Differential Scanning Calorimetry Studies on Rye Flour-Milling Streams

L. WANNERBERGER[1] and A.-C. ELIASSON[1]

Cereal Chem. 70(2):196–198

ABSTRACT

The thermal behavior of rye flour-milling streams was studied with differential scanning calorimetry. The differential scanning calorimetry-thermogram of the flour stream with the lowest levels of protein and damaged starch showed a double endotherm and was very similar to that found for the gelatinization of starch at the actual water content. The thermogram of the flour with the highest protein content and the highest amount of damaged starch was quite different and showed one broad symmetric endotherm. It could be concluded that the milling process affects the interaction between the crystalline regions and the amorphous parts in the starch granules. The results showed that an increase in gelatinization onset temperature (T_o) and peak maximum (T_m) occurred with an increased level of damaged starch. This was related to a change from a double to a single endotherm. Both T_o and T_m increased with an increased level of protein. The gelatinization enthalpy (ΔH) increased with an increased level of starch damage and with increasing protein content, but the differences in ΔH between milling streams were small.

The thermal properties of rye starch extracted from different cultivars were reported recently (Gudmundsson and Eliasson 1991). In that study, it was found that gelatinization parameters measured by differential scanning calorimetry (DSC) differed for varieties as well as for years. The gelatinization behavior of starch is known to depend not only on the water content (Donovan 1979, Eliasson 1980), but also on other components like sugar, salt, polar lipids, and fats (Osman and Dix 1960; Osman 1975; Wootton and Bamunuarachchi 1979a, 1979b, 1980; Evans and Haisman 1982; Ghiasi et al 1983; Cloke et al 1983; Davis et al 1986). Proteins affect starch gelatinization (Osman 1965) because water separates into two phases: a protein aggregate phase and a starch phase. The degree of starch gelatinization depends on the distribution of water among the colloidal components in the system and on the water activity in the corresponding aggregates. This means that the gelatinization behavior of an extracted starch is different from the gelatinization behavior in the flour. Usually the gelatinization temperature range is shifted to a higher temperature in the flour than in the starch (Eliasson 1989).

In this study, the gelatinization properties were studied by DSC for four different rye flour-milling streams together with the main flour. The thermal properties of rye flours were compared with those of wheat flours and correlated to protein content and starch damage.

MATERIALS AND METHODS

Materials

In this study, four different rye flour-milling streams, together with the main flour (M1), were investigated. Three of the flour streams were break flours (B1, B2, and B3) and one was a reduction flour (R1). The samples were supplied by NordMills (Malmö, Sweden) and analyzed for ash (AACC 1976), protein (N × 5.7, Kjell-foss method), starch (Holm et al 1986), and damaged starch (AACC 1976) (Table I). Water content was determined from weight loss after 16 hr at 105°C.

Methods

A DSC-2 calorimeter (Perkin-Elmer, Norwalk, CT) was used for measuring thermal properties. Flour and distilled water were mixed in the appropriate ratio (1:1) and transferred to a Du Pont coated aluminum sample pan. The weight of the flour-water mixture used in each pan was in the 7–20 mg range. The samples were heated from 17 to 127°C at a scanning rate of 10°C/min, with an empty pan as a reference. After the DSC run, each pan was punctured and dried 24 hr at 105°C to determine the dry-matter content. The enthalpies were calculated on a starch basis. The onset of gelatinization (T_o), the temperature at peak maximum (T_m), and the gelatinization enthalpy (ΔH) were used to characterize the gelatinization process.

RESULTS

The chemical composition of the four milling streams and the main flour is given in Table I. The range in protein content of

TABLE I
Analytical Data of Flour Streams

Flour[a]	Protein (%)[b]	Starch (%)[b]	Starch damage (FU)[c]	Ash (%)
M1	7.6	75.5	12.3	0.68
B1	4.0	86.6	5.5	0.33
B2	7.8	79.6	16.4	0.56
B3	13.8	55.1	25.6	1.79
R1	9.1	67.4	12.7	0.87

[a] M = main flour, B = break flour, and R = reduction flour.
[b] Dry basis.
[c] % Farrand units.

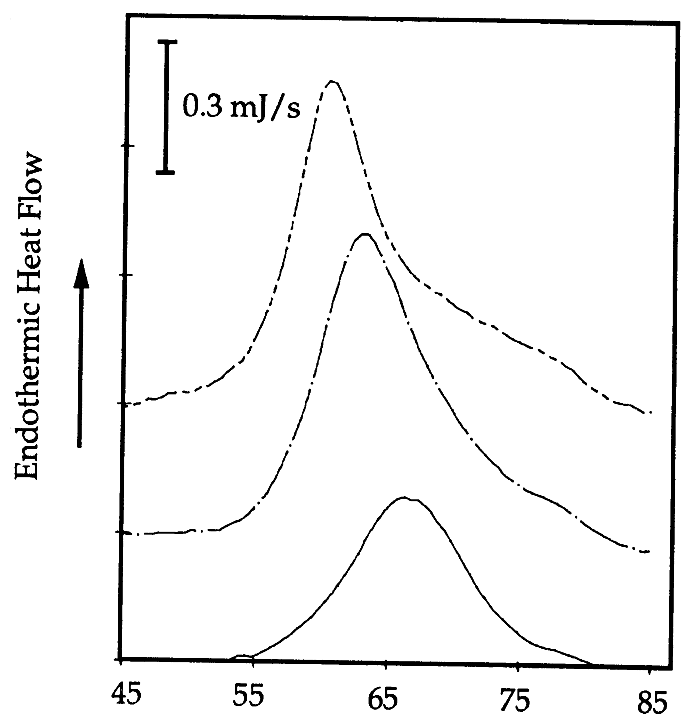

Fig. 1. DSC-thermogram for heating a 1:1 mixture of water and rye flour. — - - — = B1, —·— = B2, and — = B3.

[1]Department of Food Technology, P.O. Box 124, S-221 00, University of Lund, Sweden.

the milling streams was 4.0–13.8%, the range in level of starch damage was 5.5–25.6%, and the range in ash content was 0.33–1.79%. The variation in protein content, as well as in ash content, of the rye flour-milling streams was much larger than that of wheat flour streams investigated previously (Eliasson et al 1991). The level of starch damage was similar to the levels found in the wheat flour streams. Some of the flour streams (B3 and R1) contained high levels of nonprotein and nonstarch material.

When a mixture of rye flour and water was heated in the DSC, thermograms such as those in Figure 1 were obtained. The DSC-thermogram of flour stream B1 was very similar to that found for the gelatinization of starch at the actual water content (Donovan 1979, Eliasson 1980). However, the appearance of the thermogram of flour stream B3 (high in protein and damaged starch) was quite different. One broad but symmetric endotherm was obtained, not a double endotherm as for the other flour streams. The temperature range and enthalpy of the gelatinization are given in Table II. For the rye flour streams, T_o was 54.6–57.4°C, and T_m was 60.1–67.1°C. The variation in the gelatinization enthalpy (ΔH) was 12.5–14.5 J/g of starch. The corresponding values for the flour (M1) were 55.4°C for T_o and 63.1°C for T_m. The ΔH was 14.2 J/g of starch. As M1 is composed of the other flours, these values are reasonable.

T_o and T_m vs. starch damage are shown in Figure 2. An increased level of damaged starch increased T_o and T_m. These results are the opposite of that obtained in corresponding experiments on wheat flour streams (Eliasson et al 1991). The linear regression coefficient was 0.846 for T_o and 0.945 for T_m.

ΔH vs. the percentage of starch damage is shown in Figure 3. In this comparison there was a considerable deviation from linear relationship. The linear regression coefficient was only 0.677. ΔH increased with an increased level of starch damage, which is not in accordance with earlier results reported for wheat starch (Stevens and Elton 1971) and wheat flour-milling streams (Eliasson et al 1991). However, when the standard deviations (Table II) are taken into account, it is evident that the ΔH values did not differ much for these flour streams.

T_o and T_m were related to the protein content in the flour, as shown in Figure 4. Both T_o and T_m increased with an increased level of protein, and the linear regression coefficient was 0.930 for T_o and 0.997 for T_m. This result corresponds with that found for wheat gluten-starch mixtures (Eliasson 1983). Also, high correlation coefficients were obtained for wheat flour streams when T_o and T_m were correlated to protein content (r = 0.840 and r = 0.867, respectively) (Eliasson et al 1991). The increase in T_m with increasing protein content may be due to a delay in the diffusion of water into the starch granules because of the presence of protein on the surface of the granules.

ΔH vs. the percentage of protein in the flour streams is illustrated in Figure 5. ΔH increased with increasing protein content, and the linear regression coefficient was 0.702.

DISCUSSION

The present investigation showed that the gelatinization behavior of a rye flour depends on its composition. The gelatinization temperature of rye flour-water mixtures corresponding to the starch-water ratios in a dough was strongly related to the protein content of the flour: the higher the protein content, the

TABLE II
Gelatinization Parameters[a] of Rye Flour Streams[b]

Flour	T_o (°C)	T_m (°C)	ΔH (J/g starch)
M1	55.4 ± 0.5	63.1 ± 0.6	14.2 ± 1.1
B1	54.6 ± 0.0	60.1 ± 0.3	12.5 ± 1.5
B2	56.0 ± 0.2	63.1 ± 0.3	12.7 ± 1.6
B3	57.4 ± 0.5	67.1 ± 0.3	14.5 ± 1.9
R1	56.9 ± 0.1	64.1 ± 0.3	12.8 ± 1.4

[a]Triplicate determinations.
[b]Water-flour ratio 1:1, heating rate 10°C/min.

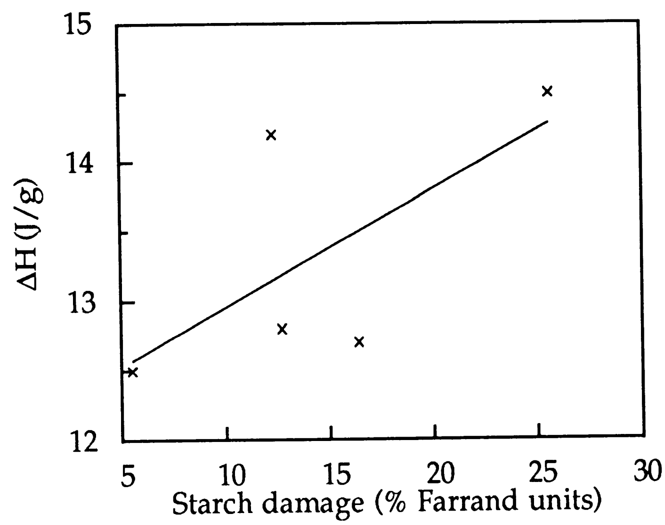

Fig. 3. Gelatinization enthalpy (ΔH) as a function of the percentage of starch damage of rye flour streams. Water-flour ratio was 1:1, heating rate was 10°C/min.

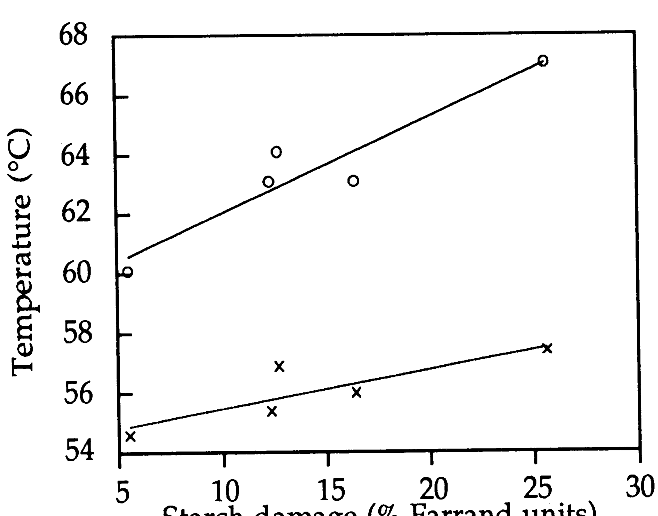

Fig. 2. T_o (x) and T_m (o) as a function of damaged starch of rye flour streams. Water-flour ratio was 1:1, heating rate was 10°C/min.

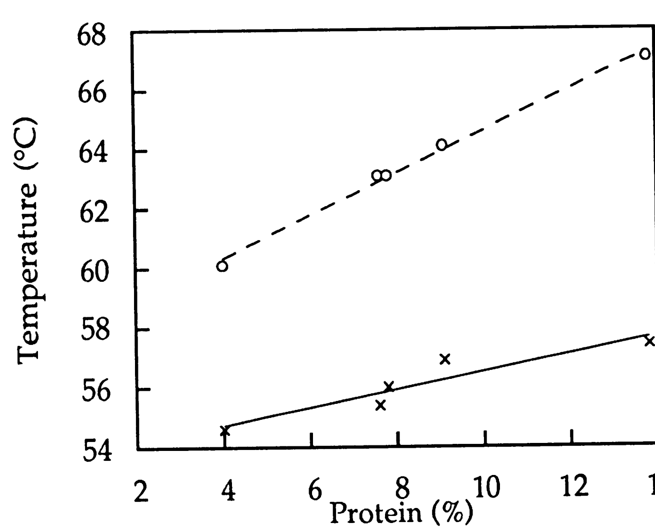

Fig. 4. T_o (x) and T_m (o) as a function of protein content of rye flour streams. Water-flour ratio was 1:1, heating rate was 10°C/min.

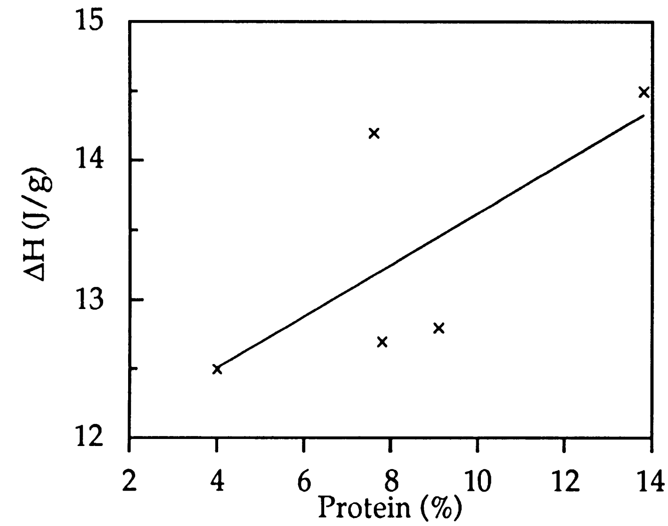

Fig. 5. Gelatinization enthalpy (ΔH) as a function of the protein content of rye flour streams. Water-flour ratio was 1:1, heating rate was 10 °C/min.

higher the T_o and T_m. T_m was more sensitive to the protein content than T_o (Fig. 4). This is the same behavior found in wheat flour-milling streams (Eliasson et al 1991). The relationship between starch damage and the gelatinization behavior was unexpected: T_o and T_m increased with increasing level of starch damage. This may be because the highest protein content also had the greatest starch damage. The protein content may override the effect of the starch damage on starch gelatinization. This is the opposite of the results found for wheat flour-milling streams. The thermograms in Figure 1 show the change in T_m very clearly. Moreover, for flour stream B3, the peak and the shoulder have merged into a single broad endotherm. This effect has been observed for a wheat flour milled to different levels of starch damage (Eliasson and Larsson, in press). The gelatinization process occurred differently for the flour with high-level starch damage. If the low-temperature side of the peak is assumed to be related to the influence of the amorphous parts of the starch granule on the gelatinization (Donovan 1979), this influence has evidently changed. As flour stream B3 contained the highest amount of damaged starch, it could be concluded that the milling process affected the interaction between the crystalline regions and the amorphous parts in the starch granules. The increases in T_o and T_m with the amount of starch damage were, thus, related to a change from a double endotherm to a single endotherm.

The level of starch damage was found to be strongly related to the protein content ($r = 0.943$). The flour with lowest protein content had the lowest level of starch damage, and the flour stream with the highest protein content had the highest level of starch damage. In the case of wheat endosperm hardness, it has been suggested that the existence of a continuous protein matrix in the cells is important. If the protein matrix is disrupted, the endosperm is soft (Stenvert and Kingswood 1977). The results we obtained for rye flour-milling streams support this hypothesis. In a flour stream with only 4.0% protein, a continuous protein matrix might not have developed. Thus, less starch damage occurs during milling.

The correlation of ΔH with percentage of starch damage and protein content gave low regression coefficients, which means that these relations are not as certain as those for temperature vs. percentage of starch damage and protein content. This is, of course, due to the high standard deviation in the measurements of ΔH. The rye flour streams were evidently quite heterogeneous, as judged from the high ash contents (as high as 1.79% in one flour-milling stream).

ACKNOWLEDGMENT

Financial support was obtained from the Swedish Council for Forestry and Agricultural Research. We are indebted to Cerealia Utveckling AB for providing the rye flours.

LITERATURE CITED

AMERICAN ASSOCIATION OF CEREAL CHEMISTS. 1976. Approved Methods of the AACC. Method 08-02, approved April 1961; Method 76-30A, approved May 1969, revised November 1972. The Association: St. Paul, MN.

CLOKE, J. D., GORDON, J., and DAVIS, E. A. 1983. Enthalpy changes in model cake systems containing emulsifiers. Cereal Chem. 60:143.

DAVIS, E. A., GRIDER, J., and GORDON, J. 1986. Microstructural evaluation of model starch systems containing different types of oils. Cereal Chem. 63:427.

DONOVAN, J. W. 1979. Phase transition of the starch-water system. Biopolymers 18:263.

ELIASSON, A.-C. 1980. Effect of water content on the gelatinization of wheat starch. Starch/Staerke 32:270.

ELIASSON, A.-C. 1983. Differential scanning calorimetry studies on wheat starch-gluten mixtures. I. Effect of gluten on the gelatinization of wheat starch. J. Cereal Sci. 1:199.

ELIASSON, A.-C. 1989. Some physico-chemical properties of wheat starch. Wheat End-use Properties. Wheat and Flour Characterization for Specific End-use. H. Salovaara, ed. University of Helsinki: Helsinki.

ELIASSON, A.-C., SILVERIO, J., and TJERNELD, E. 1991. Surface properties of wheat flour-milling streams and rheological and thermal properties after hydration. J. Cereal Sci. 13:27.

ELIASSON, A.-C., and LARSSON, K. In Press. In: Cereals in Breadmaking: A Molecular/Colloidal Approach. Marcel Dekker: New York.

EVANS, I. D., and HAISMAN, D. R. 1982. The effects of solutes on the gelatinization temperature of potato starch. Starch/Staerke 34:224.

GHIASI, K., HOSENEY, R. C., and VARRIANO-MARSTON, E. 1983. Effect of flour components and dough ingredients on starch gelatinization. Cereal Chem. 60:58.

GUDMUNDSSON, M., and ELIASSON, A.-C. 1991. Thermal and viscous properties of rye starch extracted from different varieties. Cereal Chem. 68:172.

HOLM, J., BJÖRCK, I., DREWS, A., and ASP, N.-G. 1986. A rapid method for the analysis of starch. Starch/Staerke 38:224.

OSMAN, E. M. 1965. Page 163 in: Starch: Chemistry and Technology, Vol. 2. R. L. Whistler, ed. Academic Press: London.

OSMAN, E. M. 1975. Interaction of starch with other components of food systems. Food Technol. 29:30-35, 44.

OSMAN, E. M., and DIX, M. R. 1960. Effects of fats and nonionic surface-active agents on starch pastes. Cereal Chem. 37:464.

STENVERT, N. L., and KINGSWOOD, K. 1977. The influence of the physical structure of the protein matrix on wheat hardness. J. Sci. Food Agric. 28:11.

STEVENS, D. J., and ELTON, G. A. H. 1971. Thermal properties of the starch/water system. I. Measurement of heat of gelatinization by differential scanning calorimetry. Starch/Staerke 23:8.

WOOTTON, M., and BAMUNUARACHCHI, A. 1979a. Application of differential scanning calorimetry to starch gelatinization. I. Commercial native and modified starches. Starch/Staerke 31:201.

WOOTTON, M., and BAMUNUARACHCHI, A. 1979b. Application of differential scanning calorimetry to starch gelatinization. II. Effect of heating rate and moisture level. Starch/Staerke 31:262.

WOOTTON, M., and BAMUNUARACHCHI, A. 1980. Application of differential scanning calorimetry to starch gelatinization. III. Effect of sucrose and sodium chloride. Starch/Staerke 32:126.

[Received July 10, 1992. Accepted October 6, 1992.]