Thermochimica Acta, 69 (1983) 221—228
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

CALORIMETRIC STUDIES OF HEAT AND ENZYME TREATED CEREAL-PRODUCTS

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Abstract

If the drying of "wet" harvested grain is carried out at drying temperatures which are too high, the protein content of the grain will be denatured. A series of tests, to clearly detect this break down, caused by heat and enzyme action were performed using a Heat Flux DSC.

With the DSC, it was not possible to obtain reproducible results on tests carried out on whole grains because of differences between individual grains. With tests carried out on flour from thermally treated grain the break down was already apparent and the tests showed good reproducibility, when the gluten was extracted and tested the difference was even more clearly shown.

To avoid the problem of water, surface bound to the gluten, all samples were vacuum dried at ambient temperature for a fixed time. The tests were carried

0040-6031/83/$03.00

out in open sample pans, with a N_2 atmosphere, the resulting structured endothermal peak occurs in the temperature range 20 to 200°C. The peak maxima of treated gluten is found at lower temperatures, also the enthalpy change is much less than for undamaged gluten. The detection limit for the effects of heat on gluten using DSC far exceeds that of commonly used current methods.

Introduction

Drying grain to produce supplies of grain suitable for bread making is in many areas a necessity. The reason for the current study of the drying process is that expensive energy is needed for artificial drying, the time pressure during harvest, and the possibility of heat damage to the grain. Topics of interest are

- drying temperatures
- drying media to remove the moisture
- detection of heat damage.

The removal of moisture at predetermined temperatures and in controlled atmospheres is an ideal application for thermogravimetry and simultaneous thermal analysis. Tests on the complete grain are necessary to maintain its relevance to the real situation. Only by using large sample quantities can the natural variations of single grain analysis be avoided.
Using calorimetric methods it is possible to detect heat damage on grain after separation of the temperature resistant components of the grain, e.g. on flour, even better on gluten.

Experimental

Heat damage was studied on wheat, wheat flour and gluten of wheat. To get the necessary damage on the complete grain this was partially done by rapid heating in the thermobalance at exactly reproducible grain temperatures. Gluten was available as pre-dryed powdery product as well as in wet, plastic state. Of the powdery samples, marked A1 and A2, A1 was untreated (vital) and A2 enzymatically damaged. The wet gluten samples, marked R10 and R13 were of the summer wheat type "Ralle" whereas R13 was obtained of wheat grain which was treated at 150°C for 5 minutes. Further wet gluten samples C15 and C17 were obtained from untreated flour (C15) as well as from flour (C17) treated at 150°C for 5 minutes. All gluten samples were vacuum dryed at ambient temperature and treated for the same time (10 min) before thermal analysis independent of their different initial moisture contents.

The drying process on wet wheat was recorded by the thermobalance (Netzsch STA 409). For this sample crucibles with a volume to 3,4 cm^3 were used to be able to analyse simultaneously a larger number of grains (approx. 40 wheat grains). Heating rates were up to 2 K/min, the atmosphere used was dry air (dynamic 100 cm^3/min); flour and gluten were tested with the heat flux DSC (Netzsch DSC 444) in a static nitrogen atmosphere in the temperature range 20 ... 200°C at a heating rate 5K/min. Sample crucibles used were open pans of pure aluminium, sample quantities were 20 ... 70 mg for gluten, the reference cell was empty. The DSC 444 was operated with the data acquisition system 414/1 and computer HP 85 with plotter. Peak integration in preselectable ranges and determination of characteristic temperatures was carried out automatically with this data system.

Results and Discussion

The vacuum drying of the gluten samples already shows differences between treated and untreated samples: independent to the initial moisture damaged samples show a higher mass loss (table 1)

table 1	powdery samples		plastic samples			
	A1 (untreated)	A2 (enzym.damaged)	R10 (untreated)	R13 (heat damaged)	C15 (untreated)	C17 (heat damaged)
mass loss	1,45%	1,6%	14,3%	37,3%	10,9%	14,1%

The results obtained by vacuum drying indicate that with denaturing water is less tightly bonded to gluten. This effect can be very clearly noticed for the high initial moisture of the wet gluten samples R10 and R13 as well as C15 and C17. The DSC trace for gluten in the range 20 ... 200°C exhibits a partially structured endothermal peak. The dry gluten show an equal endothermal peak with the peak starting at 30°C and ending at 170°C. There is no significant difference in peak temperature which is at 92,5°C (A1) and 95°C (A2); with the damaged gluten the reaction enthalpy is clearly reduced by 29%, compared to the undamaged sample.
Fig. 1 and 2 show the graphs plotted for the DSC runs on the dry gluten A1 and A2.

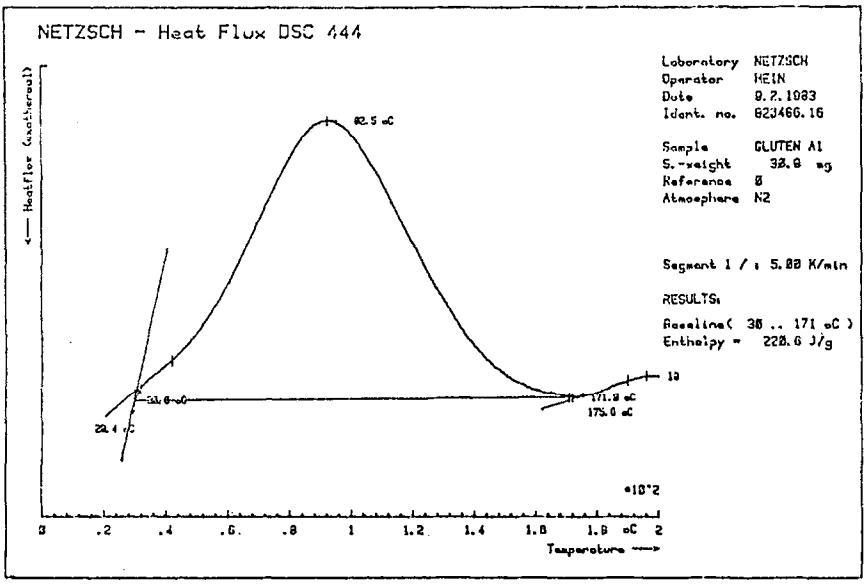

Fig. 1: wheat gluten A1 (dry gluten) endothermal reaction enthalpy 220,6 J/g

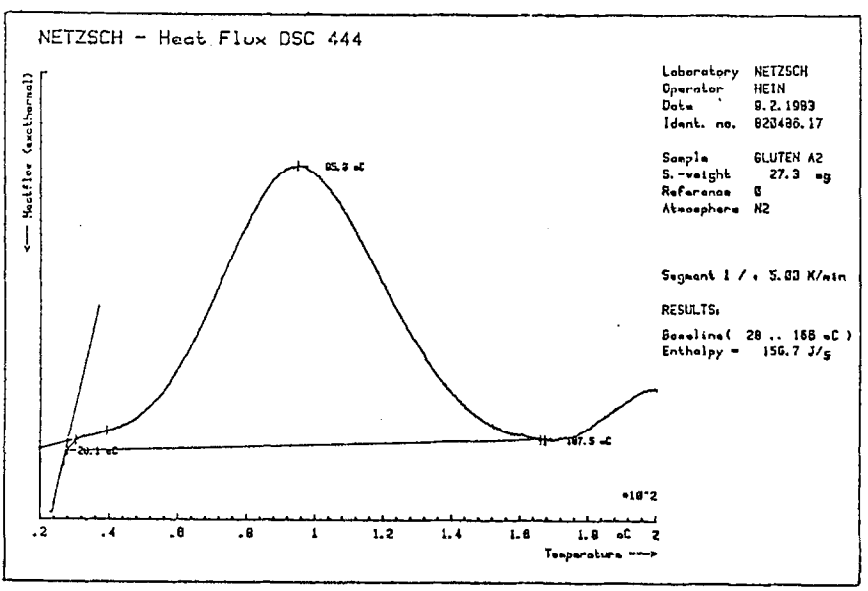

Fig. 2: wheat gluten A2 endothermal reaction enthalpy 156,7 J/g

Untreated wet gluten samples always show a structured (double-)peak with main maximum at approx. 120 ... 130°C.

Treated wet gluten - obviously dependent on the degree of damage - shows lower peak temperatures, a simpler peak shape (R13) and lower reaction enthalpy. Fig. 3 shows in a direct comparison the untreated sample R10 and the heat-treated wet gluten R13.

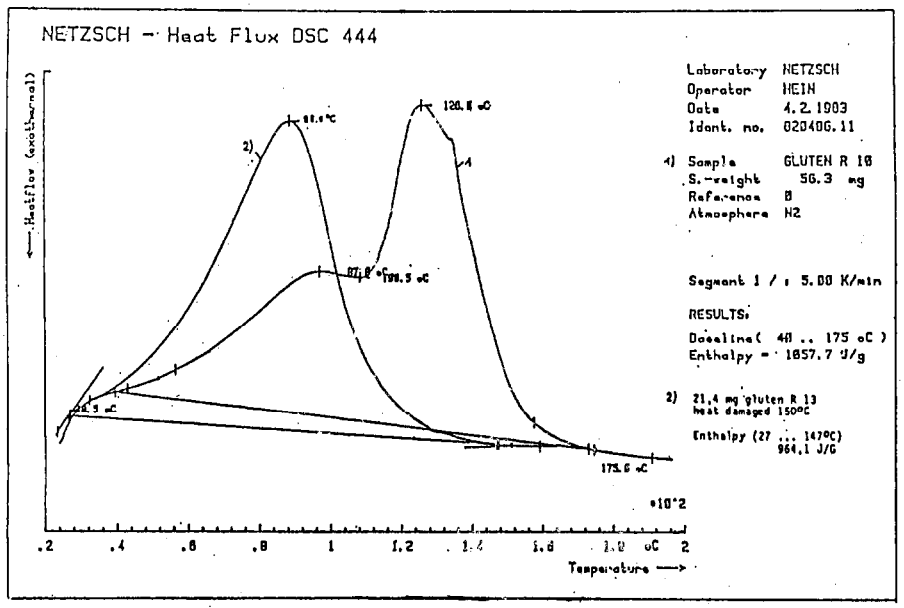

Fig. 3: wheat gluten R10 endothermal reaction enthalpy 1057,7 J/g
wheat gluten R13 endothermal reaction enthalpy 964,1 J/g

For the plastic gluten C17 which was washed out of heat-treated flour (150°C, 5 min) no corresponding distinct difference was found between the reference sample C15, as was shown by R10 and R13. By choosing the same integration limits for the enthalpy determination, the difference would exceed the values stated below.

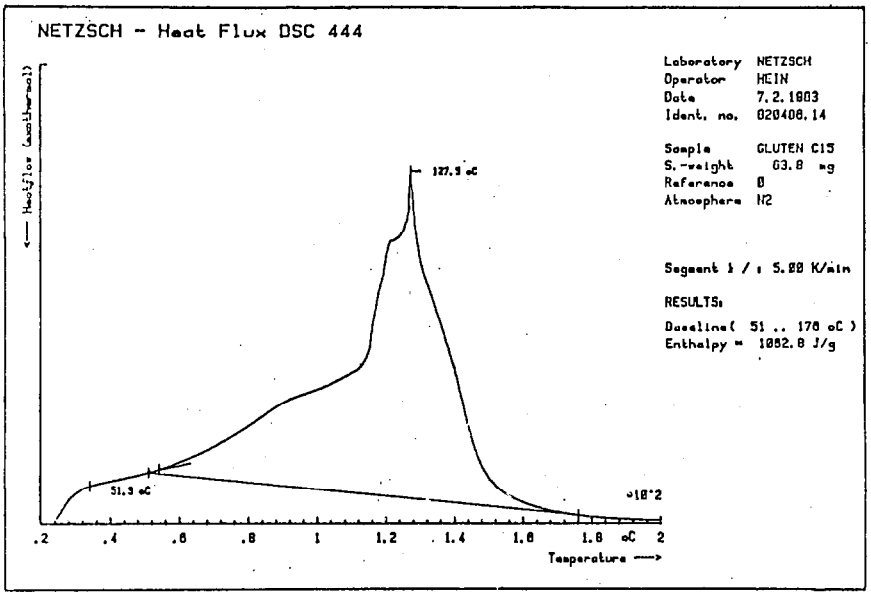

Fig. 4 wet gluten C15 endothermal reaction enthalpy 1062,8 J/g

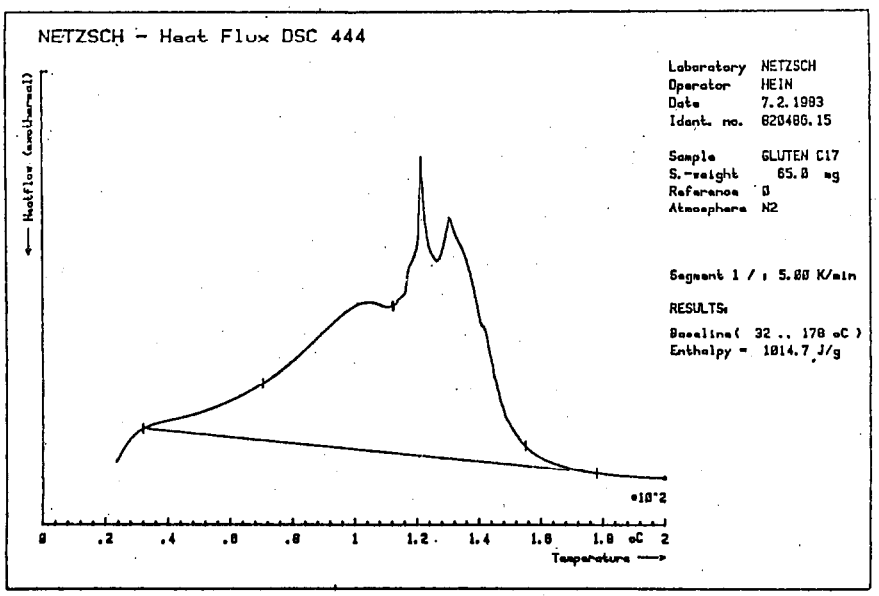

Fig. 5 wet gluten C17 endothermal reaction enthalpy 1014,7 J/g

Treating flour and grain under the same conditions, i.e. 150°C for 5 min., results in greater damage to the gluten extracted from grain, than that extracted from flour. The DSC gives a sensitive indication of these subtle differences (samples R/ samples C) and therefore shows better results than common test methods where no difference could be determined for the samples C15/C17.

The results obtained in simultaneous thermoanalytical tests of the drying process on grain indicated clearly the dependence of the mass losses to the initial moisture of the grain. The atmosphere was dry air. Tests under atmospheres of different moisture content will be continued.

Conclusion

The Heat Flux DSC offers a sensitive method for detecting damage to gluten. With special sample preparation it is also possible to obtain reproducible test results for open sample pans.

The heat influence on grain causes structural changes which can be clearly detected by DSC on protein (gluten). By DSC differences in treated wet gluten could be determined where current standard test methods have so far failed.

The basic structure changes of gluten are the subject of further work.