Thermoanalytical Study of Moisture in Grain

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ABSTRACT

Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) were employed in studying the state of water in grains. If the termperature does not exceed about 200°C., water is absorbed and released reversibly; i.e., it is free water. Soybeans are an exception and appear to contain about 5% by weight of water that is held in a different manner than in corn, wheat, oats, or sorghum. Above 200°C. pyrolysis and/or oxidation predominates. TGA weight losses below 200°C. agree reasonably well with the DTA endotherms.

Considerable information is available on the state of water in grains and on the thermodynamic properties of grains. Babbitt (1) studied the effect of hysteresis on sorption and desorption of water in wheat and flour, and Hubbard et al. (2) investigated this phenomenon in wheat and maize. Pixton and Worburton (3) recently determined the moisture content-equilibrium relative humidity for four grains. Chung and Pfost (4) discussed theories for explaining hysteresis effects on the sorption behavior of various grains. Other researchers have measured or defined bound water in various ways (5-8). More recently, Shanbhag et al. (9) used wide-line NMR to determine the amount of bound water in grains and, based on this method, defined bound water.

Knowledge of the state of water in grains is important in understanding differences in the thermodynamic properties of grains and in the development of improved conditioning, drying, and storage equipment.

The research described in this paper was undertaken in an effort to apply thermoanalytical techniques to this problem.

MATERIALS AND METHODS

Water in samples of yellow dent corn, hard red winter wheat, yellow oats, grain sorghum, and soybeans was examined by the thermoanalytical techniques, differential thermal analysis (DTA), and thermogravimetric analysis (TGA).

DTA is a rapid, sensitive technique for measuring physicochemical changes accompanied by a thermal effect. The sample and reference material are heated (or cooled) at the same programmed rate, and changes within the sample (manifested as a difference in temperature from the reference material, ΔT) are recorded as a function of the sample temperature (T). Thus, the DTA thermograms depict endothermal or exothermal changes as peaks of ΔT vs. T; the peak areas are proportional to the heat liberated or absorbed (ΔH).

The instrument used for this work is a very sensitive research model, not designed for quantitative studies. Attempts to calibrate its response at the high sensitivities used in these studies were not successful. Therefore, absolute calorimetric measurements could not be made.

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Samples are placed in a pan in contact with one thermocouple junction of a differential thermocouple. An empty pan is used as the reference material in contact with the reference side of the differential couple. When no chemical or physical change occurs within the sample upon heating, there is no electromotive force (emf.) (△T) generated between the sample thermocouple junction and the reference thermocouple junction. However, if the sample undergoes a chemical or physical change, the sample thermocouple registers the difference between the sample temperature and reference temperature, and an emf. proportional to the temperature difference is generated and recorded as △T. Electronic amplification of small emf. signals allows detection of extremely small temperature changes in samples as small as 1 mg.

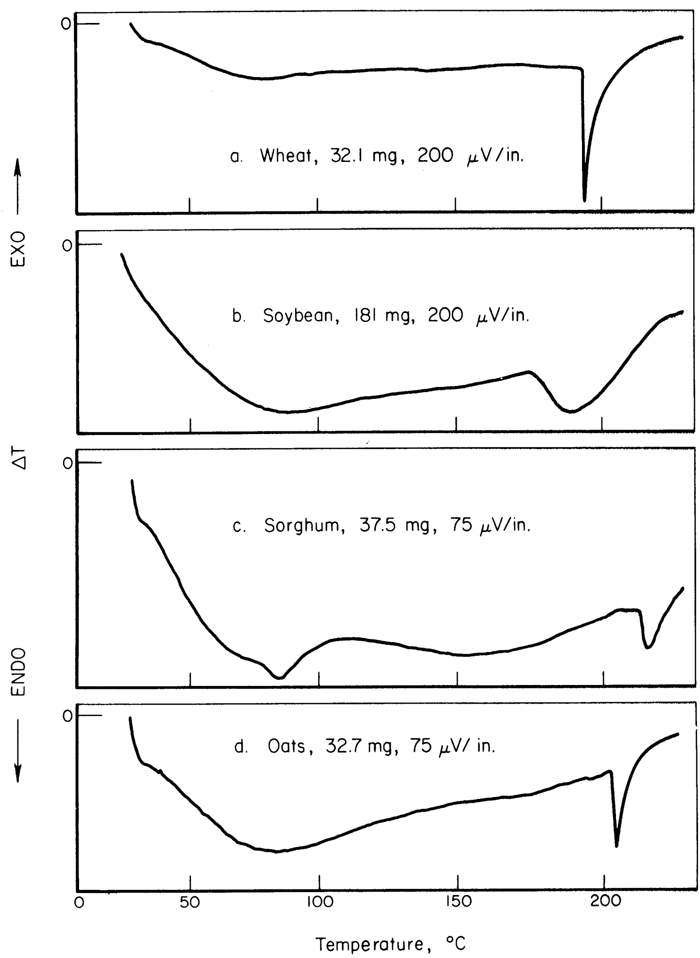

Fig. 1. DTA thermograms of intact kernels of grains. △T below the zero line depicts endothermal change and above the zero line depicts an exothermal change.

Thermogravimetric analysis (TGA) provides a continuous recording of the weight of a sample as a function of the sample temperature and environment. As in DTA, the sample is heated in a linear manner and the weight change of the sample is recorded against sample temperature in the resulting thermogram. This technique can thus provide a rapid and accurate means for determination of the water content of materials including tissue. Loss of water upon heating results in the corresponding loss in weight of the sample, and the percent weight loss is equal to the percent water content of the original sample which was released under the conditions of the experiments.

The DTA instrument used in this study was a Model LB202 DTA research instrument manufactured by the R. L. Stone Division of Columbia Scientific Industries. The sample cell, surrounded by a furnace, contains a ring-type differential thermocouple fabricated from Platinel®. The Stone H-5 cell was used for subambient studies.

The TGA data were obtained with a Cahn RG recording electrobalance housed in a glass vacuum bottle. Ancillary equipment included furnaces, temperature program controller, and recorder. Samples were suspended from the balance beam

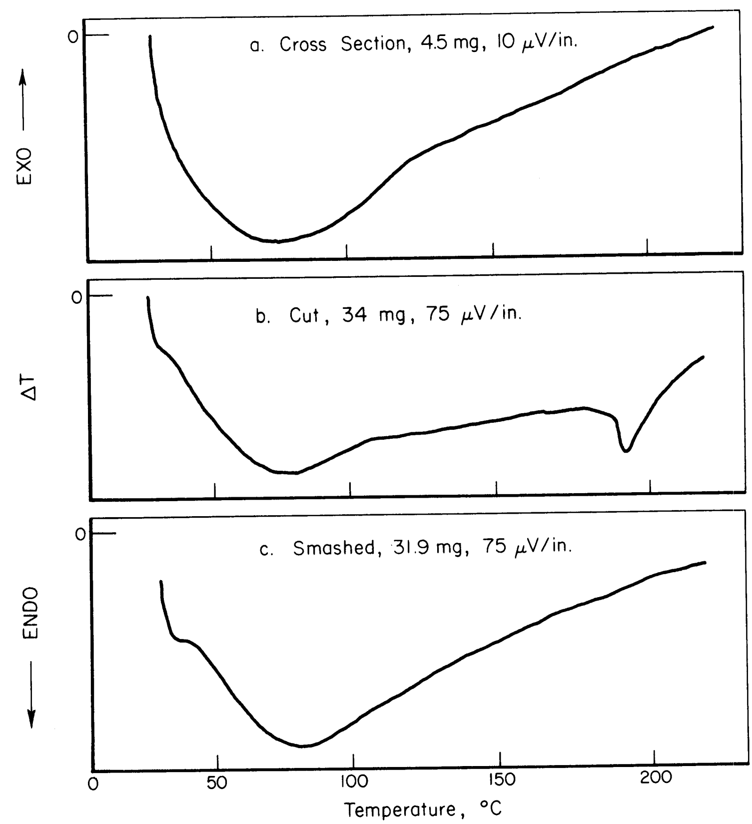

Fig. 2. DTA thermograms of partial kernels of wheat. ΔT below the zero line depicts endothermal change and above the zero line depicts an exothermal change.

on a fine wire into a heated tube attached to the vacuum bottle. The sample weight was continuously recorded as a function of the sample temperature.

Whole and crushed kernels of the grains were examined by DTA and TGA. Whole kernels of corn were not analyzed because of their large size. Heating rates of 4°C. per min. for DTA and 5°C. per min. for TGA were selected. (Higher heating rates result in an undesirable thermal lag between the sample and the environment.) Use of static air, flowing air, flowing nitrogen, and reduced pressure was investigated. The behavior of the grains was not appreciably different under these various conditions. However, if the samples were heated above 250°C. in air, extensive oxidation or pyrolysis occurred, or both. The samples were conditioned in a constant-temperature-humidity room (75°F., 50% r.h.) for several weeks before analysis.

RESULTS AND DISCUSSION

The elevated temperature DTA thermograms of the five grains studied are all similar and show no essential differences among grains except in the case of

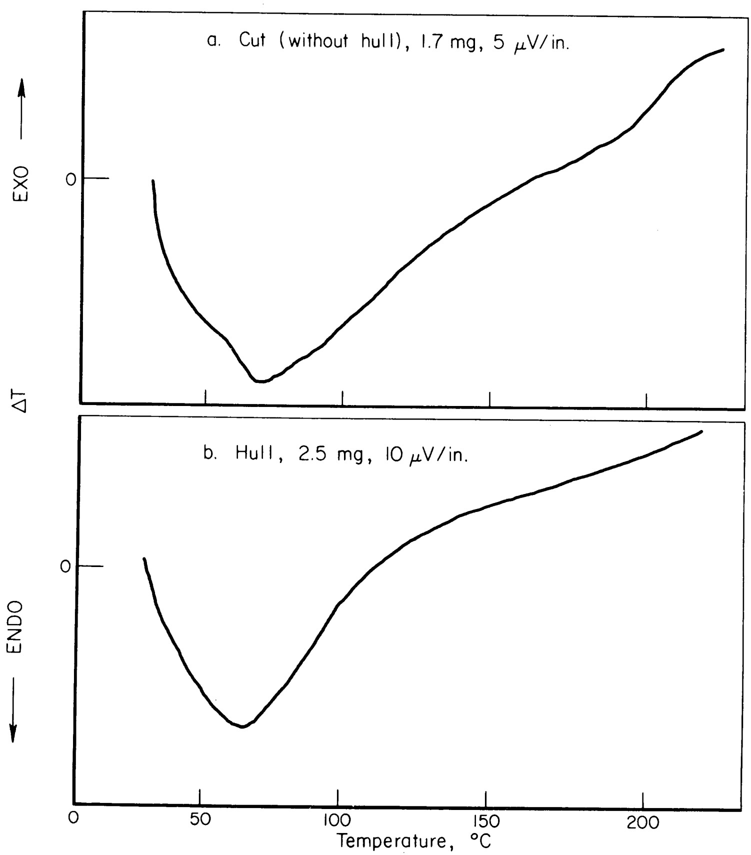

Fig. 3. DTA thermograms of partial kernels of soybeans. ΔT below the zero line depicts endothermal change and above the zero line depicts an exothermal change.

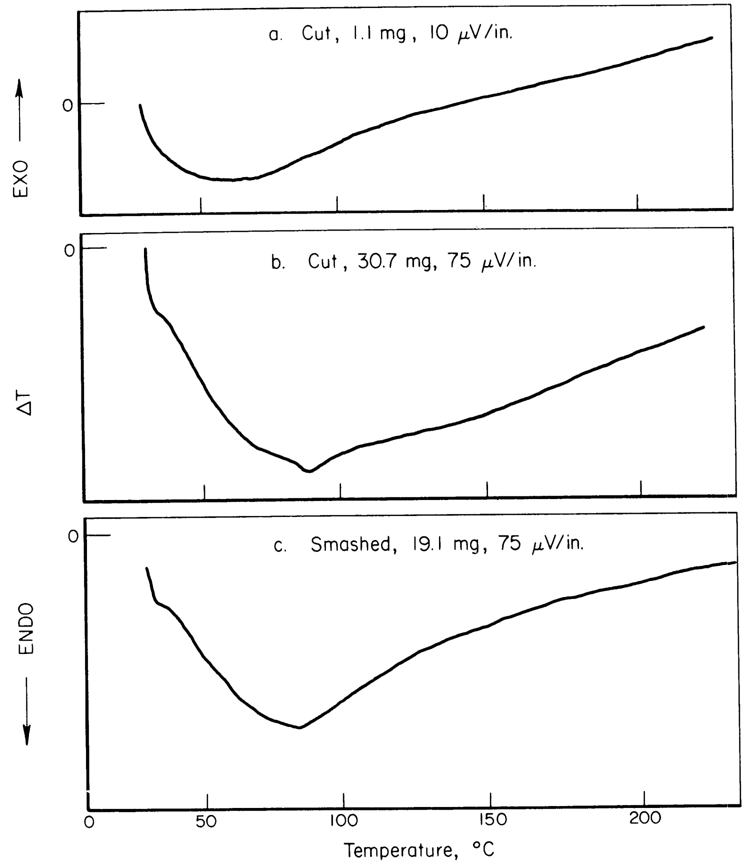

Fig. 4. DTA thermograms of partial kernels of sorghum. ΔT below the zero line depicts endothermal change and above the zero line depicts an exothermal change.

sorghum. However, there are substantial differences between the thermograms of intact grains and cut, fractured, or crushed grains. Figure 1 shows thermograms[3] of whole kernels of wheat, soybeans, sorghum, and oats. Each thermogram shows a large endotherm presumably caused by dehydration in the vicinity of 60° to 90°C. and a second, sharper endotherm in the vicinity of 200°C. Sorghum exhibits a small relatively sharp endotherm at about 85°C. superimposed on the broad initial endotherm, and a second very broad endotherm at about 130° to 180°C., neither of which is shown by the other grains.

Figures 2–6 show thermograms of partial, cut, or crushed kernels of wheat, soybeans, sorghum, oats, and corn. These thermograms also show the same large, broad endotherm as whole kernels with its maximum in the vicinity of 60° to 90°C., but the sharp endotherm at about 200°C. is usually absent. This sharp

[3]These thermograms are tracings of actual thermograms which were selected as being representative of many others obtained.

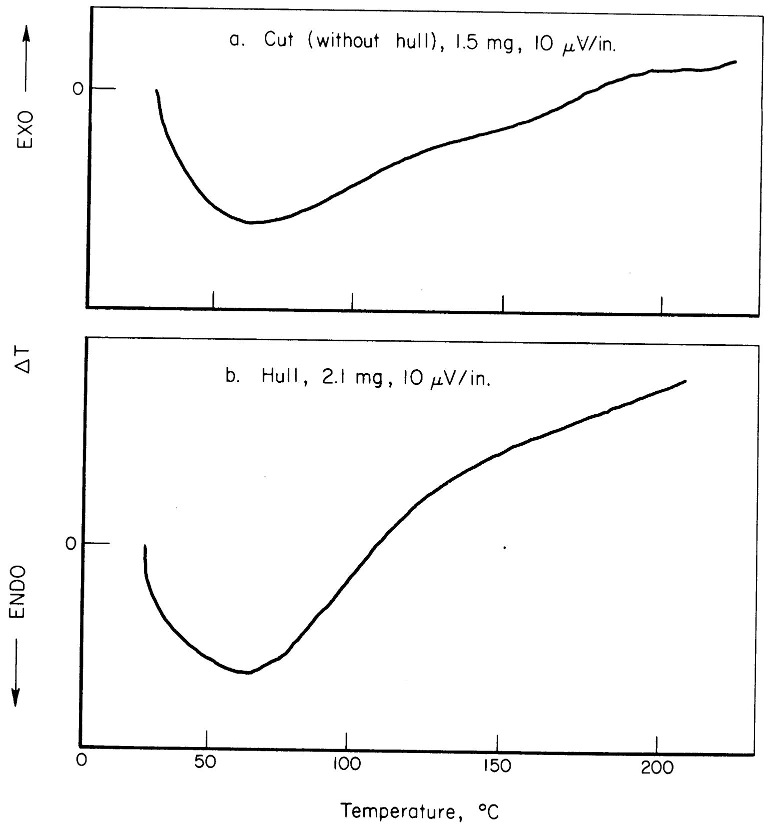

Fig. 5. DTA thermograms of partial kernels of oats. ΔT below the zero line depicts endothermal change and above the zero line depicts an exothermal change.

endotherm is apparently caused by gross rupture of the outer membrane and/or overall structure of the kernel resulting from internal pressure and sudden vaporization of water contained in the kernel. In cases where it does occur, it is invariably smaller than in the case of whole kernels of grain. In these cases it is probably due to "case-hardening" and subsequent rupturing of the cut grain surfaces.

With the exception of soybeans, the thermal effects observed by DTA below 200°C. appear reversible. When samples of grain were cooled, re-equilibrated in the constant-temperature-humidity room the thermograms were essentially duplicated, provided the temperature was not allowed to exceed about 200°C. Hence, the water released is reabsorbed upon cooling.

The five grains were also examined by subambient DTA. However, only soybeans exhibited any significant subambient endotherm or exotherms (Fig. 7). The cooling curve (upper portion) shows an exotherm at about -30°C. that probably results from crystallization of water, and the heating curve (bottom portion) shows an endotherm at about -25°C. that is presumed to result from

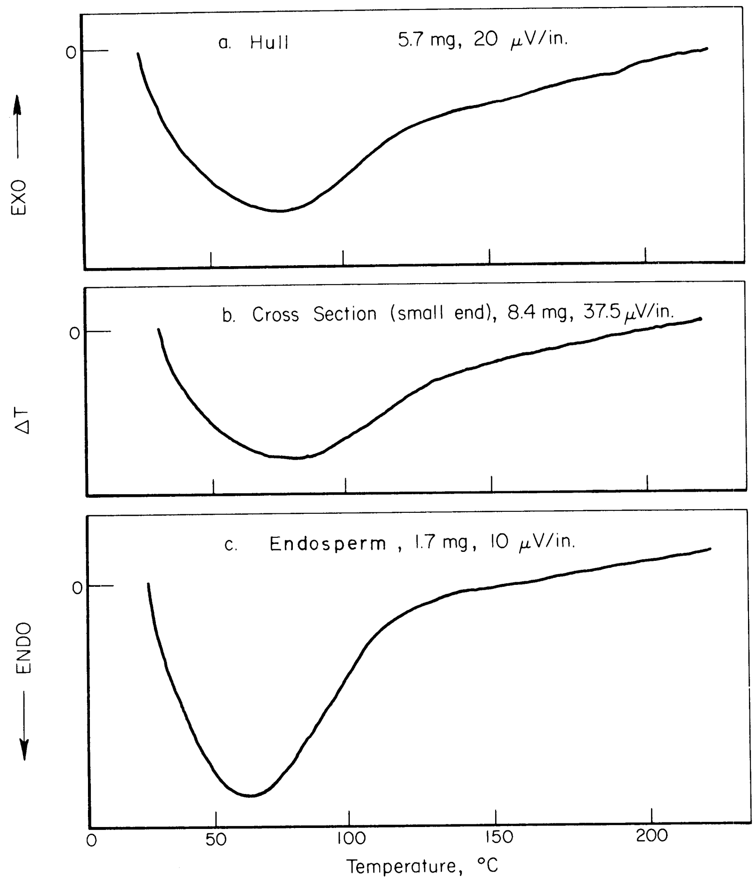

Fig. 6. DTA thermograms of partial kernels of corn. ΔT below the zero line depicts endothermal change and above the zero line depicts an exothermal change.

melting of the ice[4]. The other three grains did not show the endotherm and exotherm shown by soybeans. Thus, soybeans apparently contain moisture which is held differently than the moisture in the other grains. These differences might be expected because of the high oil content of soybeans. Chung and Pfost (4) observed differences in isotherms of various corn products, including the germ. These authors also observed that corn germ had lower heats of sorption than other parts of the corn kernel.

The magnitude of the DTA endotherm is a function of the energy absorbed as well as the weight of the sample (i.e., its heat capacity). Sample sizes ranged from 1 to 5 mg. for cut and crushed samples to about 300 mg. for whole sorghum kernels. To compare the results, the magnitude (maximum pen deflection X range factor) of

[4]It is a characteristic of the subambient DTA cell used that the cooling curve is usually above the ΔT baseline (0 on the left side of the chart), and that the heating curve is below the baseline.

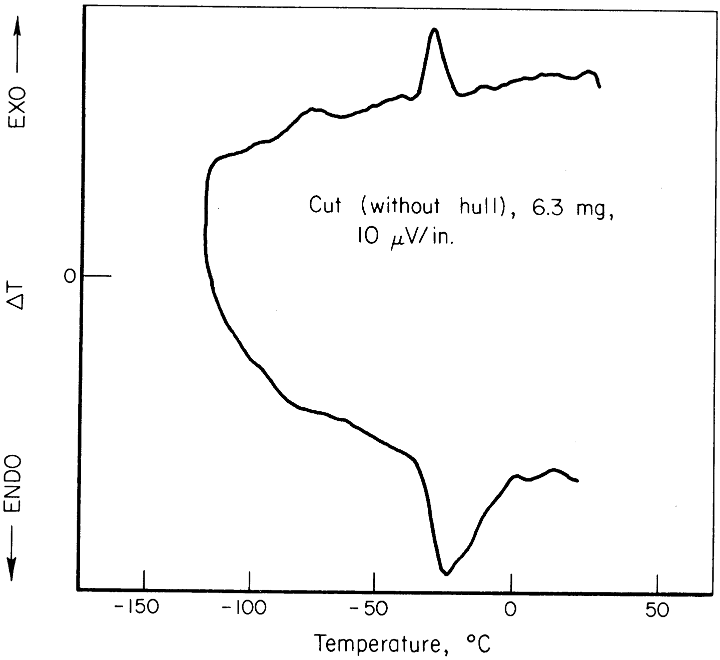

Fig. 7. Sub ambient DTA plot of soybeans.

the endotherms was divided by the weight of the samples. The resulting adjusted values are recorded in Table I. These data show that the initial endotherm is smaller for whole kernels than for crushed kernels in each case. This supports the hypothesis that part of the water is lost at a higher temperature in the case of intact kernels than for crushed kernels.

TABLE I. MAGNITUDE OF INITIAL ENDOTHERM FOR VARIOUS GRAINS

Grain	Number of Samples	Endotherm Magnitude[a] Avg.	Std. Dev.
Whole kernels			
Oats	3	44	...[b]
Wheat	5	49	2
Soybeans	1	49	...[b]
Sorghum	4	61	7
Crushed kernels			
Oats	8	63	11
Wheat	6	68	12
Corn, yellow	7	74	7
Soybeans	10	78	16
Sorghum	13	79	10
Corn, white (starch)	5	157	19

[a]These endotherm values have been normalized to 1 mg. weight for each sample.
[b]Not calculated because of the small number of samples.

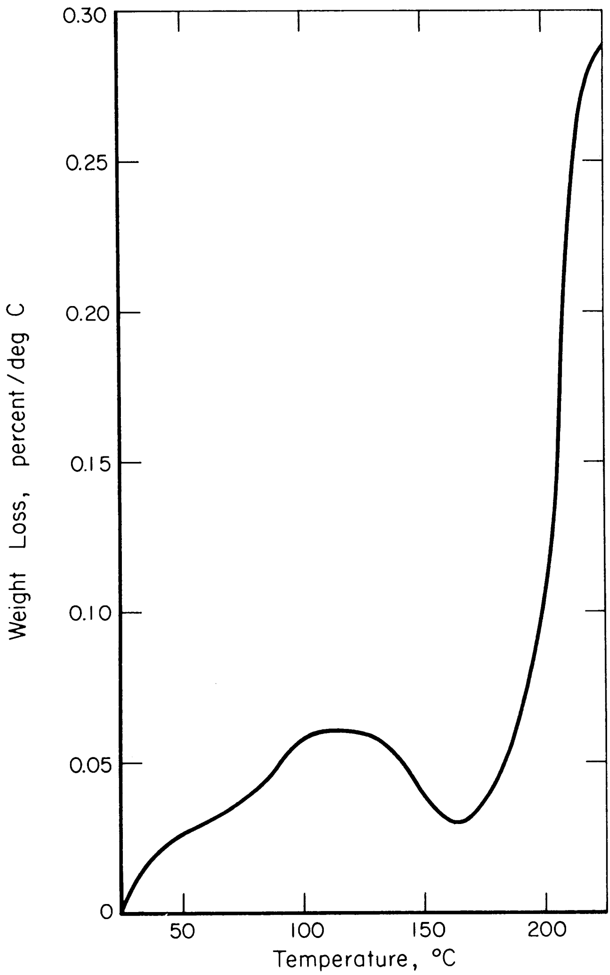

Fig. 8. Differential TGA plot for soybeans.

It appears logical to surmise that the initial broad endotherm in the DTA thermograms is caused by the latent heat of vaporization of the water lost from the grain as it is heated, since these changes were reversible in the cases studied. To test this hypothesis, the grains were also subjected to TGA. The TGA data were obtained on partial kernels, because whole kernels of corn and soybeans were too heavy for the electrobalance. In addition, it was deemed advisable to avoid the skin effect noted previously. The kernels were cross-sectioned to get fractions with compositions representative of the whole kernels. The TGA data for representative samples of the grains are shown in Figs. 8-12. These are derivative plots rather than standard weight loss plots; that is, the function plotted is rate of weight loss (percent per degree centigrade) as a function of temperature.

Except for wheat and oats, the TGA plots reach a maximum or a plateau at about 100° to 125°C. In each of the corresponding DTA thermograms, the major

TABLE II. TGA WEIGHT-LOSS[a] DATA FOR GRAIN

Kernel Grain	25°–200°C. Number of Samples	25°–200°C. % Weight Loss Avg.	25°–200°C. % Weight Loss Std. Dev.	25°–125°C. Number of Samples	25°–125°C. % Weight Loss Avg.	25°–125°C. % Weight Loss Std. Dev.
Wheat	5	5.9	2.1	4	1.3	0.3
Oats	5	6.6	1.4	5	3.7	0.6
Corn (yellow)	7	7.0	1.5	6	3.4	0.2
Soybeans	7	7.7	0.5	6	2.8	0.5
Sorghum	7	8.5	1.0	4	5.4	0.5

[a]Based on the wet weight.

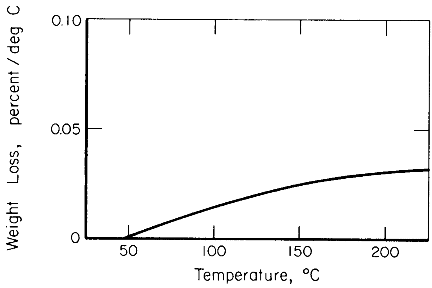

Fig. 9. Differential TGA plot for wheat.

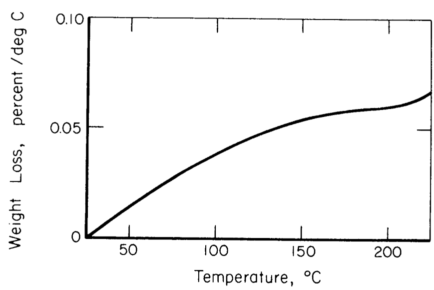

Fig. 10. Differential TGA plot for oats.

part of the endotherm extends from 25°C. to about 125°C. However, complete return to the baseline does not occur in most cases until about 200°C.

Table II gives the average weight loss data for grains in two temperature ranges, 25° to 125°C. (the approximate temperature range of the DTA endotherm), and 25° to 200°C. (the temperature at which the weight loss curve starts to rise sharply because of irreversible loss of water or pyrolysis).

Because of scatter in the data, no statistically valid comparison is possible with the small number of samples in this study. However, simple ranking of the data indicates the weight loss data generally correlate with the adjusted magnitude of the DTA endotherm shown in Table I. For both temperature ranges, oats and wheat are in reversed order compared to the DTA data; however, for the 200°C. TGA data, the difference between oats and wheat is so small that it is not significant.

Soybeans present an anomaly. Soybeans were the only grains studied that showed any ice formation in the subambient DTA studies. Yet the total water content[5] of soybeans (at 200°C.) is not significantly higher than that of the other grains, and apparently lower than any grain other than wheat at 125°C. Also, soybeans show the largest increase in rate of weight loss between 175° and 225°C. Hence, at least some of the moisture in soybeans apparently is "free" water trapped in a structure that will not permit its escape until about 200°C., but which will allow crystallization.

[5]Although the data presented in this paper are really weight loss data, it is generally recognized that at temperatures below 200°C. the effluent contains only a small percentage of components other than water.

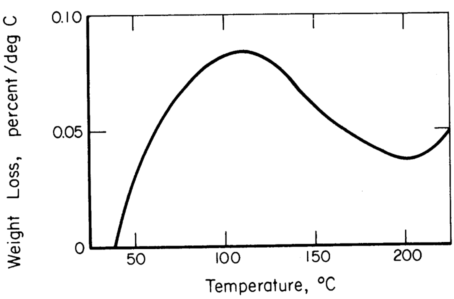

Fig. 11. Differential TGA plot for sorghum.

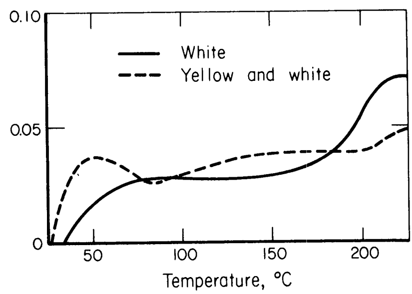

Fig. 12. Differential TGA plot for corn.

There is confusion in the literature about the meaning of the terms "free" and "bound" water in grains, free water usually being considered that water lost at about 100° to 125°C. This work suggests that there is more than one kind of "free" water and that there is probably no clear dividing line between "free" and "bound" water.

It is our feeling that the water that is reversibly lost (i.e., the water liberated when the grain is heated to about 175° to 200°C. and can be readsorbed upon cooling) should be called adsorbed water rather than "free" water. The water lost at higher temperatures is tightly bound. However, it is misleading to call it "bound" water, because most of it is present as hydrogen atoms and hydroxyl groups of the carbohydrate structure, and is released as water only upon destructive heating (pyrolysis) of the tissue. However, some of the water in soybeans appears truly to be "free" water, trapped in the interstices of the tissue, not adsorbed as in the case of the other grains.

CONCLUSIONS

Water released from grain at temperatures below 200°C. is adsorbed water; soybeans appear to contain some "free" water. Above 200°C., however, pyrolysis and/or oxidation predominate. Soybeans, unlike corn, wheat, oats, or sorghum, contains water that appears to be trapped within the structure. TGA weight loss below 200°C. agrees reasonably well with the DTA endotherms in the grains studied.

Acknowledgment

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