Thermal Behavior of Cereals Studied by Heat Flow Calorimetry

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ABSTRACT

Heat flow calorimetry was used for studying the thermal behavior of cereals above 20° C. When the samples were heated in sealed measuring cells, intense exothermic reactions were observed at about 170° C. These exothermic reactions, which are associated with roasting and carbonization of the foods, were mainly attributed to carbohydrates.

Differential thermal analysis techniques can give considerable information about the physical and chemical changes that occur in foods during thermal treatments. The principles and methods of thermal analysis have been described exhaustively (Pope and Judd 1977, Schultze 1969, Wendlandt 1974). Heat-flow calorimetry (Calvet and Prat 1956, Hemminger and Höhne 1979) was used in our study.

Thermal analysis is a valuable tool in the investigation of the exothermic reactions that occur during heat treatments (Raemy 1981). Precise knowledge of the thermal behavior of foods permits the safe design of large-scale industrial trials, such as retorting, roasting, and frying. Calorimetric data are very valuable for the analytical characterization of products and will be used in the future to obtain more information about the properties of raw materials and finished products.

This study shows how the carbohydrate content of foods influences their thermal behavior. Plant material of very different chemical composition—wheat, soybeans, and almonds—was therefore analyzed. In 1977, Baltes mentioned some results showing a relation between carbohydrate content and exothermic reactions. These indications are confirmed here, and the close relation between carbohydrate content of food and enthalpies of exothermic reactions (corresponding to the peak surfaces in the calorimetric curves) is shown.

MATERIALS AND METHODS

The instrument used in this study was a Setaram C80 heat-flow calorimeter. A diagram of this apparatus is given elsewhere (Raemy 1981).

To prevent water vaporization at 100° C, sealed cells were used that were capable of supporting a pressure increase up to 100 bar. A fixed amount of oxygen (from air) was present in the cell.

The temperature was programmed slowly (generally 1° C/min) from ambient to about 270° C. Only the most intense reactions occurring during heating of the foods are reported here. Because no comparison values are available, the threshold temperatures of the reactions and the corresponding enthalpies indicated are approximate values.

The instrument allowed the analysis of relatively large quantities of nonhomogeneous material (eg, in whole maize grains, 2–4 g of food material). Two-gram samples of cereals were analyzed, including oats, barley, and sorghum with seed coats. For very light powders, such as reconstituted maize, only 1 g of sample was used. Almonds were cut in half, but all other foods were analyzed without any treatment.

The reconstituted maize was prepared according to the following procedure. One kilogram of maize protein was added to 30 kg of cold water and vigorously mixed. After the addition of 8.7 kg of maize starch, 0.3 kg of maize germ oil was added to the suspension. The mix was sterilized by a scraped-surface heat exchanger that held the slurry at 130° C for 1 min and directly fed a bicylindrical roller dryer. The vapor pressure and the turning speed of the roller dryer were adjusted to obtain a product with less than 1% water. (Table I contains analytical data of the individual maize constituents.) The determination of the fat, protein, water, and ash in the different plant materials was done according to standard procedures (Link 1976). Carbohydrate values were obtained by difference.

Cellulose was supplied by Fluka AG (No. 22 197, Ch-9470 Buchs, Switzerland), amylose by Sigma Chemical Co. (No. A-5257, St. Louis), and amylopectin by Koch-Light Laboratories Ltd. (No. 0400-00, Colnbrook Bucks, England).

RESULTS AND DISCUSSION

Analysis of Nonprocessed Foods

Samples of untreated whole rice, wheat, maize, oats, sorghum, and barley were analyzed for their thermal behavior. Very intense exothermic reactions were observed; around 170° C enthalpies of 550–670 J/g (or 130–160 cal/g) were measured. Soybeans (seed coats included), which are about 35% carbohydrate, were also studied; the calorimetric diagrams showed weak and broad exothermic peaks corresponding to enthalpies of about 210 J/g (or 50 cal/g). In Fig. 1, three calorimetric curves for wheat, maize, and soya are shown.

For comparison, Fig. 2 represents the calorimetric curves of

TABLE I
Composition of Individual Components Used for Reconstituted Maize[a]

	Water	Carbohydrate	Protein	Lipid
Maize				
Germ oil	···	···	···	100
Protein	1	11	81	7
Starch	2	97	1	···
Reconstituted maize	1	86	10	3
Defatted reconstituted maize	···	90	10	···

[a] In percent carbohydrate, by difference.

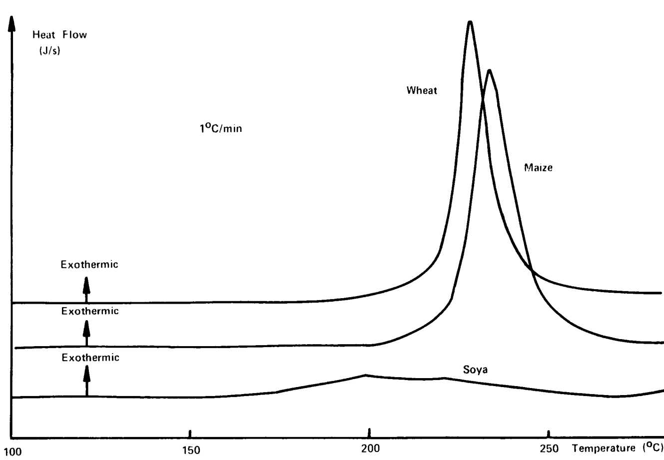

Fig. 1. Calorimetric curves of wheat, maize, and soya. All three were heated in sealed cells. Arrows indicate positive heat flow for exothermic reactions.

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nuts, almonds, and soya. The exothermic reactions detected for nuts and almonds were very weak; corresponding enthalpies were about 85 J/g (or 20 cal/g).

Figure 3 shows the calorimetric curve for raw fermented cocoa beans from Ghana. The endothermic peak, just above room temperature, is attributed to the fusion of cocoa butter. The exothermic peak above 150° C also is broad and weak.

The results, summarized in Table II, clearly show that the exothermic reactions are most pronounced for foods containing the highest percentage of carbohydrate. The apparently low reaction enthalpy for the cocoa beans is probably caused by the fact that the determination of carbohydrate was done by difference. For example, cocoa beans contain large amounts of polyphenols, which are accounted for in the determination of the carbohydrate by difference.

Analysis of Processed Foods

All plant material analyzed thus far comprised the entire grain. To further evaluate the influence of the carbohydrate content on the exothermic reactions, some refined foods were analyzed. Highly refined white wheat flour containing at least 80% carbohydrate showed an enthalpy of reactions of about 660 J/g (or 155 cal/g) at roughly the same temperature as the whole wheat.

A commercial "soluble" cacoa powder showed a thermal behavior similar to that of the raw fermented cocoa beans.

An attempt was made to analyze the thermal contributions of the individual components of maize. A homogeneous mixture of maize protein, maize germ oil, and maize starch was therefore prepared (Table I). The product was then defatted with methanol: chloroform (1:2, v/v) using a Soxhlet extractor for 3 hr. The enthalpies of reactions are listed in Table III. The exothermic reactions found with maize were observed again in the analysis of reconstituted maize, defatted reconstituted maize, and maize starch. Maize germ oil showed no marked exothermic reactions in

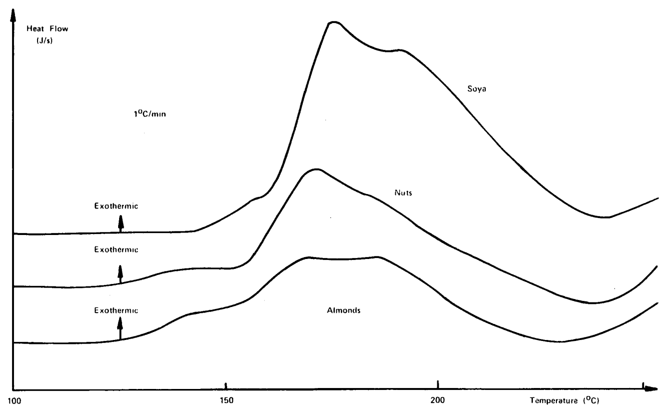

Fig. 2. Calorimetric curves of nuts, almonds, and soya. All three were heated in sealed cells. Arrows indicate positive heat flow for exothermic reactions.

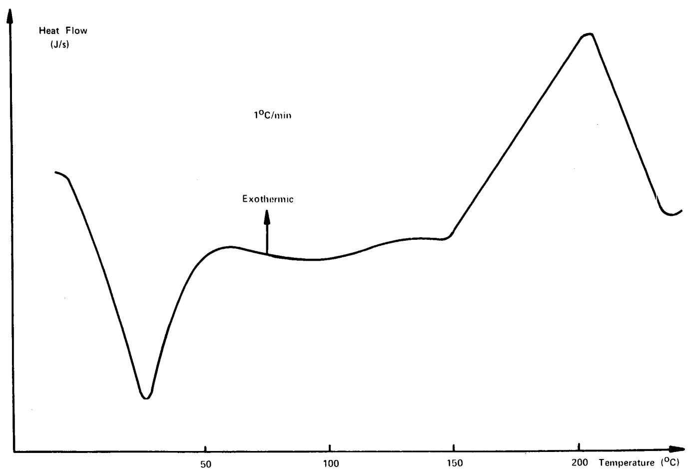

Fig. 3. Calorimetric curve of raw fermented cocoa beans that were heated in a sealed cell. Arrows indicate positive heat flow for exothermic reactions.

TABLE II
Reaction Temperatures and Enthalpies of Some Foods

Product			Carbohydrate Content (%)			Threshold Temperatures (°C)		Reaction Enthalpies	
Material	Variety	Origin	Year of Harvest	Literature[a] Value	Experimental Value	Weak Reactions	Intense Reactions	J/g	Cal/g
Wheat	Kolibri	Switzerland	1976	72	72	135	175	605	145
	Scheppers	South Africa	1976	74	74	140	175	625	150
Maize	Blizzard	Switzerland	1980	78	80	125	175	605	145
Rice (whole)	Camolino	Italy	1980	81	80	120	170	670	160
Oats	···	Switzerland	1980	68	61	125	160	545	130
Barley	···	Switzerland	1980	77	73	125	165	610	145
Sorghum	···	Hungary	1980	75	75	120	170	545	130
Soya	Fiskeby 5	···	1980	33	31	140	160	210	50
Nuts	Italian (Roma)	Italy	1980	20	24	120	150	85	20
Almonds	···	Spain	1980	22	23	120	···	85	20
Cocoa beans	···	Ghana	···	43	42	150	···	105	25

[a] Watt and Merrill 1963.

TABLE III
Reaction Enthalpies of Reconstituted Maize Components

Product	In the Reconstituted Maize (%)	Carbohydrate Content[a] (%)	Threshold Temperatures (°C) Weak Reactions	Intense Reactions	Reaction Enthalpies J/g	Cal/g
Water	1	···	···	···	···	···
Maize						
Protein	9	11	115	···	185	45
Germ oil	3	···	130	···	25	6
Starch	87	100	175	195	670	160
Reconstituted maize	100	86	155	195	675	160
Defatted reconstituted maize	100	90	155	200	710	170

[a] Experimental value.

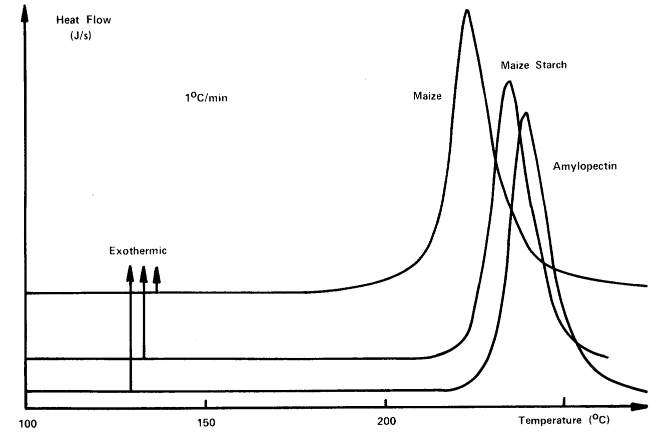

Fig. 4. Calorimetric curves of maize, maize starch, and amylopectin. All three were heated in sealed cells. Arrows indicate positive heat flow for exothermic reactions.

the same temperature range. The weak exothermic peak found in the calorimetric curve of maize protein can probably be explained by the small amount of carbohydrate remaining in this product. These results clearly indicate that the intense exothermic phenomena observed for maize are due to its high carbohydrate content.

To further show the importance of carbohydrate in explaining these phenomena, some polysaccharides of known chemical structure and purity were analyzed. Cellulose, amylose, and amylopectin showed reaction enthalpies similar to those observed for cereals. Figure 4 compares the calorimetric diagrams of maize, maize starch, and amylopectin. The chemically pure substances have a higher temperature range of reactions and show calorimetric curves with sharper peaks, as expected for relatively pure chemical substances. Figure 5 presents the calorimetric curves of amylopectin, amylose, and cellulose.

CONCLUSIONS

The thermal analysis of some cereals has shown that the exothermic reactions evidenced by heating foods containing substantial amounts of carbohydrate (more than 60%) are essentially due to reactions of the carbohydrate. The importance of protein and especially of fat for these phenomena seems to be negligible.

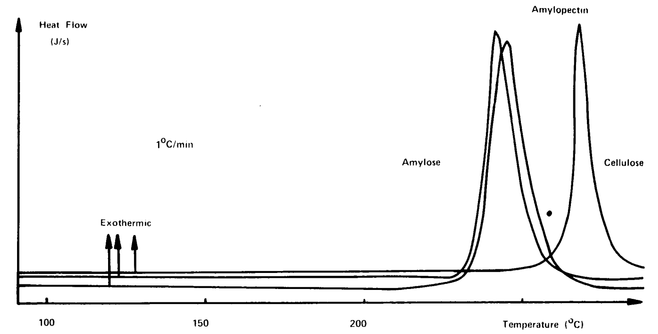

Fig. 5. Calorimetric curves of amylose, amylopectin, and cellulose. All three were heated in sealed cells. Arrows indicate positive heat flow for exothermic reactions.

No attention was given to other factors such as water content and particle size of the powders. Even if these were important in dust explosions, they probably would not modify our calorimetric measurements. The present results should help in the understanding of self-heating and thermal explosions.

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