\pm$ 0.8
2	2.1 $\pm$ 0.1	59.1 $\pm$ 1.8	62.9 $\pm$ 7.3	64.5 $\pm$ 0.9
3	2.4 $\pm$ 0.2	58.6 $\pm$ 1.2	64.1 $\pm$ 1.1	65.2 $\pm$ 1.0
5	2.9 $\pm$ 0.2	57.5 $\pm$ 1.5	64.8 $\pm$ 10.6	67.0 $\pm$ 1.2
8	3.3 $\pm$ 0.2	62.0 $\pm$ 1.3	66.5 $\pm$ 0.5	73.9 $\pm$ 0.9
10	6.9 $\pm$ 0.1	56.4 $\pm$ 1.2	70.3 $\pm$ 0.9	75.5 $\pm$ 1.0
12	7.3 $\pm$ 0.2	60.6 $\pm$ 2.1	75.6 $\pm$ 1.7	79.4 $\pm$ 1.3
14	7.3 $\pm$ 0.2	59.9 $\pm$ 2.1	81.4 $\pm$ 1.7	84.3 $\pm$ 1.0
15	7.5 $\pm$ 0.2	64.8 $\pm$ 2.4	88.5 $\pm$ 2.2	90.2 $\pm$ 0.8

<sup>a</sup> Water-to-flour ratio 2:1.

TABLE II  
Heating Rates and Average Peak Temperatures for Rice Milled Flour

$\beta$ (K/min)	$T_p$ (K)	$1/T_p$ ( $10^3 \times \text{K}^{-1}$ )	$\beta/T_p^2$ ( $10^6 \times \text{min}^{-1} \text{K}^{-1}$ )
1	331.64	3.01	9.06
2	335.78	2.98	17.76
3	337.07	2.97	26.46
5	337.88	2.96	43.81
8	339.47	2.94	69.15
10	343.30	2.91	84.68
12	348.59	2.87	98.84
14	354.41	2.82	111.33
15	361.47	2.77	115.09

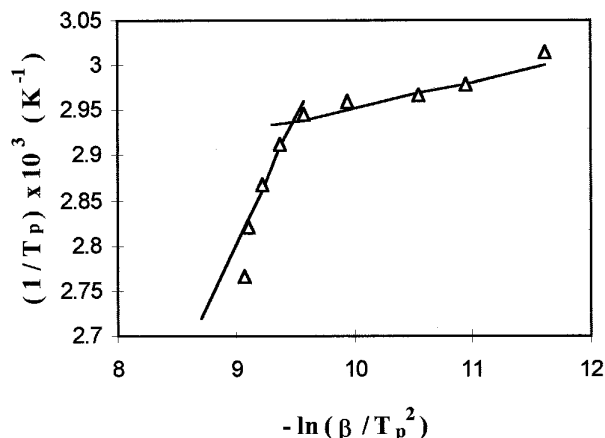


Fig. 1. Relationship between heating rate and peak temperature according to Ozawa (1970). Each point is the average of at least three replicates; full line, Eq. 6.

286.7 kJ/mol to 29.8 kJ/mol at the breaking point of 70.1°C, while the preexponential factor  $Z$  changed at this point from  $4.5 \times 10^{42} \text{ min}^{-1}$  to  $170.1 \text{ min}^{-1}$ .

Juliano and Pérez (1986) reported that higher activation energy was required for cooking milled rice at low temperature. Satterfield (1970) mentioned that a change in activation energy with temperature indicates a shift in the controlling mechanism of the reaction. Thus, the phase transition of starch containing a shift in controlling mechanism could be considered as a two-step reaction.

From these results, it can be hypothesized that at temperatures <70.1°C, the energy added to the system results in disorder of the amorphous region of the starch. At temperatures >70.1°C, the additional energy provided to the system allows the mobility of the chains in the amorphous regions, causing melting of the crystallites. In that way, gelatinization is completed. This conclusion concurred with the results of other investigators. Suzuki et al (1976) found that the values of  $E_a$  for gelatinization of white rice above and below 75°C were 82.8 and 36.8 kJ/mol, respectively. For brown rice, Bakshi and Singh (1980) reported that at >85°C,  $E_a = 43.9 \text{ kJ/mol}$ ; at <85°C, the value of  $E_a$  was 77.3 kJ/mol. More recently, Yeh and Li (1996) found for native rice starch values of  $E_a = 306.0$  and 42.6 kJ/mol below and above the breaking temperature of 76°C, respectively. The results found here are close to those found by Yeh and Li (1996) for rice starch.

## CONCLUSIONS

Kinetics of the phase transition of milled rice flour with water content of 70% (w/w) was investigated. The Ozawa model was used to estimate the kinetics parameters. This is a nonisothermal method that avoids the  $\Delta H$  determination of the conventional isothermal method (Yeh and Li, 1996).

The Ozawa model was used to evaluate the relationship between  $T_p$  and the heating rate obtained by DSC. This work shows that the Ozawa method, an alternative nonisothermal procedure, can give reliable kinetic information that is comparable to the isothermal method.

Assuming that starch gelatinization follows pseudo first-order kinetics, it appears that the phase transition of rice flour is a two-step reaction. At the first step ( $T_p < 70.1^\circ\text{C}$ ), higher activation energy is required for the disordering of internal structure, where starch granules are more temperature sensitive. Once the  $T_p$  is >70.1°C, the activation energy drops considerably and the rice flour becomes less temperature sensitive.

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