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THERMAL ANALYSIS OF PROTEIN-CARBOHYDRATE MIXTURES IN OXYGEN

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SUMMARY

Thermal analysis of wheat gluten (G), food carbohydrates and their admixtures by DSC in oxygen revealed two major exothermic peaks. Heat of combustion in the 200–400°C range decreased in the order: HPMC > hydrocellulose (HC) > cellulose > glutenin > CMC > G/HC > G/maltose ≃ glucose ≃ lactose ≃ starch > G/cellulose ≃ G/CMC ≃ G/HPMC ≃ maltose > G/glucose ≃ sucrose ≃ ascorbic acid > G ≃ G/ascorbic > G/starch > gliadin > G/sucrose. In the range 400–650°C, the order was: G/CMC > G/sucrose > gliadin > G/ascorbic > G > G/HPMC > CMC ≃ sucrose > G/starch > G/HC ≃ G/glucose ≃ maltose ≃ ascorbic ≃ G/cellulose > glucose > G/maltose ≃ G/lactose ≃ lactose > glutenin > HPMC > cellulose > starch > HC. These differences are discussed in relation to antinutritional and toxic effects of thermal browning of foodstuffs.

INTRODUCTION

During simulated crust baking of wheat gluten, exothermic browning occurs with a depletion of protein content and partial volatilization (ref. 1). In the presence of food carbohydrates, thermal degradation of gluten increased vigorously, and its extent correlated with the peak internal temperature. While heated gluten inhibited the growth of mice, baked gluten-carbohydrate mixtures merely lost any nutritive value (refs. 2,3). The predominant role of heat generation prompted us to examine the substrates by DSC in oxygen.

METHODS

Materials used were described previously (ref. 1). Hydrocellulose (HC) was a microcrystalline cellulose, and CMC and hydroxypropyl-methylcellulose (HPMC) were cellulose ethers. A Perkin-Elmer DSC-2C differential scanning calorimeter was used with gold pans containing samples (ca. 0.5–0.95 mg) under 100-mesh stainless steel screen. Oxygen flow was 50 cm^3/min, using a flow-through cover, and heating rate 20°C/min. Heat of reaction ΔH is an average of 2–4 determinations, negative values indicating an exothermic reaction.

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RESULTS

Commercial wheat gluten (83% protein) and its purified fractions glutenin and gliadin differed substantially (Table 1). Purified gluten (98% protein) had a similar DSC curve to the crude protein, except that peaks were resolved more clearly (ref. 4). A biphasic exotherm also appeared in the kinetics of internal temperature during baking of gluten (ref. 1).

TABLE 1

DSC curve for the proteins

Protein	Parameter	Peak I	Peak II		Peak III	Total combustion
Gliadin	Range (°C)	150-234	234-330	330-417	415-666	331-665
	ΔH(cal/g)	11.0	94.7	-161	-1280	-1850
	S.D. (±)	1.03	71.7	68.2	118	346
Glutenin	Range (°C)	124-234	234-431		422-634	233-639
	ΔH(cal/g)	-9.79	-908		-519	-2080
	S.D. (±)	4.65	2.4		1.9	22.1
Gluten	Range (°C)	---	238-418		401-656	234-656
	ΔH(cal/g)	---	-305		-998	-1880
	S.D. (±)	---	37.9		157	109

Thermal behaviour of food carbohydrates is described in Table 2. Endothermic peak I of anhydrous β -D-glucose, L-ascorbic acid, sucrose and maltose monohydrate corresponds to fusion, as does the 198-272°C peak of α -lactose monohydrate (cf. ref. 5). Evaporation of water of crystallization accounts for peak I of the lactose and is included in peak I of the maltose. No exothermic transition occurred below 270°C (cf. ref. 5). A vigorous exotherm attributed to combustion was resolved into two peaks, the 260-420°C region of sugars and ascorbic acid having a smaller enthalpy, and the polysaccharides (except for CMC) a higher enthalpy, than their 390-600°C peak. HC and HPMC exhibited an extremely high heat of reaction in peak III (> 2000 cal/g). Enthalpy values of the low-temperature exotherm were all higher than that of gluten, while, in the high-temperature region, gluten had the highest heat of combustion.

Admixture of carbohydrates did not affect the transition onset temperature (238°C) of the low-range exotherm of commercial gluten (Table 3). The decrease in the case of gluten-lactose (197°C) was merely a slight shoulder in the range

TABLE 2

DSC curve data for carbohydrates

Substrate	Parameter	Peak I	P e a k II		Peak III		Peak IV	Total combustion
Glucose	Range (°C)	142-177	177-263		263-401		401-581	263-581
	Δ H (cal/g)	43.5	54.1		-528		-647	-1530
	S.D. (±)	1.2	3.2		57.8		15.4	28.9
Sucrose	Range (°C)	160-198	198-279		279-399		399-600	279-600
	Δ H (cal/g)	28.1	57.7		-347		-904	-1610
	S.D. (±)	0.8	8.4		14.6		5.8	8.5
Maltose	Range (°C)	85-154	206-276		276-409		392-589	276-589
	Δ H (cal/g)	40.1	35.7		-392		-730	-1510
	S.D. (±)	1.3	4.9		0.7		70.0	28.0
Lactose	Range (°C)	83-168	168-198	198-272	272-417		396-561	272-573
	Δ H (cal/g)	35.7	-3.2	66.9	-472		-564	-1420
	S.D. (±)	0.5	0.3	0.6	58.8		14.9	97.5
Ascorbic acid	Range (°C)	177-201	201-262		262-415		388-532	201-532
	Δ H (cal/g)	51.2	-91.1		-341		-717	-2040
	S.D. (±)	4.4	15.1		50.3		60.3	94.5
Starch	Range (°C)	----	----		227-315	315-422	407-577	173-557
	H (cal/g)	----	----		-64.2	-506	-346	-1260
	S.D. (±)	----	----		3.3	17.8	4.1	3.9
Cellulose	Range (°C)	----	----		203-367		395-486	203-486
	Δ H (cal/g)	----	----		-972		-409	-1770
	S.D. (±)	----	----		24.6		3.4	16.6
HC	Range (°C)	----	----		246-388		388-526	246-525
	Δ H (cal/g)	----	----		-2044		-224	-2150
	S.D. (±)	----	----		24.5		0.2	23.6
CMC	Range (°C)	----	----		153-415		415-632	142-632
	Δ H (cal/g)	----	----		-823		-888	-1630
	S.D. (±)	----	----		17.8		112	176
HPMC	Range (°C)	----	----		218-398		391-518	150-518
	Δ H (cal/g)	----	----		-2140		-509	-3030
	S.D. (±)	----	----		39.6		2.5	65.7

of lactose fusion. Maltose, lactose and HC increased the enthalpy change of gluten's low-temperature peak relative to that of the high-temperature peak, resulting in substantially equal values for the two peaks. Cellulose and its ethers CMC and HPMC raised gluten's heat of combustion in peak II to the same extent. Sucrose, starch and ascorbic acid decreased low-temperature enthalpy of gluten, while all other additives increased the value. As regards the high-temperature exotherm (peak III, Table 3), CMC, sucrose and ascorbic acid increased the heat of reaction, while all other additives decreased it.

DISCUSSION

Although cellulose, hydrocellulose and sucrose cause the greatest over-

TABLE 3

DSC curve data for gluten-carbohydrate mixtures (4:1)

Carbohydrate	Parameter	Peak I	Peak II	Peak III	Total combustion	
Glucose	Range (°C)	85-229	229-421	385-634	229-649	
	Δ H(cal/g)	27.3	-341	-732	-1880	
	S.D. (±)	1.8	9.9	14.0	24.6	
Sucrose	Range (°C)	202-247	247-401	401-659	196-659	
	Δ H(cal/g)	-3.4	-99.5	-1380	-1930	
	S.D. (±)	0.2	20.2	68.4	55.4	
Maltose	Range (°C)	119-233	233-436	416-642	233-651	
	Δ H(cal/g)	26.8	-516	-568	-1860	
	S.D. (±)	2.5	17.9	33.8	84.7	
Lactose	Range (°C)	----	197-431	410-635	197-646	
	Δ H(cal/g)	----	-486	-558	-2120	
	S.D. (±)	----	31.2	27.7	68.0	
Ascorbic acid	Range (°C)	----	226-409	338-641	117-641	
	ΔH(cal/g)	----	-302	-1180	-2600	
	S.D. (±)	----	15.9	22.3	74.6	
Starch	Range (°C)	91-218	230-416	390-638	218-649	
	ΔH(cal/g)	-6.7	-283	-837	-1890	
	S.D. (±)	0.6	2.4	16.3	36.2	
Cellulose	Range (°C)	96-232	235-425	407-641	204-647	
	ΔH(cal/g)	10.4	-384	-703	-1930	
	S.D. (±)	0.07	4.3	28.1	44.9	
HC	Range (°C)	127-238	238-422	407-632	238-647	127-637
	ΔH(cal/g)	-24.2	-726	-754	-2290	-2470
	S.D. (±)	1.0	10.9	11.3	1.4	----
CMC	Range (°C)	112-233	238-411	411-623	238-623	111-623
	ΔH(cal/g)	-8.55±1.34	-389±4.5	-1530±4.9	-2620±15.5	-2880±9
HPMC	Range (°C)	145-239	239-418	409-627	239-639	135-639
	ΔH(cal/g)	-4.7	-413	-953	-2080	-2220
	S.D. (±)	1.5	24.2	16.4	39.5	53.6

heating and damage of gluten during crust baking (ref. 1), they had mutually incongruous effects on the 200-400°C exothermic peak (Table 3). The results suggest that DSC curve data for gluten-carbohydrate mixtures do not reflect their behaviour in a baking oven, indicating that the mechanism of the synergistic baking phenomena does not involve chemical reaction between gluten and carbohydrate additives. It is rather the low-temperature heat of combustion of the pure carbohydrates (Table 2) that corresponds coherently to their effect on gluten baking, since their enthalpy values are all greater than that of gluten alone. Thus combustion of carbohydrate while blended with the protein would generate greater heat, thereby raising the internal temperature of the mixture and aggravating chemical and nutritional damage to gluten. Accordingly, the mechanism of the synergistic phenomena of baking damage would simply in-

volve a physicochemical thermal interaction.

To explain the paradoxical detoxification effect of the carbohydrates on heated gluten (refs. 2,3), it is suggested that toxic material formed by gluten during baking is volatilized due to the raised temperature caused by combustion of carbohydrate.

Carbohydrate ingredients in food would, therefore, appear to depreciate the nutritional value of protein during high-temperature processing, in particular destroying essential amino acids such as lysine (ref. 1), but, at the same time, the protein toxicity of the food is ameliorated.

The implication that chemical reactions between protein and carbohydrate may not be involved in high-temperature browning of food lends further support to the view (ref. 1) that now questions the generally accepted association of Maillard-type reactions (between protein amino groups and reducing sugars) with this browning phenomenon.

The effects of the sodium L-ascorbate form of vitamin C on the thermal stability of gluten and its dietary value and safety were completely different to those of all the food carbohydrates (including L-ascorbic acid) described above (refs. 1-3). Thermal analysis of protein-sodium ascorbate mixtures will be the subject of a separate communiaation (ref. 4).

CONCLUSIONS

Beneficial practices that may tentatively be considered for food processing and domestic preparation could include the following steps:

(a) general preference for medium-heat treatments such as boiling and pressure cooking;

(b) general curtailment of the use of higher-temperature treatments;

(c) general reduction of temperatures used in higher-heat food treatments, with a specific recommendation to minimize exposure to temperatures of 200°C and above.

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Corrections Added in Proof

In Table 2, the Range of Peak IV for Starch was 407-557^{o}C and of Peak III for Cellulose was 203-407^{o}C. In Table 3, Peak I for Cellulose had Range 96-207^{o}C, ΔH - 5.9 cal/g and S.D. $\pm$ 0.2 .