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Impact of Micronization on Rapidly Digestible, Slowly Digestible, and Resistant Starch Concentrations in Normal, High-Amylose, and Waxy Barley

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This study determined the effect of micronization (high intensity infrared heating) on the concentrations of rapidly digestible starch (RDS), slowly digestible starch (SDS), and resistant starch (RS) in normal barley (NB), high-amylose barley (HAB), and waxy barley (WB). The gelatinized starch contents and the thermal properties of the micronized samples also were determined. Samples of each barley type were tempered to each of three moisture contents (approximately 17, 31, or 41%), and then each tempered sample was micronized to each of three surface temperatures (100, 120, or 140 °C). Micronized barley samples were substantially lower in RS and in SDS and, therefore, higher in RDS than corresponding unprocessed samples. In general, higher concentrations of RDS and of gelatinized starch were associated with higher initial moisture contents and higher surface temperatures. The lowest concentrations of RS were observed in micronized WB samples. Similar concentrations of RS were observed in corresponding NB and HAB samples. Micronization resulted in slight increases in the onset (T_o), peak (T_p), and completion (T_c) gelatinization temperatures and in substantial reductions in the gelatinization enthalpy (ΔH), the latter reflecting the levels of gelatinized starch in micronized samples, particularly in samples micronized at higher moisture contents and to higher surface temperatures. Endothermic transitions were evident only in samples tempered to 17% moisture or 31% moisture (surface temperature of 100 °C only).

KEYWORDS: Infrared heating; micronization; thermal processing; slowly digestible starch; resistant starch; starch gelatinization; retrogradation

INTRODUCTION

Micronization (high intensity infrared heating) employs radiant heat as the main source of heating (*1*). The application of infrared heating to the drying of different materials, such as foodstuffs, coatings, adhesives, ink, paperboard, baked goods, and textiles, has been reported. In the food industry, infrared drying has been applied to legumes, cereals, flour, vegetables, pasta, meat, and fish (*2*, *3*). Cenkowski and Sosulski (*4*) reported the effect of micronization on the cooking characteristics of pea. Micronization has been used in the feed industry and in the production of flaked foods such as breakfast cereals. Cruzy Celis et al. (*5*) used micronization to produce a ready-to-eat breakfast cereal from sorghum.

Depending on the wavelength, infrared radiation is categorized as near-infrared (750−3000 nm), mid-infrared (3000−25000 nm), or far-infrared (25000−100000 nm). The energy of the radiation is inversley proportional to the wavelength (*2*, *6*). Infrared heating employs wavelengths from 1800 to 3400 nm (*1*, *7*). The material heated by infrared radiation should have low reflectivity to minimize the required heating energy. In terms of absorptivity and transmissivity, materials behave differently. Materials with high absorptivity have low transmissivity and vice versa. For heating and drying of nonfood materials, such as paints and coatings, higher absorptivity is preferred. As absorptivity increases, the temperature of the material increases and, consequently, less energy is consumed. However, a higher transmissivity is preferred in heat-sensitive materials, such as foodstuffs having a thick, moist texture, in order to reduce heat absorption and associated heat damage (*2*). Infrared radiation penetrates foodstuffs, such as grains, and results in excited water molecules and rapid heating. As a result, the water vapor pressure increases inside the material and it cooks. This heating in grains leads to swelling and, ultimately, expansion if sufficiently prolonged (*5*, *7*).

Starch is the major component in many foodstuffs, such as cereals and pulses, and is completely or partially hydrolyzed by amylases in the gastrointestinal tract of humans. The digestibility of starchy materials varies, and several factors affect starch digestibility in foodstuffs, including the physicochemical properties of starch, storage conditions, resistant starch content, starch−protein interactions, and the presence of fiber and antinutritional factors, e.g. enzyme inhibitors (*8*−*11*). From a nutritional point of view, starch may be classified as rapidly digestible starch (RDS), slowly digestible starch (SDS), and resistant starch (RS) (*10*−*12*).

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Analytically, RDS is that portion of starch converted to glucose during 20 min of in vitro enzyme hydrolysis using a standardized protocol. It predominates in freshly cooked, starchy foods and is digestible in the small intestine. SDS is that portion of starch converted to glucose between 20 and 120 min of in vitro enzyme hydrolysis. This type of starch predominates in most raw cereal products and is largely digestible in the small intestine. Starch not hydrolyzed after 120 min of in vitro enzyme hydrolysis is termed RS, which is not digested in the small intestine (*10*, *13*). RS may be classified as one of four types. Type 1 RS is comprised of intact starch granules which are not digestible due to their inaccessibility to amylase enzymes. This type of RS occurs in coarsely ground cereal and other flours. Type 2 RS consists of starch granules which resist amylase attack and is found in raw potato and green banana. Type 3 RS is retrograded starch which is formed by the association of starch chains during the cooling and storage of cooked starch pastes (*13*−*16*). Under favorable conditions, the formation of extensive junction zones between starch molecules results in a significant degree of crystalline order (*17*). Although both amylose and amylopectin can retrograde during cooling and storage of starch pastes, it has been shown that amylose chains exhibit a greater tendency to associate and form hydrogen bonds. Because starches vary in their proportions of amylose and amylopectin, they also vary in their tendency to retrograde, and starches having higher amylose contents tend to retrograde more extensively and form higher levels of type 3 RS (*14*, *17*, *18*). Type 4 RS is comprised by physically or chemically modified starches such as esterified and cross-linked starches (*15*, *18*−*20*). Processing conditions have a marked effect on RS content (*12*, *21*). Starch not hydrolyzed by amylases in the small intestine enters the large intestine where it is fermented, similar to dietary fiber (*10*, *11*). Fermentation of RS produces short chain fatty acids, primarily acetate, propionate, and butyrate, which are thought to play an important role in human health (*9*, *22*). RS contributes to reductions in glycemic index, the insulinemic response, and the energy value of foods. Furthermore, RS increases the bulk of the intestinal contents, which reduces passage time (*23*). It has been reported that RS can reduce the risk of hypercholesterolemia and colorectal cancer (*9*, *24*).

The objective of this study was to determine the effect of micronization conditions, namely initial moisture content and final surface temperature, on starch digestibility, i.e. levels of RDS, SDS, and RS, and starch gelatinization in normal, high-amylose, and waxy barley, along with the thermal properties of starch in micronized barleys. Differential effects of micronization on starch digestibility and gelatinization in the three barley types were anticipated due to the substantial differences in their amylose contents.

MATERIALS AND METHODS

Materials. Barley samples (CDC McGwire: normal starch barley, denoted NB; SB 94893: high-amylose starch barley, denoted HAB; CDC Fibar: waxy starch barley, denoted WB) were obtained from the Crop Development Centre, University of Saskatchewan, Saskatoon, SK, Canada. All samples had been harvested in 2008. The samples (25 kg) were stored in airtight plastic bags at approximately 4 °C until processed.

Tempering. Deionized water in quantities sufficient to obtain the desired initial moisture contents (approximately 17, 31, or 41% and denoted MC_i) was added to barley samples, which were then mixed uniformly in a tumbler for 3 h. The final moisture content was measured using a halogen moisture analyzer model HB43-S (Mettler-Toledo, Inc., Columbus, OH) to ensure the sample had reached the desired moisture content (±1%). To confirm the manufacturer's calibration (performed annually) of the rapid moisture analyzer, the moisture contents of several check samples were determined with the analyzer and by method 44−15A of the AACC (*25*). The samples then were stored in airtight containers for approximately 48 h at room temperature to ensure equilibration (*6*).

Infrared Heating. The pilot-scale micronizer used in this study was described by Fasina et al. (*1*). The system was prewarmed for approximately 15 min prior to processing. Approximately 2 kg of tempered sample was loaded into the hopper. Uniform flow of grain from the hopper was provided by vibration. By adjusting the hopper vibration amplitude and the gap at the hopper outlet, the flow rate was controlled, which determined processing time and final surface temperature (T). Vibration of the conveyor varied the grain orientation continuously and ensured that all grain surfaces were heated uniformly. The flow rate was controlled such that the grain moisture content was reduced to less than 11.5% and the surface temperature of the grain reached the desired value (100, 120, or 140 °C), which was monitored with an infrared thermometer. The samples were cooled to room temperature and then stored in airtight plastic bags at 4 °C until analyzed.

Chemical Analysis. Unprocessed and processed grain samples were ground using an impact grinder (Falling Number, Huddinge, Sweden) to obtain flour passing through a 425 μm sieve. Moisture content was determined according to method 44−15A of the AACC (*25*). Protein content was measured by method 46−30 of the AACC (*25*) using a LECO model FP-528 nitrogen/protein determinator (LECO Corporation, St. Joseph, MI). A nitrogen-to-protein conversion factor of 5.7 was used. Total starch content was determined by method 76.13 of the AACC (*25*) using a Megazyme total starch assay kit (Megazyme International Ireland Ltd., Bray, Ireland). Apparent amylose content was determined using the method of Chrastil (*26*). Ash and crude fat were measured according to methods 08−12 and 30−25, respectively, of the AACC (*25*). Crude fat content was determined with a Goldfish apparatus (Labconco Corp., Kansas City, MO) and *n*-hexane.

In Vitro Starch Digestibility. The RDS, SDS, and RS contents were determined by the enzymatic procedure of Englyst et al. (*13*) as modified by Chung et al. (*27*) with minor modifications.

Gelatinized Starch Content. Gelatinized starch content was measured according to the method of Shetty et al. (*28*) as modified by Chiang and Johnson (*29*) and Lue et al. (*30*) with minor modifications.

Differential Scanning Calorimetry (DSC). Samples of approximately 3 mg were weighed into aluminum hermetic pans. Double-distilled water was added to the samples using a microsyringe to increase the moisture content of the suspension to 70%. Pans were sealed and allowed to equilibrate at room temperature for approximately 6 h prior to heating. The absorbed heat was recorded relative to an empty pan as reference.

Thermal analysis was conducted using a differential scanning calorimeter (Q2000 modulated differential scanning calorimeter, TA Instruments, New Castle, DE) equipped with refrigerated cooling and auto sampler accessories. The instrument was calibrated using a standard sample of indium obtained from the manufacturer. The measurements were performed at a heating rate of 10 °C/min from 5 to 180 °C. Analyses were conducted in duplicate. The enthalpy (ΔH) of phase transition (gelatinization) was calculated from the DSC thermograms using Universal Analysis software (version 4.5A, TA Instruments) based on the dry mass of the sample. The onset temperature (T_o), peak temperature (T_p), and conclusion temperature (T_c) of gelatinization also were determined from the thermograms.

Statistical Analysis. Sample processing was conducted using a completely random experimental design with factorial treatment structure and two replicates. There were two variable factors, the moisture content (MC_i) of grain samples prior to infrared heating (17, 31, or 41%) and the surface temperature (T) of processed grain (100, 120, or 140 °C). Analysis of variance (ANOVA) and comparison of means (Duncan's) were performed using the Statistical Analysis System (SAS) (version 9.2, SAS Institute Inc., Cary, NC) and the GLM procedure to evaluate the effect of MC_i and T on measured parameters. Averages of two determinations are presented in the form of mean ± standard error.

RESULTS AND DISCUSSION

Table 1 presents the chemical composition of the three barley samples. NB was substantially higher in starch, and lower in protein than HAB or WB. The starch contents of the barley samples were either similar to (NB) or lower than (HAB and WB) that of the hulless barley (67% starch) used in micronization studies by Fasina et al. (*1*), whereas the concentrations of protein

Table 1. Composition of Barley Samples

constituent (% db)	normal barley	high-amylose barley	waxy barley
total starch	65.1 ± 3.1	58.2 ± 1.9	46.3 ± 1.4
free glucose	0.4 ± 0.1	0.4 ± 0.0	0.5 ± 0.0
protein	13.3 ± 0.0	17.3 ± 0.0	16.4 ± 0.1
crude fat	2.3 ± 0.1	2.7 ± 0.2	3.2 ± 0.1
ash	1.6 ± 0.0	2.2 ± 0.0	2.4 ± 0.0
apparent amylose[a]	28.7 ± 0.4	46.5 ± 0.3	0.7 ± 0.1

[a] Percent of starch.

Table 2. Rapidly Digestible Starch (RDS), Slowly Digestible Starch (SDS), and Resistant Starch (RS) Contents (g/100 g Dry Matter) of Micronized Normal Barley (NB), High-Amylose Barley (HAB), and Waxy Barley (WB) Processed at Different Moisture Contents and to Different Surface Temperatures[a]

sample	MC_i (% wb)	T (°C)	RDS	SDS	RS
NB	unprocessed		6.6 ± 0.1	41.6 ± 0.1	17.0 ± 0.0
	17.5	100	22.9 ± 0.6 e	31.2 ± 0.2 a	11.0 ± 0.3 bc
		120	32.7 ± 0.9 d	21.2 ± 0.1 b	11.3 ± 0.5 bc
		140	48.0 ± 1.0 abc	2.3 ± 0.4 f	14.8 ± 0.2 a
	32.1	100	45.4 ± 1.8 bc	7.8 ± 0.7 cd	11.9 ± 0.1 b
		120	44.4 ± 0.7 c	8.5 ± 0.6 c	11.9 ± 0.9 b
		140	49.5 ± 1.9 a	3.3 ± 0.6 ef	12.6 ± 0.8 b
	42.5	100	48.6 ± 0.6 ab	7.1 ± 0.1 cde	9.4 ± 0.5 c
		120	48.3 ± 1.1 abc	4.7 ± 0.0 cdef	12.1 ± 0.3 b
		140	48.6 ± 0.3 ab	3.9 ± 0.2 def	12.7 ± 0.4 ab
HAB	unprocessed		10.7 ± 0.4	23.5 ± 0.5	24.0 ± 0.8
	17.4	100	25.2 ± 0.0 e	19.7 ± 0.3 a	13.3 ± 0.3 a
		120	33.0 ± 0.3 d	12.8 ± 0.7 b	12.3 ± 0.6 ab
		140	39.9 ± 0.2 bc	7.7 ± 0.5 c	10.6 ± 0.7 bc
	30.7	100	33.3 ± 1.0 d	11.5 ± 1.2 b	13.4 ± 0.2 a
		120	39.5 ± 0.2 c	6.7 ± 0.5 c	12.0 ± 0.3 abc
		140	42.5 ± 1.0 ab	4.8 ± 1.6 c	10.9 ± 0.2 bc
	42.3	100	43.2 ± 1.0 a	4.7 ± 0.3 c	10.4 ± 0.3 dc
		120	43.8 ± 0.5 a	3.9 ± 0.2 c	10.4 ± 0.5 dc
		140	44.4 ± 1.2 a	4.9 ± 0.3 c	8.9 ± 0.6 d
WB	unprocessed		16.3 ± 0.5	20.8 ± 0.2	9.2 ± 0.7
	17.4	100	38.5 ± 1.1 c	6.4 ± 0.2 a	1.4 ± 0.9 a
		120	41.5 ± 0.3 abc	3.4 ± 0.2 ab	1.4 ± 0.9 a
		140	43.1 ± 0.9 ab	3.1 ± 0.2 ab	0.2 ± 0.0 a
	31.0	100	40.1 ± 0.8 bc	4.5 ± 0.3 ab	1.6 ± 0.2 a
		120	42.6 ± 0.2 abc	3.2 ± 0.0 ab	0.5 ± 0.2 a
		140	41.6 ± 0.3 abc	4.3 ± 0.3 ab	0.5 ± 0.0 a
	39.8	100	38.4 ± 0.4 c	5.9 ± 0.1 a	2.1 ± 0.4 a
		120	40.9 ± 0.8 abc	4.9 ± 0.1 ab	0.5 ± 0.1 a
		140	44.8 ± 0.8 a	1.4 ± 0.3 b	0.1 ± 0.0 a

[a] MC_i: initial moisture content. T: surface temperature. For a particular barley sample, means in the same column followed by the same letter are not significantly different (Duncan's multiple range test, $P > 0.05$).

and crude fat in NB, HAB, and WB were higher (hulless barley contained 9.4−9.5% protein and 1.6−1.7% crude fat). The apparent amylose contents of NB, HAB, and WB were consistent with their designation as normal, high-amylose, and waxy barley, respectively. The higher amylose content of HAB has the potential to enhance the RS level after processing (*31*).

Table 2 presents RDS, SDS, and RS concentrations in unprocessed and micronized barleys. All micronized samples were higher in RDS, and lower in SDS and RS, than corresponding unprocessed samples. Micronized NB and HAB samples exhibited similar concentrations of RDS, SDS, and RS for most corresponding treatments. WB samples were markedly lower in RS than corresponding NB and HAB samples. Levels of RDS and SDS in WB samples tended to be similar to those in corresponding NB and HAB samples micronized at higher moisture contents, whereas in most cases the level of RDS in WB was higher, and that of SDS lower, than in corresponding NB and HAB samples micronized at the lowest moisture content. In NB and HAB, the concentration of RDS increased, and those of SDS and RS declined, with an increase in MC_i or T ($P < 0.01$, **Tables 2** and **3**). The interaction of MC_i and T also had a significant effect on the concentrations of RDS and SDS in NB and HAB, and the concentration of RS in NB ($P < 0.01$, **Table 3**). In WB, the concentration of RDS increased, and those of SDS and RS declined, with an increase in T ($P = 0.05$, **Tables 2** and **3**). No significant effect of MC_i or the interaction of MC_i and T on concentrations of RDS, SDS, and RS was observed for WB (**Table 3**).

The concentrations of gelatinized starch in micronized samples of NB, HAB, and WB are presented in **Table 4**. For any particular treatment, the concentration of gelatinized starch was highest in WB and lowest in HAB, which corresponded to the amylose contents of starch in the three barley types. Both MC_i and T had a significant effect on the concentration of gelatinized starch in micronized barley samples, with higher concentrations of gelatinized starch associated with higher MC_i and higher surface T ($P < 0.01$, **Table 5**). A significant interaction between MC_i and T was detected ($P < 0.01$, **Table 5**).

Thermograms from differential scanning calorimetry (DSC) of unprocessed and micronized barley samples are presented in **Figure 1**. Endothermic transitions were evident only in samples tempered to 17% moisture or 31% moisture (surface temperature of 100 °C only). Micronization resulted in slight increases in T_o, T_p, and T_c and substantial reductions in ΔH (**Table 6**). The increases in T_o, T_p, and T_c, the reductions in ΔH, and the disappearance of endothermic transitions from DSC thermograms, at higher MC_i and T, are consistent with the increases observed in gelatinized starch concentration (**Table 4**). These results also are in agreement with those of Fasina et al. (*1*), who stated that T_p was directly, and ΔH inversely, proportional to initial moisture content and surface temperature after micronization.

Micronization reduced the SDS and RS contents in the three barley types compared to levels in unprocessed samples (**Table 2**). This was attributed to the significant degree of starch gelatinization achieved (**Table 4**) and to the low degree of starch retrogradation, i.e. formation of type 3 RS (*14*, *15*, *19*), which would be expected at the low moisture contents of the micronized samples (<11.5%). This result was in agreement with results reported by Chung et al. (*32*), where RS contents in gelatinized and partially gelatinized rice starches were lower than that in unprocessed rice starch. Furthermore, micronization may have reduced the level of type 1 RS in the barley samples as a direct result of the thermal energy applied or indirectly due to an increase in kernel friability because RS was assayed in ground samples. Type 1 RS is physically inaccessible to digestive enzymes, which includes starch in cells with undamaged cell walls. Because the gastrointestinal tract of humans has no enzymes capable of digesting the cellulose, hemicellulose, or lignin in the cell wall, the starch in intact cells is protected from amylolytic digestion (*13*, *14*, *16*, *18*, *19*). Type 2 RS consists of raw starch granules that show high resistance to α-amylase hydrolysis. This type of RS is found in some starches, including those from potato, green banana, and high-amylose maize (*15*, *18*). Any type 2 RS in the barley samples may have been eliminated during micronization.

Micronized WB had the lowest concentrations of SDS and RS (**Table 2**). This was attributed to the low concentration of amylose in WB starch. Retrogradation of starch reduces its digestibility (*32*, *33*). The tendency of starch to retrograde is affected by amylose content and chain length, as has been discussed by

Table 3. Effect of Initial Moisture Content (MC_i) and Surface Temperature (T) on Rapidly Digestible Starch (RDS), Slowly Digestible Starch (SDS), and Resistant Starch (RS) Levels in Micronized Barleys[a]

		RDS		SDS		RS	
source of variation	DF	sum of squares	*P*-value	sum of squares	*P*-value	sum of squares	*P*-value
				normal barley			
MC_i	2	687.21	<0.01	613.09	<0.01	369.79	<0.01
T	2	301.37	<0.01	465.10	<0.01	211.96	<0.01
$MC_i \times T$	4	366.68	<0.01	436.89	<0.01	91.75	<0.01
residuals	9	21.68		27.20		14.41	
total	17	1376.95		1542.28		687.91	
				high-amylose barley			
MC_i	2	369.79	<0.01	245.37	<0.01	19.65	<0.01
T	2	211.96	<0.01	117.12	<0.01	15.25	<0.01
$MC_i \times T$	4	91.75	<0.01	75.74	<0.01	1.45	0.63
residuals	9	14.41		22.86		4.87	
total	17	687.91		461.09		41.22	
				waxy barley			
MC_i	2	0.52	0.92	0.25	0.94	0.08	0.95
T	2	53.52	<0.01	21.92	0.03	6.59	0.05
$MC_i \times T$	4	17.14	0.31	15.97	0.18	1.59	0.73
residuals	9	27.72		18.10		7.03	
total	17	98.90		56.24		15.29	

[a] DF: degrees of freedom, *P*: probability.

Table 4. Gelatinized Starch Concentrations in Micronized Normal Barley (NB), High-Amylose Barley (HAB), and Waxy Barley (WB) Processed at Different Moisture Contents and to Different Surface Temperatures[a]

sample	MC_i (% wb)	T (°C)	gelatinized starch (%)
NB	17.5	100	10.6 ± 0.2 e
		120	12.3 ± 0.2 de
		140	63.4 ± 2.2 ab
	32.1	100	18.3 ± 0.0 d
		120	56.9 ± 1.9 bc
		140	69.6 ± 2.0 a
	42.5	100	55.7 ± 0.7 c
		120	64.8 ± 0.1 a
		140	70.2 ± 5.4 a
HAB	17.4	100	9 0.6 ± 0.2 e
		120	12.6 ± 0.1 e
		140	20.0 ± 0.3 d
	30.7	100	12.6 ± 0.1 e
		120	19.5 ± 2.1 d
		140	36.0 ± 0.5 b
	42.3	100	25.9 ± 0.2 c
		120	38.9 ± 1.1 b
		140	45.5 ± 1.5 a
WB	17.4	100	20.2 ± 0.1 f
		120	25.2 ± 0.3 e
		140	43.0 ± 0.6 c
	31.0	100	32.9 ± 0.1 d
		120	78.2 ± 2.5 b
		140	96.3 ± 1.1 a
	39.8	100	76.8 ± 1.0 b
		120	97.6 ± 1.2 a
		140	99.0 ± 1.1 a

[a] MC_i: initial moisture content. T: surface temperature. For a particular barley sample, means in the same column followed by the same letter are not significantly different (Duncan's multiple range test, $P > 0.05$).

several researchers (*9*, *34*). It was shown by Hu et al. (*9*) that RS content increases, and glycemic index decreases, as amylose content increases. Amylose forms complex regions and semicrystalline structures more readily than does amylopectin (*33*). Therefore, starches having higher amylose contents are more resistant to digestion. These previous reports are in agreement with results from the current study where SDS concentration was in the order of NB > HAB > WB and RS concentration was in the order of HAB ≥ NB > WB. The RS contents of micronized NB and HAB were greater than those of hydrothermally treated barleys (1.6−3.0% db) (*35*) and retrograded barley starch (3.3% db) (*36*).

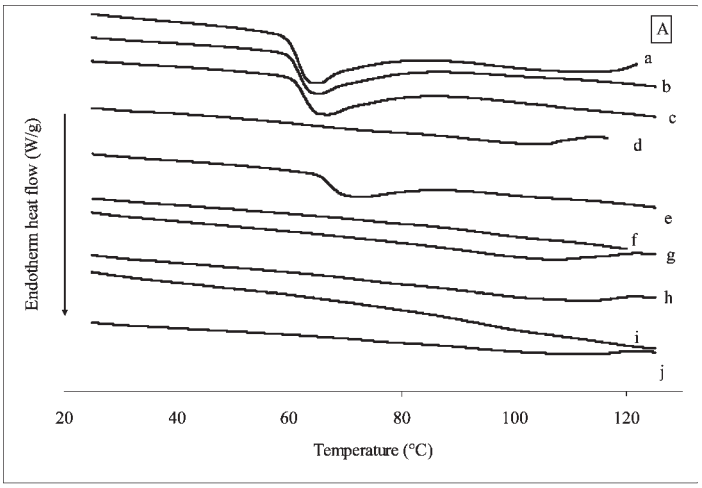
The concentration of gelatinized starch was higher in barley samples micronized at higher MC_i or at higher T (**Table 4**). This result is in agreement with those of Fasina et al. (*1*). With the exception of the sample micronized at a MC_i of 17% and to a T of 140 °C, WB samples exhibited substantially higher gelatinized starch concentrations than did corresponding samples of NB or HAB (**Table 4**). In contrast, with the exception of the sample micronized at a MC_i of 17% and to a T of 120 °C, HAB exhibited the lowest gelatinized starch concentrations (**Table 4**). These results again are consistent with the low amylose content of WB starch and the relatively high amylose content of HAB starch. Gelatinization of starch is a consequence of starch hydration at elevated temperatures and the resultant disruption of the double helix structure in starch crystallites (*37*, *38*). The lower degree of starch gelatinization in HAB was attributed to the presence of a greater degree of double helix structure and the associated greater energy requirement for double helix disruption. Conversely, the presence of less double helix structure in granules of WB starch would facilitate gelatinization. Differences in gelatinization characteristics among the three barley types may also be attributable to differences in the molecular structure of amylopectin, the ratio of crystalline to amorphous regions, and interactions among the aforementioned factors (*39*).

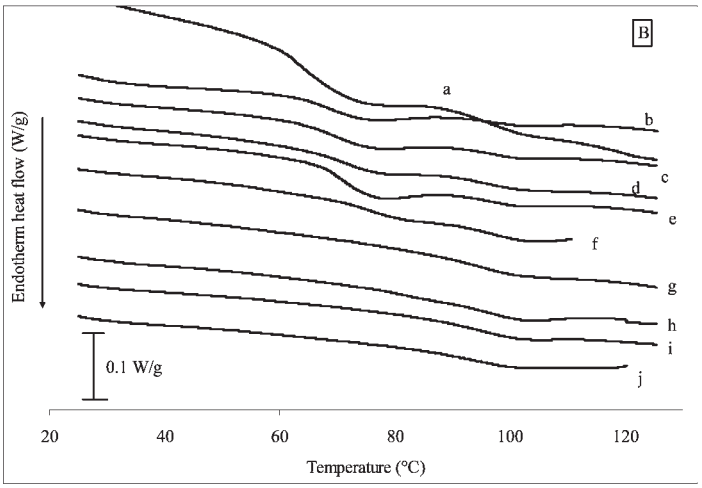
Results from DSC analysis (**Table 6** and **Figure 1**) were consistent with those from determination of gelatinized starch concentrations (**Table 4**). The lack of a visible endothermic transition in thermograms for barley samples micronized at higher MC_i and to higher T, and the associated lower ΔH values,

Table 5. Effect of Initial Moisture Content (MC_i) and Surface Temperature (T) on Gelatinized Starch Levels in Micronized Barleys[a]

		normal barley		high-amylose barley		waxy barley	
source of variation	DF	sum of squares	*P*-value	sum of squares	*P*-value	sum of squares	*P*-value
MC_i	2	3650.76	<0.01	1577.72	<0.01	11715.77	<0.01
T	2	4743.42	<0.01	957.52	<0.01	4044.87	<0.01
$MC_i \times T$	4	1931.24	<0.01	133.50	<0.01	1416.14	<0.01
residuals	9	83.26		16.44		23.24	
total	17	10408.68		2685.18		17200.02	

[a] DF: degree of freedom. *P*: probability.





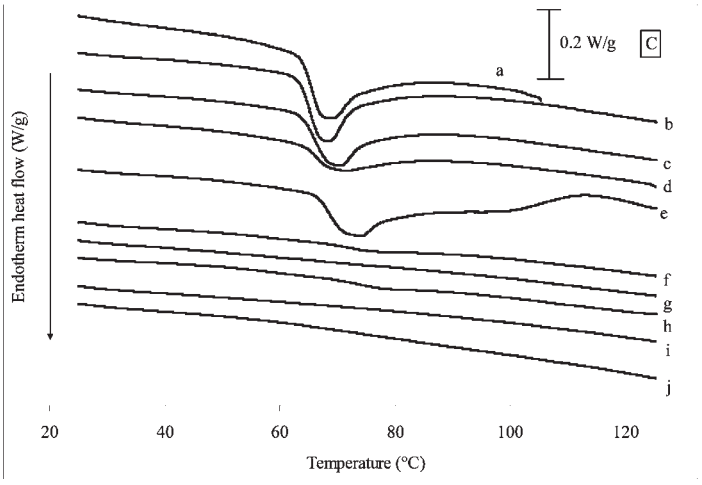


Figure 1. DSC thermograms of micronized normal barley (**A**), high-amylose barley (**B**), and waxy barley (**C**) processed at different initial moisture contents (MC_i) and surface temperatures (T).

Table 6. Thermal Properties of Unprocessed and Micronized Barleys[a]

MC_i (% wb)	T (°C)	T_o (°C)	T_p (°C)	T_c (°C)	ΔH (J/g)
		normal barley			
unprocessed		60.3 ± 0.1	64.2 ± 0.1	81.4 ± 0.5	9.6 ± 0.2
17.5	100	60.4 ± 0.2	64.6 ± 0.1	83.4 ± 0.8	9.1 ± 0.2
	120	61.7 ± 0.3	65.8 ± 0.0	80.3 ± 0.1	5.7 ± 0.3
	140	nd	nd	nd	nd
32.1	100	65.9 ± 0.2	71.0 ± 0.1	84.1 ± 0.0	3.9 ± 0.1
		high-amylose barley			
unprocessed		61.0 ± 0.1	72.6 ± 0.2	86.5 ± 0.0	2.9 ± 0.0
17.4	100	63.4 ± 0.6	74.4 ± 0.8	89.7 ± 1.5	2.2 ± 0.5
	120	64.9 ± 0.1	75.9 ± 0.1	89.9 ± 0.2	1.6 ± 0.0
	140	66.9 ± 0.1	76.5 ± 0.3	86.6 ± 0.5	0.7 ± 0.1
30.7	100	68.5 ± 0.3	76.4 ± 0.2	85.4 ± 0.4	1.3 ± 0.1
		waxy barley			
unprocessed		64.0 ± 0.1	68.0 ± 0.3	84.9 ± 0.1	8.2 ± 0.1
17.4	100	63.6 ± 0.2	67.5 ± 0.1	75.7 ± 0.8	5.2 ± 0.2
	120	64.0 ± 0.0	69.2 ± 0.0	81.9 ± 1.5	5.2 ± 0.7
	140	64.6 ± 0.1	70.9 ± 0.2	81.7 ± 1.4	2.9 ± 0.2
31.0	100	66.7 ± 0.0	73.5 ± 0.3	86.0 ± 1.7	5.0 ± 0.5

[a] A significant endothermic peak was not detected in DSC thermograms for the treatments which are not shown in the table. MC_i: initial moisture content. T: surface temperature. T_o: onset temperature. T_p: peak temperature. T_c: conclusion temperature. ΔH: enthalpy of phase transition. nd: not detected.

corresponded to the higher gelatinized starch concentrations in samples processed under these conditions. It is noteworthy that no endothermic transition was visible in thermograms of samples where as much as 50−60%, or more, of the starch remained ungelatinized. This suggests that DSC is not a sensitive method for determining the degree of starch gelatinization. The observation that RDS concentrations were higher, and SDS and RS concentrations lower, at higher MC_i and higher T (**Table 2**) was also consistent with the trends in the gelatinized starch and DSC results.

In conclusion, this study revealed that micronized samples of NB, HAB, and WB were higher in RDS, and lower in SDS and RS, than corresponding unprocessed samples. Therefore, micronization clearly is not an effective process for reducing starch digestibility in barley and similar grains and, rather, has the opposite effect. The observed increases in starch digestibility were attributed to starch gelatinization during micronization without significant retrogradation during subsequent storage. Micronized NB and HAB samples processed under similar conditions exhibited similar RDS, SDS, and RS concentrations. Micronized WB samples were markedly lower in RS than corresponding NB or HAB samples. Increasing MC_i or T enhanced starch digestibility in NB and HAB. Increasing T enhanced starch digestibility in WB. The degree of starch gelatinization achieved during micronization was, therefore, influenced by the amylose content of starch. Increases in starch digestibility were associated with increases in gelatinized starch content and reductions in ΔH values determined from DSC thermograms. DSC was not sufficiently sensitive to accurately predict gelatinized starch content in micronized barley samples.

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