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Mechanized fermentation systems for the production of experimental soy sauce koji

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Summary

Mechanized methods are proposed for improving the technology of soy sauce production at the koji stage. A comparative study on roller and rotary fermenters has been conducted from three viewpoints, namely enzyme levels, chemical composition and soy sauce produced. The taste, aroma and colour of the soy sauce samples from these mechanized fermenters were similar and compared satisfactorily with good commercial soy sauce. The equipment shows promise for controlled solid substrate fermentations.

Introduction

The traditional methods for production of soy sauce have been reviewed by several workers (Yokotsuka, 1960; Hesseltine, 1972; Yong & Wood, 1975). Koji, the first part of the two-stage fermentation process for production of soy sauce, is an enzyme preparation resulting from growing a strain of the mould *Aspergillus oryzae* on cooked, sterile soybean–wheat mixture at 30°C for about 3 days. The mature koji is mixed with about an equal volume of brine to form the mash or moromi. The latter is inoculated with lactic acid bacteria and yeast and kept for up to 2 years at ambient temperature or for 3–4 months if warmed. At the end of moromi fermentation, the mash is pressed leaving a cake; the extract is soy sauce or shoyu which is then pasteurized and bottled.

The 'koji process' is an example of a solid state fermentation process which has existed for centuries, and the process may either be with or without continuous agitation or shaking of the fermenting mass (Hesseltine, 1972; Aidoo, Hendry & Wood, 1982). The use of a rotating drum for koji culturing was reported to prodce low enzyme levels because as the drum rotates it destroys the growing mycelium (Terui, Shibasaki & Mochizuki, 1958; Arima, 1964). However the authors were of the opinion that the rotating drum as used at one time for the production of gluconic acid (Herrick, Hellbach & May, 1935) would be worth investigation as a device for koji culturing. The advantages would be that more substrate could be used and less space would be required than in the conventional tray method. Also it would provide better mixing of the whole mass of koji, allow rapid growth of the mould on the substrate and give information on prospects for continuous koji production. The main argument against continuous agitation seems to be the suggestion that it damages the developing mould mycelium to such an extent as to kill it. However, the results of some very preliminary

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experiments with a rotating jar which were carried out in ignorance of this claim (B. J. B. Wood, unpublished data) seemed to show that the mould grew so rapidly and well that the principal problem was an excessive rise in temperature caused by the mould's rapid metabolism, occasionally reaching such high temperatures as to kill the mould mycelium. Temperatures well in excess of 45°C were sometimes attained when a 20 litre jar was charged with about 3 kg of most koji and operated in an incubator maintained at 30°C.

Materials and methods

Rotating and roller fermenter designs

The roller fermenter was a 20 litre vessel (Quickfit and Quartz) inclined at 20° to a rigid frame and rotated using a variable speed motor (Fig. 1a). The apparatus for air inlet for the fermenter (Fig. 1b) was composed of a 22 cm stainless steel tube which passed through a polytetrafluoroethylene (PTFE) stopper to fit a Quickfit adapter B24/19 which was connected to the 20 litre flask. The PTFE stopper rotated on the metal tube and the latter was prevented from itself rotating by a metal rod. The Quickfit adapter, the stainless steel tube with the PTFE stopper and the vessel were steam sterilized separately at 15 psig for 15 min. The fermenter carried a maximum charge of 1.8 kg of koji.

The rotary fermenter comprised a control shaft with eight paddles surrounded by two concentric 1 m long glass tubes sealed at both ends by metal plates. The metal ends had pockets for temperature probe, air inlets and outlets and hand hole for collection of samples (Fig. 2). The paddles were arranged such that there was a space of about 0.5 cm between the inside of the wall of the inner tube and the rotating paddles. The paddles were rotated by a variable speed motor and fermentation temperature was controlled by passing cooling water through the outer jacket. The volume of space in the inner tube was 20 l and the outer space, 15 l. The fermenter carried a maximum charge of 2.0 kg of koji.

Koji fermentation

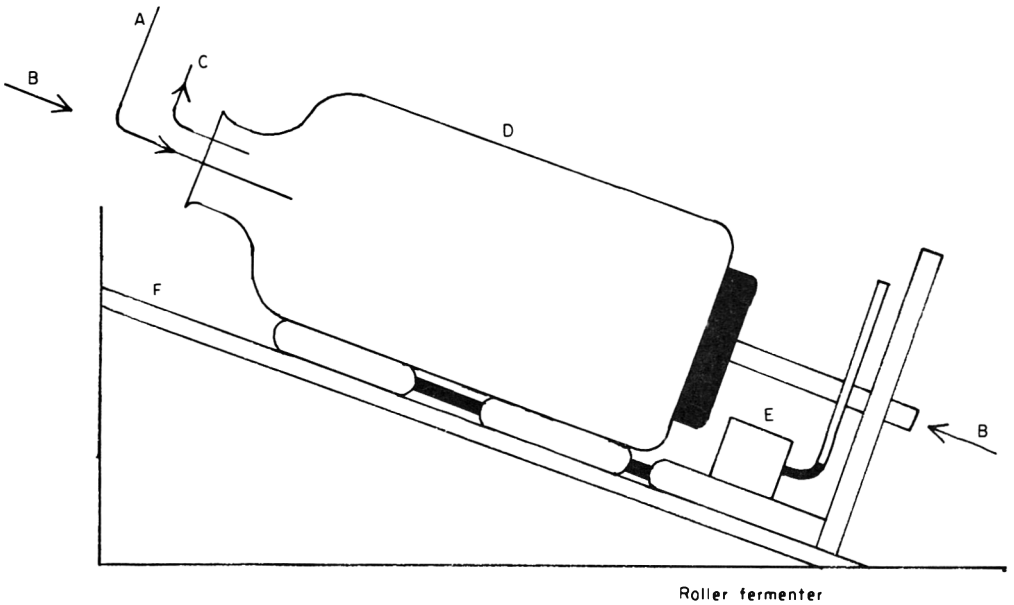
The method of koji culturing was as described by Yong & Wood (1976). The *Aspergillus oryzae* strain used in the present work was the one which they employed in their studies.

Moromi fermentation

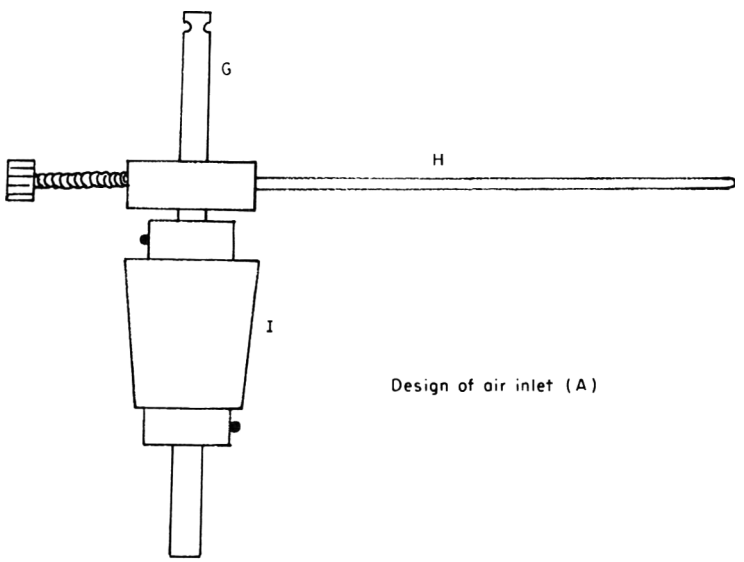
Moromi or soy mash was prepared by mixing koji with a 22% (w/v) solution of sodium chloride. Lactic acid was added to lower the pH to 4.5 and the mixture was then inoculated with yeast, *Saccharomyces rouxii*, strain NRRL, Y-27, and incubated at 40°C for 1 month (see Yong & Wood (1976) for details).

Assay of koji enzymes

Crude enzyme extracts from koji samples were prepared by the method described in Aidoo *et al.* (1981). The assay procedure used to measure sucrase activity in the koji was that reported by Yong & Wood (1975). Alpha-amylase activity was determined by measuring the dye released from a Cibachron Blue-Amylase complex (Klein, Foreman & Searcy, 1969) using the reagents and procedures reported by Roche Diagnostic (1975).



Roller fermenter



Design of air inlet (A)

Figure 1. Diagrammatic representation of rotating vessel or roller fermenter. A: Inlet for sterile, humified air. B: Axis of rotating flask. C: Air out. D: 20 litre flask. E: Variable speed motor. F: Rigid frame at 20°. G: Stainless steel tube. H: Metal rod. I: Rotating polytetrafluoroethylene (PTFE) stopper to fit adapter B24/19.

Proteinase activity was then measured as follows: Hammerstein casein (2.0 g) was with the 'Bio-Rad' Protein Assay Kit (Bio-Rad, 1977). The protein assay is a dye binding one based on differential colour change in response to various concentrations of proteins. One part of dye reagent concentrate was diluted with four parts of distilled water. 'Bio-Rad' protein standard was reconstituted with 20 ml distilled water to give a protein concentration of 1.4 mg/ml and dilutions ranging from 0.2 to 1.4 mg/ml were prepared. Exactly 0.1 ml of test protein solution, standard protein solution and blank

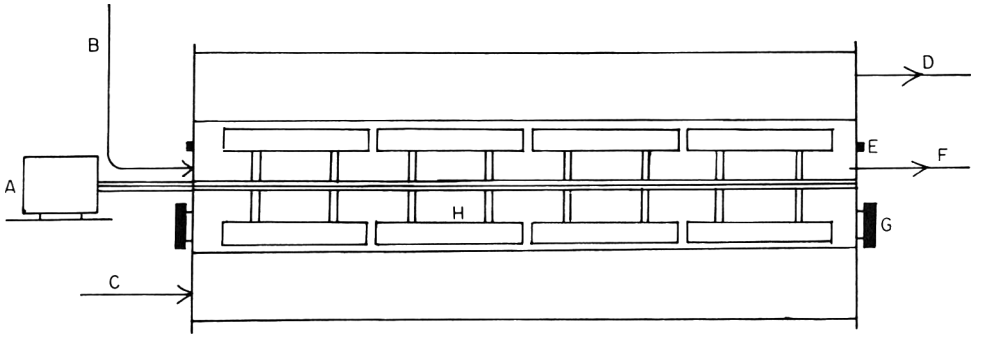


Figure 2. Diagrammatic representation of rotary fermenter. A: Variable speed motor. B: Inlet for sterile, humidified air. C: Inlet for cooling water. D: Outlet for water. E: Pocket for temperature probe. F: Outlet for air. G: Sampling port. H: Rotary paddle.

were transferred into separate test tubes and 5.0 ml of the diluted dye reagent was then added to each tube. The tubes' contents were mixed and after 30 min room temperature incubation the absorbance of the solutions was read at 595 nm against a blank made of 0.1 ml of phosphate buffer (pH 7.0) and the dye reagent. A plot of absorbance *versus* mg protein gave a straight line graph.

Proteinase activity was then measured as follows: Hammerstein casein (2.0 g) was dissolved in 80 ml of phosphate buffer (pH 7.0) and boiled gently for 5 min. It was cooled and made up to 100 ml with the buffer solution in a volumetric flask. Meanwhile 2% casein solution (2 ml) in a boiling tube was immersed in a water bath at 35°C. After 10 min, 1 ml of the koji enzyme extract was added and an aliquot of 0.1 ml was quickly transferred for 'Bio-Rad' assay. The reaction mixture was incubated at 35°C for 30 min after which 0.1 ml of the mixture was again quickly transferred for 'Bio-Rad' assay. The amount of casein hydrolysed was used as a measure of proteinase activity. One unit of proteinase activity is defined as that which will hydrolyse 1 mg of protein/ml from 2% casein in 1 min at 35°C, pH 7.0.

Sodium chloride and total acidity were determined by the method of Onaga, Luh & Leonard (1957). All other analyses were as described by Yong & Wood (1977). All assays and analyses were carried out on duplicate fermentations, and for each sample duplicate determinations were made of the item concerned.

Results and discussion

Both fermenters proved reasonably easy to operate but the rotary fermenter was easier to sample from. No instances of contaminants growing in fermenters were recorded; this was achieved by careful aseptic procedure when sampling, and by maintaining a positive air pressure inside the vessels at all other times, aided by the short duration of fermentations.

Temperature control was a major source of difficulty and the results in Table 1 show that considerable rises in koji temperature took place during the period of active mould growth. The roller fermenter showed a tendency to higher temperatures than did the rotary fermenter under otherwise similar operating conditions; we attribute this to the greater thickness of the layer of koji in the inclined bottle. In practice the water jacket for the rotary fermenter could not be operated because of leaks between the jacket and the koji. (Subsequently a modified design was produced and is currently being tested.)

Table 1. Changes in levels of some koji enzymes by the use of roller and rotary fermenters with similar fermentation conditions*

Time after inoculation (hr)	Roller				Rotary			
	Temp. (°C)	Enzyme activity (Unit/g dry wt koji)			Temp. (°C)	Enzyme activity (Unit/g dry wt koji)		
		α-amylase	Sucrase	Proteinase		α-amylase	Sucrase	Proteinase
0	28.5 (1.2)	0.00	0.20 (0.05)	0.00	30.0 (0.9)	0.00	0.00	0.00
16	31.0 (0.8)	0.20 (0.0)	0.30 (0.05)	0.15 (0.03)	30.0 (0.6)	0.10 (0.06)	0.12 (0.06)	0.10 (0.02)
24	33.0 (0.5)	0.70 (0.21)	1.30 (0.44)	0.58 (0.10)	32.0 (1.0)	0.30 (0.07)	1.10 (0.36)	0.48 (0.08)
40	42.0 (0.8)	—	—	—	39.0 (1.1)	3.85 (0.50)	3.50 (0.51)	1.62 (0.21)
42	40.0 (1.6)	3.70 (0.51)	3.80 (0.51)	1.73 (0.24)	39.0 (1.6)	—	—	—
48	40.0 (1.1)	4.00 (0.26)	4.21 (0.32)	1.74 (0.25)	38.0 (0.9)	5.70 (0.89)	3.92 (0.29)	1.83 (0.27)
52	39.0 (1.7)	4.52 (0.44)	5.70 (0.45)	2.18 (0.23)	37.0 (2.1)	—	—	—
53	39.0 (1.1)	—	—	—	37.0 (2.0)	5.80 (0.79)	5.28 (0.65)	2.40 (0.24)
65	38.5 (2.1)	—	—	—	37.0 (1.9)	6.31 (0.83)	6.51 (0.84)	2.58 (0.21)
66	38.0 (0.9)	6.30 (0.81)	7.41 (0.85)	2.40 (0.26)	37.0 (1.1)	—	—	—
70	38.5 (1.7)	8.50 (0.67)	7.20 (1.02)	2.42 (0.27)	37.5 (2.1)	8.00 (0.69)	6.70 (1.02)	2.65 (0.18)
72	37.0 (1.8)	—	—	—	36.0 (1.5)	7.81 (0.57)	6.65 (0.79)	2.70 (0.28)
74	36.5 (2.0)	8.30 (0.79)	6.90 (0.92)	2.60 (0.21)	36.0 (1.1)	—	—	—

*Inoculation rate of 1.0×10^{10} spores/1.8 kg charge and fermentation temperature, 30°C. Humidified air introduced at a rate of 1.0 l/min and the speed of rotation, 4 rpm.

Results represent the average from duplicate experiments with all analyses being performed in duplicate. Standard deviations in parentheses.

Enzyme levels in both fermenters are given in Table 1. The levels of α-amylase activity in the roller and rotary fermenters were similar and increased steadily during the fermentation. Sucrase activity also increased from the onset of fermentation but then decreased slightly towards the end. Proteinase levels, like those of α-amylase and sucrase, were also comparable in both fermenters and increased steadily throughout the fermentation.

It was found that the levels of koji enzymes (carbohydrases and proteinases) correlated well with changes in the concentration of reducing sugars, soluble and amino nitrogen in both culturing methods. There was a rapid increase in reducing sugar concentrations during the early stage of koji fermentation in both fermenters and this is due to the activity of extracellular sucrase on sucrose present in the soybean (Yong & Wood, 1975). The rotary fermenter gave a higher reducing sugar level than the roller, however the latter showed high moisture levels throughout the fermentation (Table 2). Total soluble nitrogen in both fermenters increased steadily until the end of fermentation. Amino acids, which contribute to flavour in soy sauce, were determined and calculated as amino nitrogen and there was no marked difference in their levels in the two fermenters.

Table 2. Chemical composition of kojis produced on roller and rotary fermenters

	Roller				Rotary			
Time after inoculation (hr)	Moisture (% w/w)	Reducing sugar (mg/g dry wt)	Nitrogen (mg N/g dry wt) Total	Amino	Moisture (%)	Reducing sugar (mg/g dry wt)	Nitrogen (mg N/g dry wt) Total	Amino
0	43.0 (1.4)	6.3 (1.00)	5.7 (0.8)	0.2 (0.0)	42.8 (0.0)	3.6 (0.3)	3.2 (0.6)	0.2 (0.0)
16	42.9 (0.9)	25.6 (1.5)	8.0 (0.9)	0.7 (0.0)	40.0 (1.1)	17.6 (0.5)	5.5 (0.5)	0.5 (0.0)
24	45.5 (1.0)	38.3 (1.5)	11.6 (1.5)	1.0 (0.1)	41.9 (1.0)	31.0 (1.1)	9.1 (0.4)	0.8 (0.1)
40	—	—	—	—	44.0 (0.9)	44.2 (0.9)	16.4 (1.1)	1.9 (0.1)
42	45.0 (1.7)	35.0 (2.4)	15.6 (0.8)	1.8 (0.2)	—	—	—	—
48	45.8 (2.2)	37.2 (1.1)	16.3 (0.7)	2.2 (0.3)	44.0 (0.5)	42.3 (1.8)	18.2 (1.3)	2.0 (0.2)
52	47.0 (1.4)	35.0 (1.2)	18.0 (1.1)	2.5 (2.5)	—	—	—	—
53	—	—	—	—	45.5 (1.0)	38.5 (2.5)	19.0 (0.8)	2.5 (0.2)
65	—	—	—	—	46.5 (1.4)	40.0 (1.3)	21.1 (1.3)	2.7 (0.1)
66	48.5 (2.5)	32.0 (1.0)	20.0 (0.9)	2.8 (0.4)	—	—	—	—
70	48.8 (2.4)	30.8 (1.9)	21.1 (1.5)	2.9 (0.4)	47.0 (1.8)	39.0 (0.8)	21.6 (1.0)	3.0 (0.3)
72	—	—	—	—	47.0 (1.4)	39.2 (1.1)	22.0 (1.4)	3.1 (0.2)
74	48.5 (2.3)	27.6 (0.8)	22.0 (1.5)	3.1 (0.5)	—	—	—	—

All conditions, etc. as in Table 1. Standard deviations in parentheses.

Chemical compositions of soy sauce prepared from kojis made by the roller and rotary methods and a commercial soy sauce ('Tamari', also prepared from a soybean–wheat koji and purchased in Edinburgh) are shown in Table 3. Reducing sugars and sodium chloride contents of the soy sauce from the two culturing methods were almost the same. Although there were slight differences in the levels of total amino nitrogen, the taste, aroma and colour of the samples were quite similar (soy sauce from roller fermenter looked slightly darker). The sauce from the rotary fermenter had slightly more total acids than that from the roller. Reducing sugar and sodium chloride contents in the 'Tamari' and the laboratory-made samples were nearly the same but total acids

and nitrogen-containing compounds differed. The 'Tamari' soy sauce looked more viscous and the colour more intense than that of the laboratory-made samples. However the taste, aroma and chemical compositions of soy sauce from the mechanized koji culturing methods were almost the same and compared well with that of 'Tamari' soy sauce.

The results reported in this study show that the koji mould will grow rapidly despite the continuous agitation employed in both types of fermenter. Unpublished experiments (Sumbo H, Abiose) with a rice koji destined for miso production showed that on this substrate the mould would not grow in continuously agitated roller or rotary fermenter incubations.

Table 3. Chemical composition of soy sauce prepared from the mechanized methods of koji cultures and commercial soy sauce

Koji method	pH	Total acids as lactic acid (g/100 ml)	Total nitrogen (g/100 ml)	Amino nitrogen (g/100 ml)	Reducing sugar (g/100 ml)	Sodium chloride (g/100 ml)
Tray	4.52 (0.08)	0.97 (0.14)	1.03 (0.16)	0.60 (0.13)	5.84 (0.81)	18.23 (1.03)
Roller	4.50 (0.11)	0.93 (0.17)	1.21 (0.19)	0.52 (0.10)	6.02 (0.58)	18.12 (0.98)
Rotary	4.57 (0.19)	1.01 (1.07)	1.00 (0.10)	0.48 (0.02)	5.92 (0.34)	18.04 (0.90)
'Tamari' soy sauce	4.68 (0.00)	1.83 (0.02)	1.42 (0.02)	0.68 (0.01)	6.00 (0.10)	18.23 (0.01)

'Roller' and 'rotary' kojis derive from the runs described in Tables 1 and 2. The 'tray' koji was prepared according to the method of Yong & Wood (1976) using the same inoculation rate as employed in the mechanized kojis. Moromis were incubated at 40°C for 1 month, then pressed and the filtrate pasteurized and refiltered as described by Yong & Wood (1976). Analyses were performed on this filtrate. Standard deviations in parentheses.

Comparison of the results in this study with those previously reported for tray kojis (Yong & Wood, 1977) shows that rather similar changes occur in all three systems, with the two mechanized culturing methods giving generally higher levels of reducing sugars, amino nitrogen and total soluble nitrogen. Ammonia levels were no different in the three fermentation systems. On the other hand the water content of the koji remained fairly steady throughout the fermentation on the mechanized fermenters whereas it shows substantial decreases during tray fermentations (Yong & Wood, 1976). Although we have no experimental evidence to show that the higher moisture levels maintained in the mechanized fermenters are beneficial, this would seem to be a reasonable inference to draw and might help to account for the biochemical differences noted above.

The rotary fermenter was used in a comparison of mould growth at ambient temperatures of 25 and 30°C. Tables 4 and 5 show the results of this experiment. Temperature in each case shows a similar pattern of change. During most of the fermentation, the kojis showed a difference of about 5°C in temperature corresponding to the differences in ambient temperature, but during the period of greatest temperature elevation (which may be presumed to correspond to the period of greatest metabolic activity) temperature differences as great as 7°C were observed (Table 4). In experiments using different levels of spore inoculation, the overall trends were very similar and detailed results are not reproduced here, but it is worth noting that after 40 hr incubation, koji temperatures at ambient temperatures of 25 and 30°C were 33 and

Table 4. Temperature changes in koji fermentations on the rotary fermenter at different ambient temperatures

Time after inoculation (hr)	Ambient temperature	
	25°C	30°C
	Koji temperatures	
0	26.0 (0.5)	29.5 (0.7)
5	26.0 (0.8)	30.5 (0.4)
10	29.0 (1.5)	32.0 (0.8)
15	30.0 (1.0)	33.0 (0.6)
20	31.0 (0.8)	37.0 (1.6)
25	31.5 (1.0)	36.0 (1.5)
30	32.0 (0.6)	37.0 (1.6)
35	33.0 (1.3)	38.5 (0.9)
40	34.0 (0.8)	38.0 (1.1)
45	33.0 (1.4)	39.0 (2.1)
50	33.0 (1.0)	40.0 (1.0)
55	33.0 (1.0)	40.0 (2.1)
60	33.0 (2.1)	38.0 (1.8)
65	33.0 (1.8)	37.5 (0.5)
70	33.0 (1.7)	38.0 (1.7)
75	33.0 (2.0)	39.0 (1.5)
80	33.0 (1.2)	38.0 (1.1)

Charge: 2 kg inoculated with 5×10^{10} *Aspergillus oryzae* spores. Standard deviations in parentheses.

Table 5. Effect of environmental temperature on enzyme levels in experimental koji

Time after inoculation (hr)	α-amylase		Sucrase		Proteinase	
	25°C	30°C	25°C	30°C	25°C	30°C
0	0	0	0	0	0	0
17	0.21 (0.03)	0.21 (0.06)	0.72 (0.12)	0.20 (0.04)	0	0
24	0.62 (0.03)	0.32 (0.04)	1.50 (0.25)	0.50 (0.17)	0.26 (0.04)	0.35 (0.08)
30	2.18 (0.17)	—	6.40 (0.6)	—	0.70 (0.05)	—
40	—	3.18 (0.58)	—	5.55 (0.53)	—	1.36 (0.21)
42	5.40 (0.60)	—	5.45 (5.45)	—	1.55 (0.28)	—
48	—	4.72 (0.95)	—	8.70 (1.10)	—	1.55 (0.18)
50	5.82 (1.01)	—	8.26 (0.58)	—	2.05 (0.22)	—
52	—	4.80 (0.80)	—	9.30 (0.81)	—	2.20 (0.12)
64	6.55 (0.92)	—	10.80 (0.98)	—	2.67 (0.29)	—
65	—	6.00 (0.72)	—	10.10 (0.52)	—	2.64 (0.14)
70	—	6.81 (0.64)	—	10.60 (1.57)	—	2.80 (0.10)
72	7.62 (0.91)	—	10.90 (1.20)	—	2.78 (0.11)	—

Apparatus: rotary fermenter; charge: 2 kg inoculated with 5×10^{10} spores of *Aspergillus oryzae*. The temperatures shown are those of the rooms in which the apparatus was located for the particular experiment (cf. Table 4). Enzyme activities are in units/g dry weight of koji. Standard deviations in parentheses.

42°C, respectively, a difference of 9°C, when a spore level twice that used in the experiments of Table 4 was employed.

In general the lower ambient temperature seemed to give better yields of protease and α-amylase. Sucrase yields showed a less clear pattern but at the beginning of the fermentation, when this enzyme is probably at its most important for the mould (Yong & Wood, 1975) levels were appreciably higher at the lower temperature. Since enzymes produced in the koji stage of fermentation are important for the moromi stage and hence for the quality of the finished soy sauce, these results may have practical significance for the operation of a mechanized koji production system of the type described here.

An advantage of the rotary fermenter over the tray fermenter used in previous studies (Yong & Wood, 1976) is that effluent gases are easily sampled for analysis. A very limited study of this kind was possible through the generosity of Foxboro Analytical Ltd, Milton Keynes, U.K. who loaned us a Foxboro infra red analyser which was set up to measure carbon dioxide when effluent gas was presented in a cell with a 0.1 m pathlength. Instrument readings were converted to carbon dioxide concentration using a calibration provided by the company based on a calibration procedure described by Wilks Scientific Ltd (1977). The results obtained (Table 6) although very preliminary in nature, suggest that this may be a useful technique for studying solid substrate fermentations.

Table 6. Carbon dioxide production in a koji fermentation

Age of koji (hr)	Instrument reading	Carbon dioxide production (mg/hr)
50	0.21	490
58	0.23	580
70	0.25	650

Apparatus: rotary fermenter; charge: 2 kg inoculated with 10^{10} spores of *Aspergillus oryzae*; are flow rate 1.5 l/min; detector Foxboro Analytical Ltd infrared analyser. the calibration is not a linear function of carbon dioxide concentration. Duplicate observations on a single fermentation.

However, the very preliminary nature of these results must be stressed. In order for the reproducibility and hence the usefulness of this analysis in the study of solid substrate fermentation to be properly established, a more extensive study would be needed. Such a study would involve numerous fermentations under a range of environmental conditions, and would seek to establish correlations between these measurements and other growth related phenomena, such as chitin production.

The observations in this report show that the two types of apparatus described here have promise for the production of koji, and possibly for the growth of organisms on solid substrates generally, under controlled environmental conditions. Studies are continuing in an effort to refine the designs still further.

Acknowledgments

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Comparison of drying kinetics of soybeans in thin layer and fluidized beds

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Summary

The drying behaviour of soybeans previously water soaked to a moisture content above that of the naturally moist product was studied. A comparison was performed between thin layer and fluidized bed drying (up to 20 cm depth). In both cases, thin layer or fluidized beds of variable heights, a satisfactory description of the drying kinetics was obtained using Fick's second law for diffusion out of spheres. However, it was found that the diffusion coefficients so obtained showed a tendency to decrease with increasing bed height. This is attributed to the drop in the temperature in the fluidized bed which affects the diffusion coefficients. Activation energies were found to be fairly independent of bed height and were in the range 6.9–7.4 Kcal/mol.

Introduction

Fluidized beds have been widely used in drying of different kinds of materials such as solutions, suspensions, granular materials and others. In general, the performance of this operation is satisfactory for any drying controlling mechanism (i.e. surface or internal controlled mechanism) because the uniformity of temperature achieved in the bed gives a product of better quality than comparable conventional driers. Fluid bed drying has found many applications in the food industry: the drying of cereals and other field crops (Van Arsdel, Copley & Morgan, 1973), milk products (Hayashi & Wada, 1980) are some areas where fluidization has been applied successfully.

The mathematical description of fluidized beds is difficult due to the complicated flow pattern of gas and solid movement and the bypassing of bubbles in the bed. Various empirical correlations had been developed to predict drying rates of food particles (i.e. rice, sorghum) in fluidized beds (Laquerrica, Floors & Cerni, 1974; Brunello & do Nascimento, 1977). However, basic research on drying of food particles in aggregate fluidized beds has been relatively scarce.

The purpose of this work was to study the drying kinetics of a food-like system in an aggregative fluidized bed and to compare the results with those obtained in thin layer drying. Soybeans were used as a food model due to their regular (sphere-like) geometry which facilitates mathematical calculations. However, their moisture content was intentionally increased (by adding water) before drying to emphasize the difference which may exist between thin layer and fluid bed systems.

Materials and methods

Soybeans, Williams variety, were received with the following characteristics: moisture content 0.12 g water/g dry solid; density 1.21 g/cm^3 and average diameter 0.684 cm.

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Before the drying experiments water was added to the samples to increase their moisture content in order to magnify the differences in drying behaviour between a single layer and a fluid bed. This was done by soaking the grains in water at room temperature for 10–30 min depending on the desired final moisture content. After soaking, the samples were placed in a sealed plastic container and stored in a refrigerator for 48–72 hr to attain a uniform internal moisture profile. The refrigerated condition inhibited microbial spoilage during equilibration. Two levels of moisture content were used for most drying experiments, namely 0.42 and 0.62 g water/g dry solid (gw/gds); as mentioned, these moisture values are above the product naturally moist. The moisture content of the samples were determined gravimetrically with a precision balance (± 0.0001 g), using a vacuum oven method at 70°C over magnesium perchlorate.

Thin layer drier

This was a conventional through-circulation drier which was described in detail in previous publications (Suárez, Viollaz & Chirife, 1980a,b).

Batch fluidized bed

The fluidized bed consisted of a cylindrical steel vessel of inner diameter 22 cm, height 25 cm, fitted on a drilled plate distributor. Beneath this distributor, air passed through a smoothing section with deflecting baffles. Air was supplied by a centrifugal fan and regulated by a butterfly valve placed on the gas duct between the fan and the vessel. Pressure taps were installed to measure the pressure drop in the bed and distributor. Air flow was measured on a 0–3000 l/min flowmeter placed between the fan and the vessel. Air was electrically heated and temperature controlled by an electronic proportional controller (± 0.3°C). Mercury thermometers (± 0.1°C) were provided to measure dry and wet bulb temperatures of the inlet and exit air. To create adiabatic process conditions, the whole equipment was insulated.

The drying process was monitored by periodically withdrawing samples of the bed and determining their moisture content. The minimum fluidization velocity was estimated from a plot of bed pressure drop against the superficial gas velocity; its value was 1.84 m/sec. The theoretical minimum fluidization velocity obtained from usual literature correlations (Kunii & Levenspiel, 1969) was 1.68 m/sec. The temperature of the solids in the bed was obtained by measuring the exit temperature of the air. It is known that thermal equilibrium between the solids and the fluid is usually achieved when the bed height approaches 15–20 particle diameters (Heertjes, de Boer & Haas van Dorser, 1953). This condition was fulfilled in most of the fluid bed experiments.

Equilibrium moisture content

Selected values of equilibrium moisture content at the various drying temperatures were determined by equilibration with saturated salt solutions which provided known constant relative humidities. The measurements corresponded to the desorption branch of the isotherms and the details of the experimental technique have been published elsewhere (Iglesias, Chirife & Lombardi, 1975).

Results and discussion

Thin layer drying

By studying the effect of different air velocities on the rate of drying it is possible to determine which resistance is controlling the overall process (Vaccarezza, Lombardi &

Chirife, 1974). It was experimentally determined that in the range of air velocities used (8–13 m/sec) the main resistance is due to internal moisture movement because the drying rate was not affected by increasing air velocity (results are not shown here), even for the higher initial moisture content used (0.62 gw/gds).

Accepting that the moisture movement inside the solid is Fickian, the analytic solution of Fick's second law for diffusion out of spheres for constant boundary conditions may be used in order to obtain the diffusion coefficients (Luikov, 1965).

$$u = \sum_{n=1}^{\infty} 6/(n\pi)^2 \exp(-(n\pi)^2 D_{\text{eff}}\,\theta/R^2), \tag{1}$$

where u is the dimensionless moisture content $((\bar{u}-u_e)/(u_o-u_e))$, $\bar{u}$ is the mean moisture content at a given time, u_e is the surface moisture content, u_o is the initial moisture content, all given on a dry basis, D_{eff} is the effective diffusion coefficient (cm^2/sec), R is the radius of the particle (cm) and θ is the time (sec).

Moisture effective diffusion coefficients in soybean were found by comparing experimental and predicted (equation 1) drying curves by using a digital computer. For each calculation the diffusivity was allowed to vary until the sum of the squared deviation between the experimental and the theoretical values of the mean moisture content was a minimum.

The values of equilibrium moisture content for each drying condition (u_e) were determined as described in Materials and methods.

Typical results comparing the predicted and experimental drying curves for soybeans of two different initial moisture contents (0.42 and 0.62 gw/gds) are shown in Fig. 1. These curves indicate the accuracy with which the diffusion theory with constant diffusivity predicts the drying behaviour.

It is known that a Biot number (Bi) for mass transfer greater than 100 indicates that the diffusion inside the solid represents the controlling step for the moisture transport and the solid surface moisture content is that corresponding to equilibrium conditions and practically constant (Luikov, 1965). The Bi is defined as

$$Bi = k_g R/D_{\text{eff}} m, \tag{2}$$

where k_g is the external mass transfer coefficient (g water/cm^2 sec atm) and m is the slope of the sorption isotherm (g water/cm^3 atm). Substituting in equation (2) it can be shown that for the typical drying conditions studied in the present work, Bi is always > 3000, which confirms the experimentally observed absence of external control to mass transfer.

It is to be noted that for the evaluation of the diffusion coefficients any heat transfer effects were neglected and the drying process treated as a purely mass transfer one. Various workers (Vaccarezza, Lombardi & Chirife, 1974; Suárez *et al.*, 1980b) have demonstrated that for drying conditions and systems similar to those used here, the temperature of the grain may be safely assumed to be constant and uniform throughout the particle with little error.

To obtain the dependence of the diffusion coefficient on temperature, an Arrhenius dependence was assumed.

$$D_{\text{eff}} = D_x \exp(-E_a/R_g T), \tag{3}$$

where D_x is the pre-exponential factor (cm^2/sec), R_g is the gas content (Kcal/mol K), T

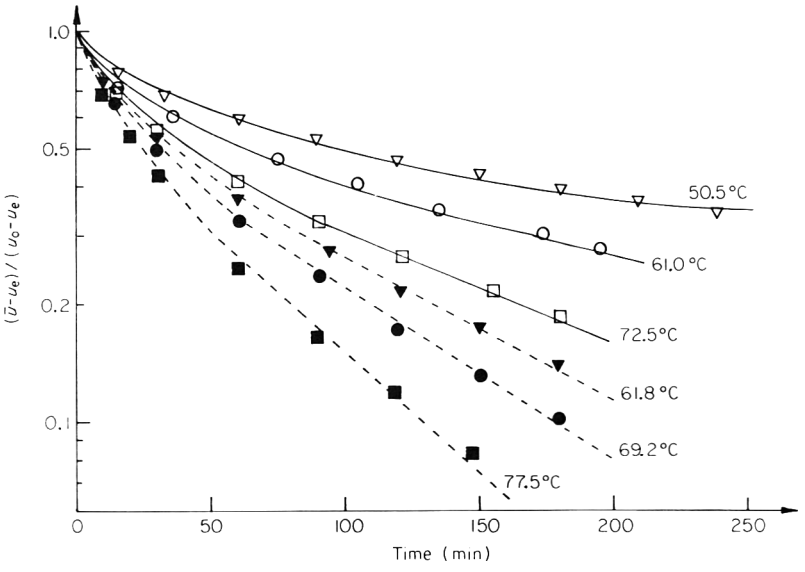

Figure 1. Comparison of predicted and experimental drying curves for soybean in thin layer; u_0 = 0.42 gw/gds (———, predicted; ▽, O, □, experimental); u_0 = 0.62 gw/gds (— — —, predicted: ▼, ●, ■, experimental).

is the absolute temperature (K) and E_a is the activation energy for diffusion of moisture out of soybean grains (Kcal/mol). Figure 2 shows a plot of the calculated diffusion coefficients *versus* the reciprocal of absolute temperature for soybean grains of two initial moisture contents, namely 0.42 and 0.62 gw/gds. Each set of values was fitted to equation (3) by a linear regression technique and the activation energies so calculated are shown on Table 1, together with various literature values for water diffusion in grains and other foods of relatively low moisture contents. It may be noted that the obtained values of the activation energy for diffusion of water in soybeans are practically the same for the samples having different initial moisture content—i.e. 0.42 and

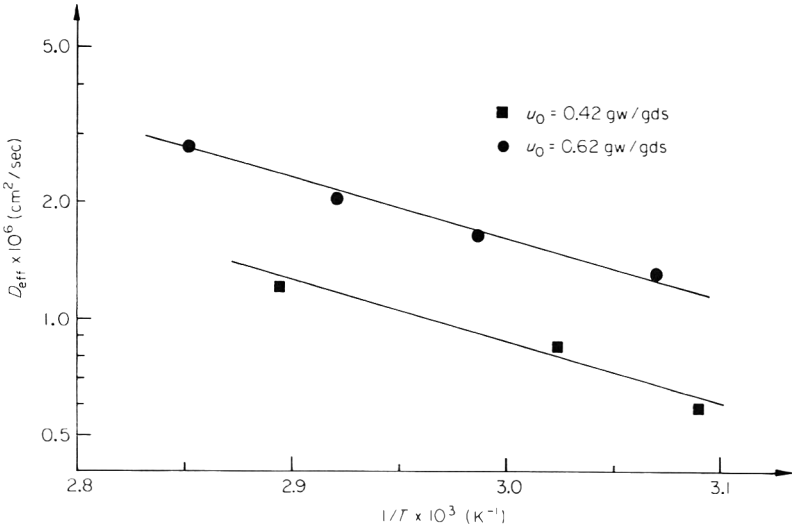

Figure 2. Effect of temperature on the diffusivity of water in soybean grains dried in thin layer.

Table 1. Activation energies for diffusion of water in various grains during thin layer drying

Material	Initial moisture content (gw/gds)	E_a (Kcal/mol)	Reference
Cotton seed (endosperm)	0.24	13.8	Farinati (1982)
Sorghum	0.21	7.5	Suárez *et al.* (1980b)
		endosperm 5.8	
Rough rice	0.27–0.31	bran 10.2	Singh Wang & Zuritz (1980)
		hull 14.8	
Rough rice	0.22	9.9	Aguerre *et al.* (1982)
Soybeans	0.29	8.7	Suárez *et al.* (1980a)
Soybeans	0.42	7.2	this work
Soybeans	0.62	6.9	this work

0.62 gw/gds. Suárez *et al.* (1980a) dried soybeans of 0.29 gw/gds initial moisture content which were humidified by water vapour adsorption and reported a somwhat higher activation energy (8.7 Kcal/mole, see Table 1). However, it is not certain whether this difference is due to the lower moisture range studied or to structural changes in grains due to the different methods of humidification (water vapour *versus* water soaking).

Figure 3 shows a plot of D_{eff} *versus* initial moisture content at two different temperatures; the values corresponding to the lower moisture content (0.29 gw/gds) were taken from a previous work (Suárez *et al.*, 1980a). It can be seen that at both temperatures the diffusion coefficients increase exponentially with increasing the initial moisture content. It is interesting to note that this type of dependence has been proposed by Misra & Young (1980) to solve numerically the simultaneous moisture diffusion and shrinkage during soybean drying. Other workers also found that at relatively low moisture content the diffusion coefficient in foods undergoing drying, drastically decreases with decreasing moisture content (Steffe & Singh, 1980).

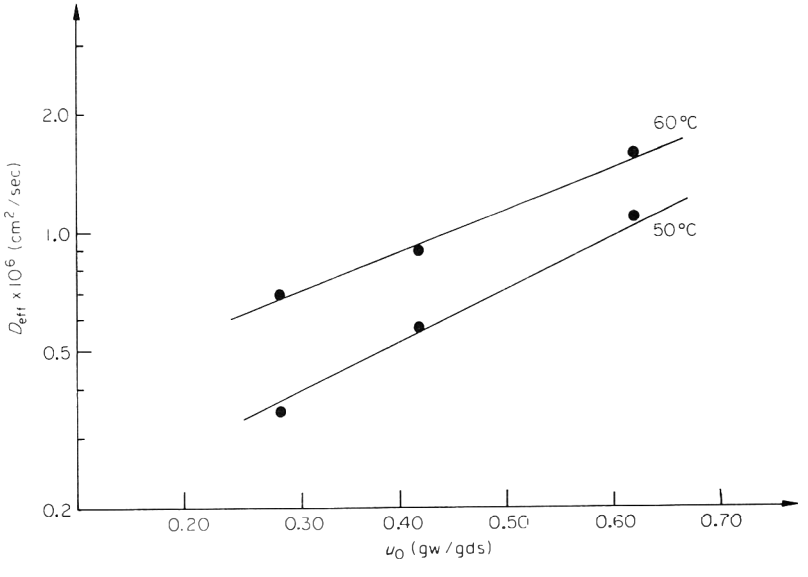

Figure 3. Effect of the initial moisture content on the diffusion coefficient of water in soybean dried in thin layer.

Fluidized bed drying

In fluidized beds the drying regime is determined by the magnitude of two rate processes, the heat transfer and the moisture diffusion within the solid. When the heat transfer is the limiting process there will be a constant rate drying period and when the diffusion of the moisture inside the solid is slow enough to control the process a falling rate drying period will occur. The fixed bed height (L_o) and the superficial air velocity (v_o) are the variables that determine the constant rate period and the diffusivity of the water in the material is the characteristic parameter for the falling rate period. With the values of L_o, v_o and D_{eff} the drying regime can be determined at a given drying air condition (Kunii & Levenspiel, 1969).

Figure 4 shows the drying behaviour of soybean (of two different initial moisture contents) in fluidized beds having 10 and 14 cm fixed bed height (L_o). Although in these experiments the air velocity is lower and the bed deeper than in thin layer runs, no constant rate period is observed. The absence of a constant rate period was confirmed by determining the exit temperature of the air as a function of drying time. As shown in Fig. 5 the exit temperature of the air increases continuously from the beginning of drying. It was also observed that increasing the air velocity (v_o) from 1.9 m/sec (which for the experimental conditions corresponds to the minimum bubbling velocity) to 2.6 m/sec did not affect the drying rate of soybean beds of heights up to 20 cm (results are not shown here). This again indicates that the drying of soybean in this type of fluidized bed is mainly controlled by the internal movement of moisture.

Figure 6 shows a comparison of the experimental and predicted drying curves for various soybean beds of approximately 10 cm height and two initial moisture contents (0.42 and 0.62 gw/gds) dried at different air dry bulb temperatures. Predicted curves were obtained with Fick's second law (equation 1), as used before in thin layer drying experiments. Diffusion coefficients so obtained were correlated with temperature using

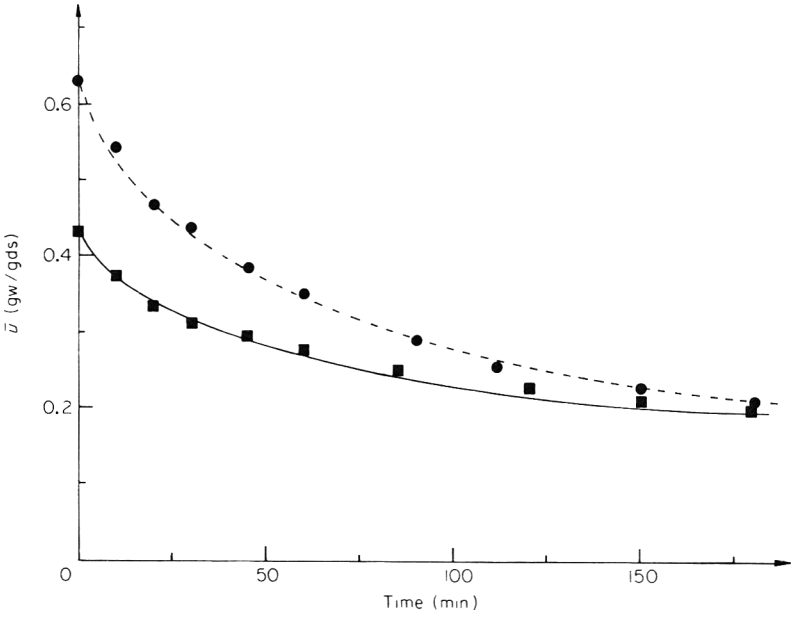

Figure 4. Moisture content of soybeans as a function of time during fluidized bed drying: ———, u_o = 0.431 gw/gds, L_o = 14 cm, v_o = 2.50 m/sec, T_{db} = 43.8°C.

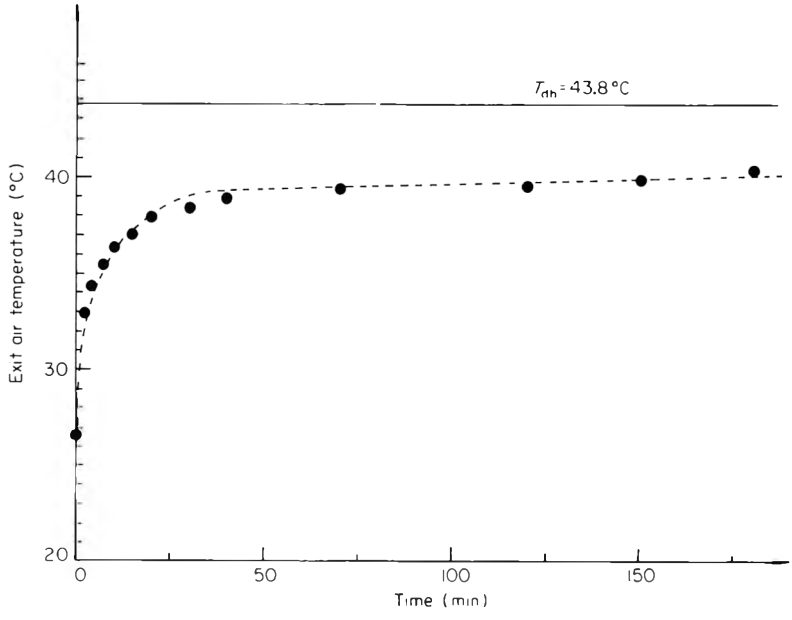

Figure 5. Evolution of exit air temperature during fluidized bed drying of soybeans: u_o = 0.629 gw/gds, L_o = 14 cm, v_o = 2.50 m/sec, T_{db} = 43.8°c.

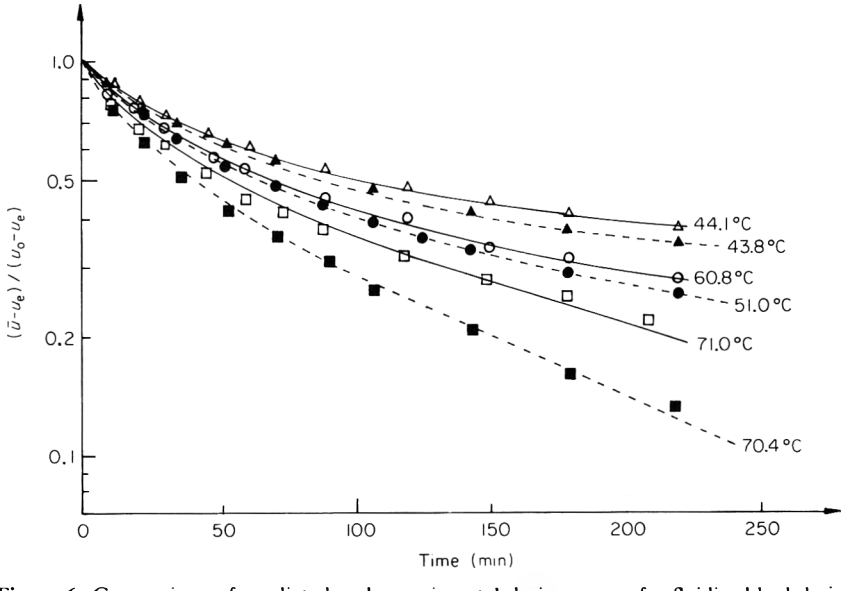

Figure 6. Comparison of predicted and experimental drying curves for fluidized bed drying (L_o = 10 cm, v_o = 2.5 cm/sec) of soybeans; u_o = 0.42 gw/gds (———, predicted: △, O, □, experimental); u_o = 0.62 gw/gds (— — —, predicted: ▲, ●, ■, experimental).

the Arrhenius relationship and are shown in Fig. 7. It is to be noted that the activation energy obtained in these experiments were practically the same as those found for the thin layer runs (7.4±0.9 Kcal/mol for u_o = 0.42 gw/gds and 7.0±0.5 Kcal/mol for u_o = 0.62 gw/gds). However, the diffusion coefficients obtained from the drying of soybean in fluidized beds were somewhat lower than those corresponding to thin layer

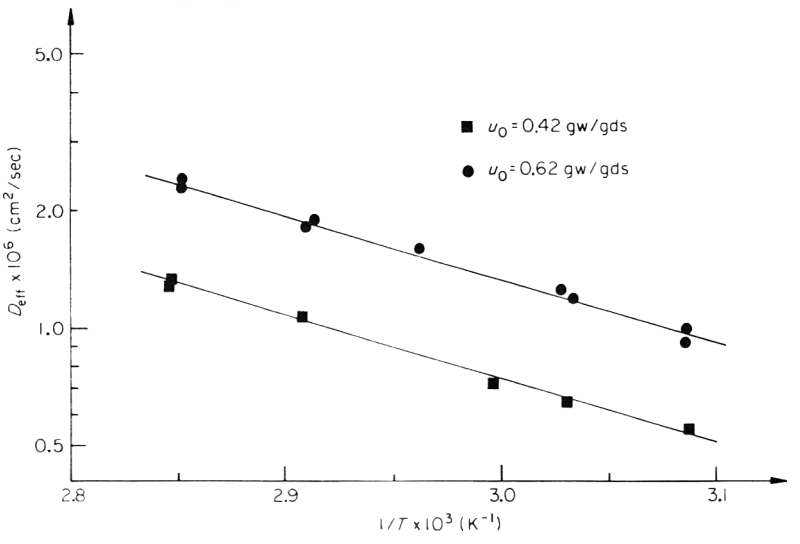

Figure 7. Effect of temperature on the diffusivity of water in soybean grains in fluidized bed (L_0 = 10 cm).

drying—i.e. at 70°C and for both initial moisture contents the D_{eff} in an 8–10 cm bed were about 20% lower than for thin layer.

Table 2 shows the diffusion coefficients calculated from drying runs of fluid beds of variable height. It can be seen that for each set of drying conditions (i.e. initial moisture content and air temperature) the diffusion coefficient decreases very slightly with increasing bed height. This effect is attributed to the lower mean temperature of the solids in the deeper beds, which means a correspondingly lower diffusion coefficient. This can best be observed in Fig. 8 which shows the evolution of exit air temperature for two beds of 8 and 18 cm height being dried at 50°C. It can be observed that at any time after an initial adjustment time, the exit air temperature in the 18 cm bed is about 4°C lower than in the 8 cm bed. This temperature difference accounts (using the Arrhenius equation) for the observed differences (Table 2) in diffusion coefficients obtained from drying data of beds of different height.

Table 2. Effect of bed depth on the diffusion coefficient of water in fluidized bed drying of soybeans

Run	u_0 (gw/gds)	T_{db} (°C)	L_0	D_{eff} (cm²/sec)
1	0.638	50.0	0	1.0×10^{-6}
2	0.631	50.0	18	8.7×10^{-7}
3	0.872	63.0	11	2.2×10^{-6}
4	0.845	63.5	17	1.9×10^{-6}
5	0.523	78.4	10	2.6×10^{-6}
6	0.523	78.2	18	2.3×10^{-6}

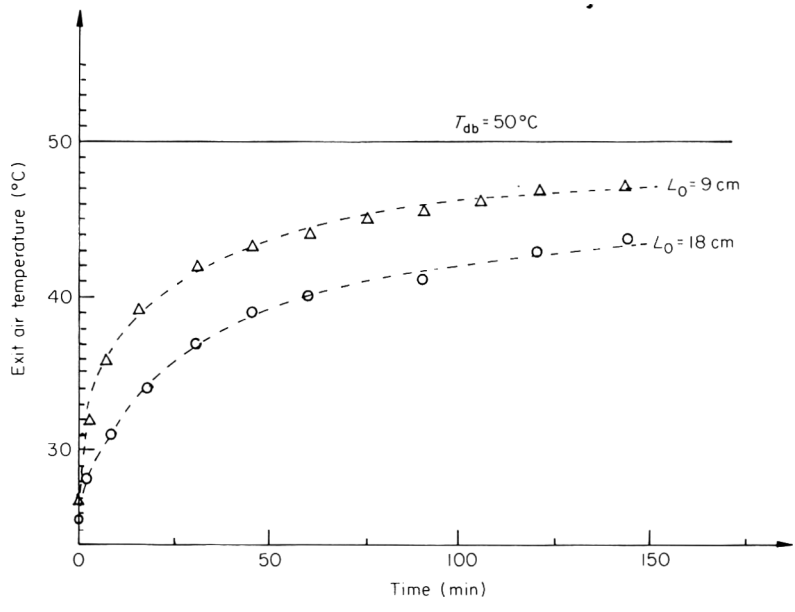

Figure 8. Effect of the bed height on the exit air temperature during fluidized bed drying of soybeans.

Figure 9 shows a plot of diffusion coefficients obtained from drying soybean in fluidized beds of variable initial moisture content at three different air temperatures and bed heights. As observed previously for thin layer experiments, the D_{eff} increases exponentially with increasing the initial moisture content.

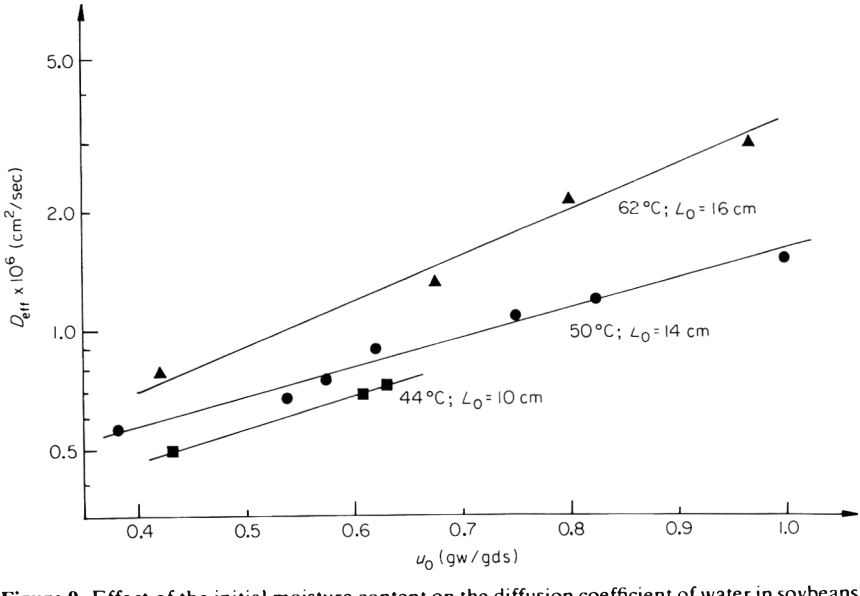

Figure 9. Effect of the initial moisture content on the diffusion coefficient of water in soybeans dried in fluidized beds of various heights.

Conclusions

The following conclusions were obtained for the drying kinetics of soybean having an initial moisture content in the range of 0.42–0.62 gw/gds. The drying curves for thin layer or fluid bed up to 20 cm height can be very well described using Fick's second law for diffusion out of spheres. The diffusion coefficients for thin layer experiments were slightly higher than those for beds up to 20 cm height and this is attributed to the temperature drop in the bed; activation energies were essentially the same for beds of all thickness in the range studied. It was observed, in agreement with other literature data, that the diffusion coefficient for water in soybean increases with increasing initial moisture content. No significant errors are to be expected if kinetic data obtained from thin layer experiments are used to predict drying behaviour in aggregative fluidized beds up to 20 cm height. However, caution should be exercised in projecting data to much deeper fluidized beds in which the heat transfer effects should be considered along with the mass transfer.

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Physico-chemical studies on sugar glasses. I. Rates of crystallization

THELMA M. HERRINGTON* AND ANTHONY C. BRANFIELD

Summary

The rates of progress of the nucleation front of sucrose glasses containing various proportions of dextrose, fructose or confectioner's glucose have been measured and considered in relation to their water contents. At high water contents samples containing dextrose had lower rates than samples containing the same amount of glucose syrup solids. It was also found that there was a value of the water content below which crystallization did not occur for samples prepared from glucose syrups, but not from samples prepared from dextrose or fructose.

Introduction

Glasses containing sucrose are readily prepared by adding dextrose, D-fructose or confectioner's glucose, which is partly degraded starch syrup containing polymers of glucose, called dextrins, as well as glucose. Experimental work suggests that the addition of dextrose, fructose or confectioner's glucose not only facilitated production of the sugar glass, but also inhibited ready crystallization of the sugar glasses once formed. The readiness to crystallize and rate of crystallization depends on the type and amount of additive used as well as on the water content of the sample. Although much work has been done in the past on the behaviour of sugar glasses under various conditions most of the work has been qualitative (Halla & Mehl, 1930; Clark, 1932; Grover, 1947; Hermans & Weidinger, 1950). The initial composition of the sugar glass has not always been specified and the methods of determining the water contents are suspect.

Extensive work on the crystallization of sucrose and glucose glasses has been carried out by Makower & Dye (1956) and Heiss & Schachinger (1955). They considered the behaviour of mixed sucrose glasses on exposure to atmospheres of various humidities. Makower & Dye (1956) obtained their sucrose glasses by a spray drying process in the form of hollow spheres (average diameter 2 μm), which were stored in atmospheres of various humidities. They showed that each particle reached an equilibrium water content corresponding to the particular humidity at which it was stored, and the rate of crystallization measured was then that of a particle of that equilibrium water content as no further water absorption took place. They found that the time for nucleation of crystals was longer than the time for equilibrium to the atmosphere: in other words the glass completely formed a viscous phase before crystallization occurred. It is not so clear to what extent the water, released on crystallization of the anhydrous sucrose

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crystals, dissolves any remaining non-crystalline portion of the particle. Makower & Dye (1956) claimed that any water diffuses into the atmosphere as soon as it is released, so that the non-crystallized portion of the particle remains at its equilibrium water content. In the work of Heiss & Schachinger (1955), although the sample studied might have contained only 3% w/w water, the rate of crystallization was measured in an atmosphere of such high relative humidity that the equilibrium water content could well be 10% w/w. Thus the rate of crystallization measured is not that of a glass of 3% w/w water content, but a complex rate depending on the rate of dissolution of the glass by a syrupy layer, which in turn is in equilibrium with a moist atmosphere.

Palmer, Dye & Black (1956) made an X-ray diffractometer and microscopic investigation of the crystallization of sucrose glass stored at 30% relative humidity (r.h.), which corresponds to an equilibrium water content of 8% w/w. They showed that crystallization was preceded by a syrupy layer and during the rapid crystallization that took place they stated that the crystalline layer acted to retain water.

From the results of these workers on the water absorption of sucrose glasses, some common factors are clear. The water adsorption is affected by the invert sugar content (dextrose and fructose); with increasing concentration of invert sugar the water activity of the supersaturated solution (or glass) relative to sucrose is decreased and hence equilibrium with a given atmosphere will require greater take-up of water. The lower the water content of the glass, the slower the initial uptake of water from the atmosphere. It was also found that increasing the quantity of dextrose polymers decreased the rate of water absorption and of crystallization. Heiss & Schachinger (1955) also found that the addition of pectin decreased the rate of crystallization but had no effect on water absorption.

Kargin (1957) has shown that glassy cellulose initially adsorbs water from the atmosphere much more readily than does glassy dextrose. He suggested that rigid cellulose chains form loosely packed glasses and the tighter bound dextrose glass was more able to resist water absorption.

The aim of the present work was to measure the rate of crystallization of different samples of sugar glasses, after crystallization had been initiated, and to relate the stability of the samples to the water content and to the proportions of the various component sugars. Measurements were made on samples sealed in glass tubes and, as the samples were isolated from the atmosphere, the rate of crystallization is purely a function of the physical and chemical structure of the sugar glass. In the present work the samples were sealed from the atmosphere, so water absorption did not occur as in the work of Heiss & Schachinger (1955). However, our experimental conditions do not compare with those of Makower & Dye (1956). In the present work, crystallization was initiated deliberately and allowed to proceed until a good crystal front had developed.

Crystallization results in a release of water; this has been confirmed in the X-ray diffraction work of Clark (1932). Unlike the situation in the work of Makower & Dye (1956), the released water could not escape; it formed a viscous layer between the crystalline and glassy phases by dissolving the glass. It is this viscous layer of high water content that plays an important part in the mechanism of crystallization.

According to the nucleation theory of Becker & Doring (1935) and Turnbull & Fisher (1949),

$$J = \frac{\rho k T}{h} \exp[-(G_D + \Delta D_K)/kT], \qquad (1)$$

where J is the rate of nucleation per unit volume, ρ is the number of molecules per unit

volume, T is the absolute temperature, G_D is the Gibbs activation energy for diffusion of a molecule and ΔG_K is a measure of the Gibbs energy change accompanying crystallization. Now

$$\Delta G_K \alpha 1/S^2, \tag{2}$$

and the supersaturation, S, is defined by:

$$S = (n_{ss} - n_s)/n_s, \tag{3}$$

where n_{ss} is the number of moles of the crystallizing substance in the supersaturated state and n_s is the number of moles at saturation. Thus the more supersaturated the solution (i.e. the smaller the number of moles of water), the smaller is ΔG_K and the larger is J.

Materials and methods

All the glasses studied in this work contained sucrose as the major component with varying amounts (up to 40%) of the second component to act as crystallization inhibitor. The second components used were dextrose, D-fructose and various types of commercial confectioner's glucose as syrups.

The confectioner's glucose syrups are prepared by the incomplete hydrolysis of maize starch. Each syrup consists of a mixture of dextrose, maltose and dextrose polymers. The syrups are classified by comparing their reducing properties with dextrose and are expressed as % dextrose equivalent (DE). The syrups contain about 80% w/w solids. The syrups were analysed for water content both by a vacuum oven drying method (Triebald & Aurand, 1963) and by the Karl Fischer method (Peters & Jungnickel, 1955) which gave slightly higher values for the water content. The dextrose and maltose contents of the syrups were measured using gas liquid chromatography of the trimethyl silyl derivatives of the syrups, using the method of Brobst & Loft (1966). Unfortunately a column could not be prepared to analyse for maltotriose and maltotetrose.

The syrups used in this work were: (a) 42% DE glucose syrup (CPC plc, Product A1201); (b) 35% DE glucose syrup (Tunnel Refineries, Product 170); (c) 25% DE malto dextrin compound (Tunnel Refineries); and (d) 42% DE 'high maltose' syrup (CPC plc, Product AX/11J 'Morsweet').

The compositions of the syrups are given in Table 1. The dextrose and maltose contents are expressed as a weight percentage (% w/w) of the total solids composition, but the water content is quoted as weight percentage of the total weight of syrup. The figures in brackets in Table 1 are the manufacturers' values, which were not available for products (b) and (c). In the Results section when the compositions of samples containing glucose syrup are referred to, they are always quoted with respect to the solids content of the glucose syrup, which is calculated from the measured water content. Thus in calculating the weight percentage composition of the samples, it is the weight of solids contained in the glucose syrup, which is referred to and *not* the total weight of glucose syrup used. Thus:

$$\%\ \text{w/w of non-sucrose component} = \frac{\text{weight of non-sucrose solid} \times 100}{\text{weight of non-sucrose solid} + \text{weight of sucrose}}$$

For the samples containing dextrose and D-fructose the mole ratios compared with sucrose are also given. It is not possible to do this with samples containing

Table 1. Composition of confectioner's glucose (% w/w)

	Type of glucose syrup			
	Standard			High maltose
Component	42% DE	35% DE	25% DE	42% DE
Glucose	17	14	5.4	5.7
Maltose	14	13	7.0	43.0
Maltotriose	11			15.0
Maltotetrose	10			5.0
Water	18.7	19.3	5.0	19.1

The glucose and maltose contents are given as a weight percentage of the total solids composition, but the water content is quoted as weight percentage of the total weight of the syrup.

confectioner's glucose since they are a mixture of components of different relative molar masses. In all cases sucrose and water are the only other components present. The water content of the final sample is weight percentage of water with respect to total weight of the sample.

The sucrose used was commercial grade (Tate and Lyle Ltd) of 99.95% purity. The impurities were:

Invert sugar	0.010%
Ash (salts of calcium and sodium)	0.008%
Organic (colouring and colloidal matter)	0.012%
Water	0.020%
D(+) glucose was B.D.H. Analar Grade (anhydrous)	
Specific rotation $[\alpha]_D^{20^\circ}$	+52.5° to 53.0°
Water insoluble matter	0.003%
Sulphated ash	0.03%
Other impurities (sulphate, sulphite chloride)	0.006%
Weight loss on drying	0.1%
D(−) fructose was B.D.H. product (low in glucose)	
Specific rotation $[\alpha_D]^{20^\circ}$	−92° to −89°
Glucose	1%
Sulphated ash	0.2%
Weight loss on drying	1%

The water used was distilled and deionized; its conductivity was $< 10^{-6}\Omega^{-1}\,cm^{-1}$. It was degassed before preparation of the sugar glasses.

Preparation of sugar glasses

An aqueous solution containing the required proportion of solids content was boiled under reduced pressure; the water vapour produced during the boil was carried away by a stream of air. The time period of the boil determined the water content of the glass, but was usually in the region of 10–20 min. After boiling, samples of the melt were drawn up, using reduced pressure, into pre-heated glass tubes of approximately 6 mm

internal diameter, which were then sealed with rubber caps. The tubes were previously coated internally with 'Silicone Releasil Fluid' (Hopkins and Williams Ltd, Chadwell Heath, Essex) to prevent the sweet sticking to the glass surface.

A major difficulty in some of the boils was the presence of bubbles, with diameters of the order of 1 mm, in the final melt. When samples were taken these bubbles were transported with the melt into the sample tubes and their presence made measurements of crystallization rates impracticable. These bubbles had become trapped in the melt while in the process of rising from the base of the flask when the air pressure was allowed to rise to atmospheric at the end of the boil. Attempts were made to collapse the more stubborn bubbles by applying pressure, as used by Parks, Huffmann & Cattoir (1928) in their work on glucose glasses, and then to collect the samples by applying *circa* 1 atm. excess pressure to the surface of the melt to force it into the sample tubes. This neither caused the bubbles to collapse nor proved a practical method of collection. The glucose syrups and the water used in preparing the initial solutions were degassed before boiling but samples were still obtained infested with bubbles. The best results were obtained by allowing the pressure to rise slowly to atmospheric on completion of the boil.

Analysis of the sugar glasses

The water content of the samples was determined by a Karl Fischer method. A modified form of Karl Fischer reagent (Peters & Jungnickel, 1955) with a base of methyl cellosolve was used as it deteriorated less quickly than the standard reagent. The solvent used to dissolve the sweet was a 1 : 1 mixture of methanol and formamide.

Invert sugar, the product of the hydrolysis of sucrose, is a mixture of equal parts of fructose and glucose. Because both fructose and glucose tend to inhibit crystallization in the glassy state, it was necessary to determine the extent to which inversion occurred in the boiling process. The sugar glass samples were analysed for their fructose content, which when doubled, gave the invert sugar content. The method of analysis was based on a method developed by Hinton & Macara (1931) using Luff's reagent. Ten different samples were analysed by this method, the samples being taken from boils of varying lengths and sugar composition. The maximum amount of invert sugar measured was 0.6% w/w and the value was generally of the order of 0.3% w/w invert sugar. Sucrose inversion is not therefore a problem under the boiling conditions used in this work.

Determination of the rate of progress of the nucleation front

Crystallization was initiated by seeding one end of the sample, contained in its glass tube, with small sucrose crystals, replacing the rubber cap and then storing the end of the sample at a high temperature for a period of 1–4 hr. When sufficient development had occurred the samples were stored for several days at the temperature at which measurements were to be made. The samples were fixed vertically in an air thermostat and the positions of the crystal front measured at different times using a small cathetometer.

To ascertain that this method of measuring the rate of progress of the nucleation front was valid the following experiments were conducted.

1 There was no increase in weight of the samples which were kept in the air thermostat for a period of weeks. This showed that the rubber caps prevented moisture adsorption.
2 For the same nucleation front, the rate of progress in an upward direction in the tube was the same as in the downward direction.
3 Varying the diameter of the glass tube which contained the samples had no effect on

the rates. Measurements were made on a crystal front initiated in the centre of a sample contained in a wide diameter tube, where the crystal front made no contact with the surface of the glass tube. The results were in agreement with those obtained from measurements on glasses of similar composition where the crystal front was across the diameter of the tube. This demonstrated that there was no surface effect on the rate.

4 Measurements were repeated on samples contained in tubes not coated with release agent. The results showed that the release agent had no effect on the rate.

5 Some samples were crystallized initially by exposing the end to an atmosphere of known relative humidity until a crystal front developed. The end was then re-sealed. After an initial high value, the rate equilibrated to the value that would have been obtained from crystallization initiated by seeding.

Results

The rates of progress of the nucleation front were plotted against water contents for the various glass systems. The samples containing the standard confectioner's glucose (42% DE) were studied in the greatest detail and the results used as a framework against

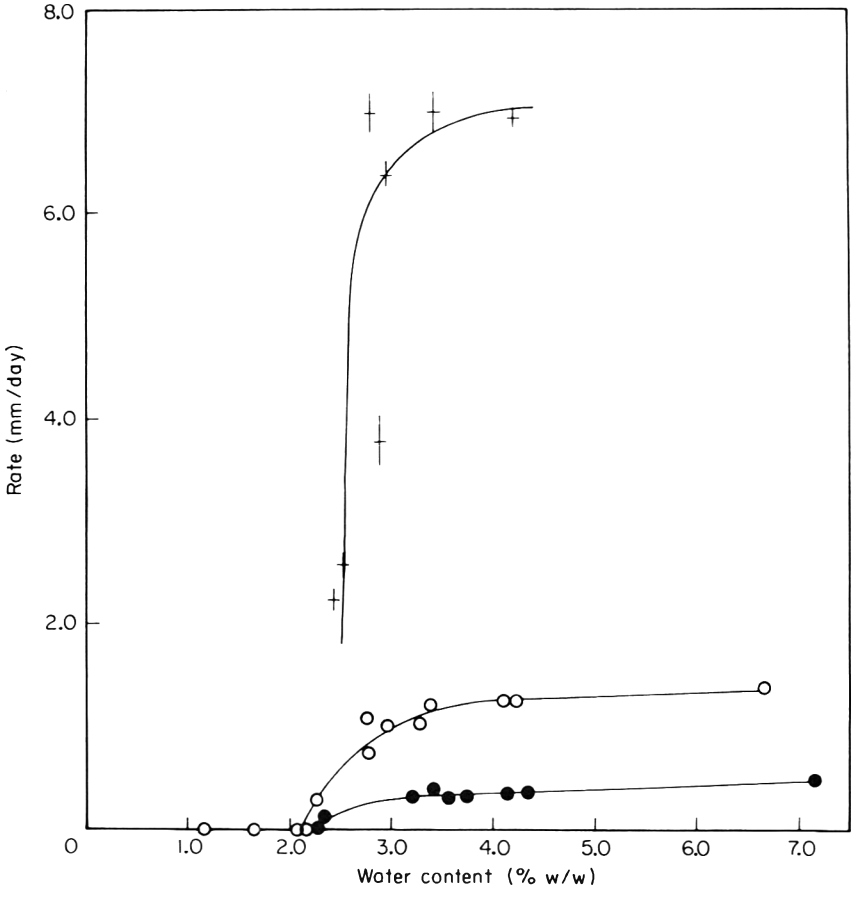

Figure 1. Variation of the rate of progress of the nucleation front with temperature for samples containing 14% w/w confectioner's glucose (42% DE). ●, 20°C; O, 30°C; +, 50°C.

which comparisons were made of further rate determinations on samples containing different component sugars and syrups.

As can be seen from Figs 1–8, for all the systems studied the rates tended towards a constant value at high water contents. From Fig. 1 the temperature change of these near constant values can be seen and Figs 2 and 3 show the change with increasing proportions of the 42% DE confectioner's glucose. From Figs 4 and 5 it is seen that the rates at higher water contents are similar for samples containing the same proportions of the different types of confectioner's glucose. However at these higher water contents, from Figs 6 and 7, and comparatively from Fig. 8, it is seen that dextrose and especially D-fructose samples have slower rates than the corresponding confectioner's glucose samples. The rates at 6% water content for samples containing 14% w/w D-fructose compare with those for samples containing 30% w/w of the confectioner's glucose and the 14% w/w dextrose samples had similar rates to the 20% w/w confectioner's glucose samples.

The second characteristic depicted by these results occurred with samples prepared from confectioner's glucose. With these samples there was a value of the water content below which the nucleation front did not proceed at a measurable rate after initial development. This may be termed the 'threshold value' of the water content. The 'threshold' values that were found for the different systems studied are given in Table 2. From Table 2, it is seen that the 'threshold' water content increases markedly with increasing proportions of confectioner's glucose, but decreases only slightly with increasing temperature. Also, the 25% DE confectioner's glucose has a higher

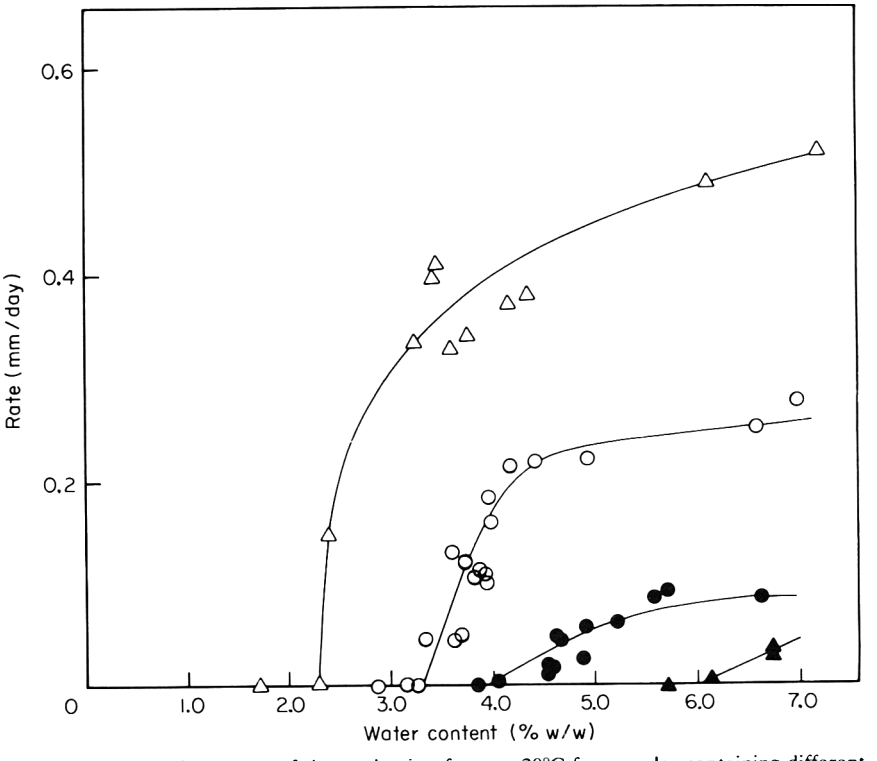

Figure 2. Rates of progress of the nucleation front at 20°C for samples containing different proportions of confectioner's glucose (42% DE). △, 14% w/w; ○, 20% w/w; ●, 30% w/w; ▲, 40% w/w.

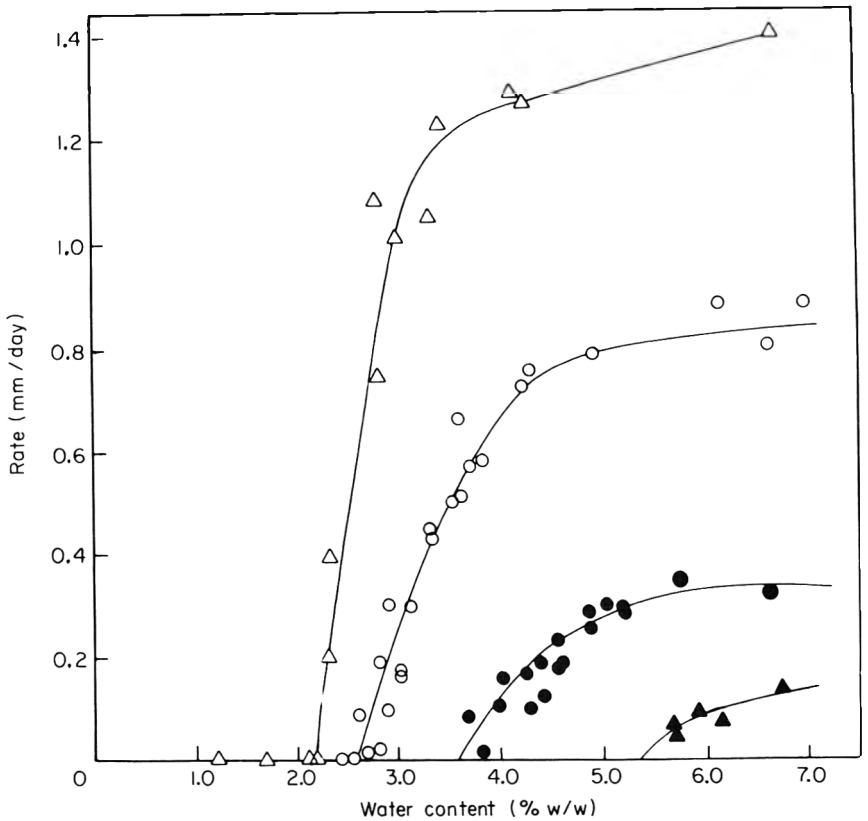

Figure 3. Rates of progress of the nucleation front at 30°C for samples containing different proportions of confectioner's glucose (42% DE). △, 14% w/w; ○, 20% w/w; ●, 30% w/w; ▲, 40% w/w.

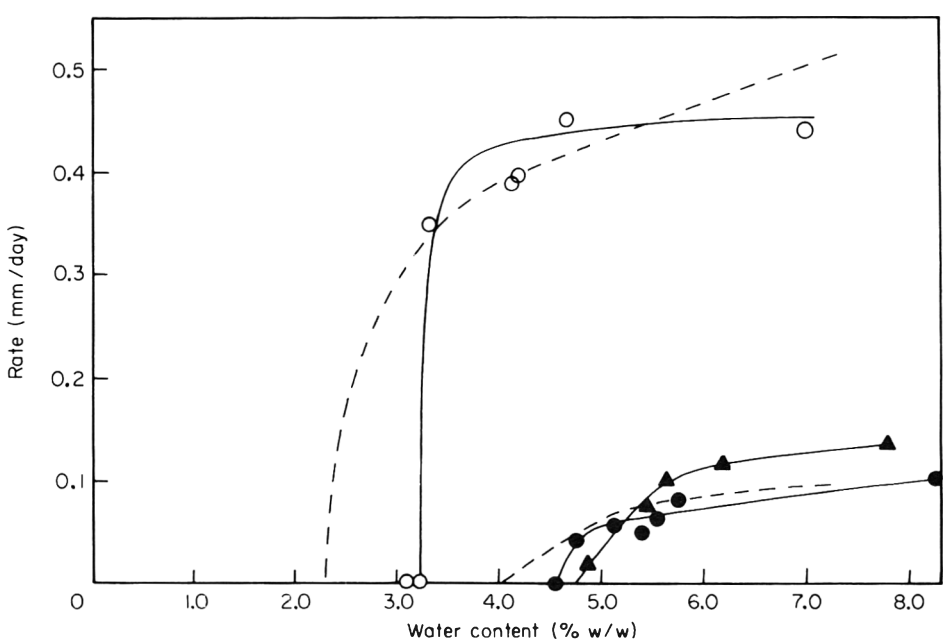

Figure 4. A comparison of the rates at 20°C of samples containing different types of confectioner's glucose. ○, 14% w/w confectioner's glucose (25% DE); ▲, 30% w/w confectioner's glucose (35% DE); ●, 30% w/w 'high maltose' confectioner's glucose (42% DE); ---, corresponding rates for standard confectioner's glucose (42% DE).

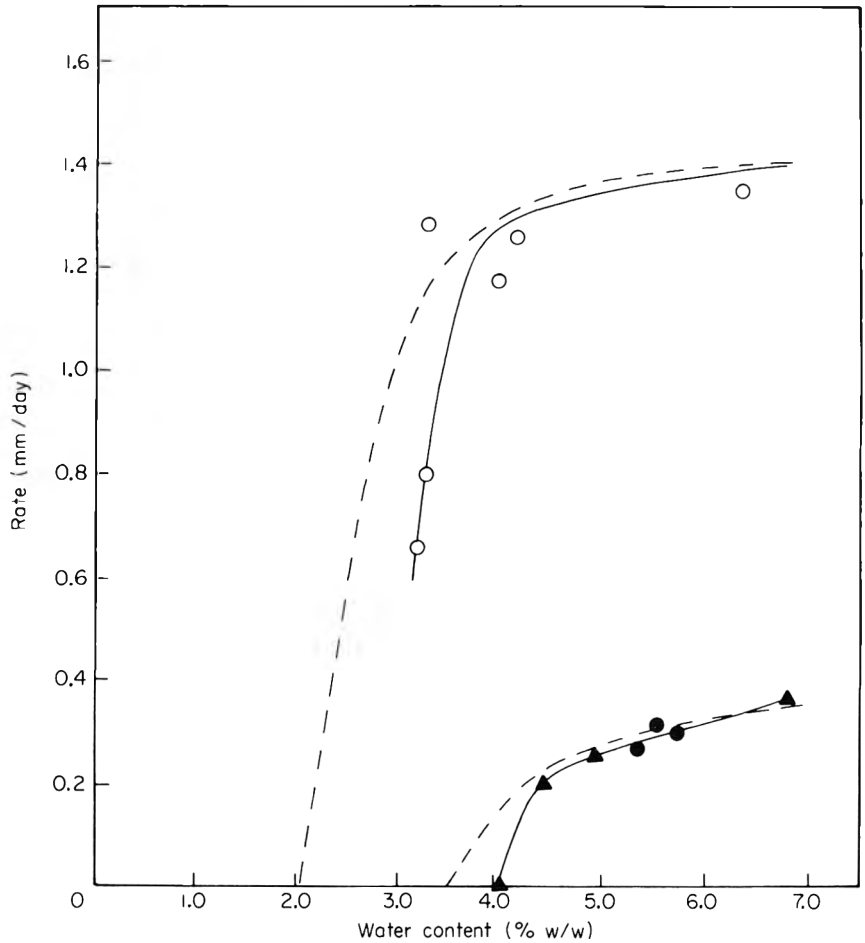

Figure 5. A comparison of the rates at 30°C of samples containing different types of confectioner's glucose. O, 14% w/w confectioner's glucose (25% DE); ▲, 30% w/w confectioner's glucose (35% DE); ●, 30% w/w 'high maltose' confectioner's glucose (42% DE); – – –, corresponding rates for standard confectioner's glucose (42% DE).

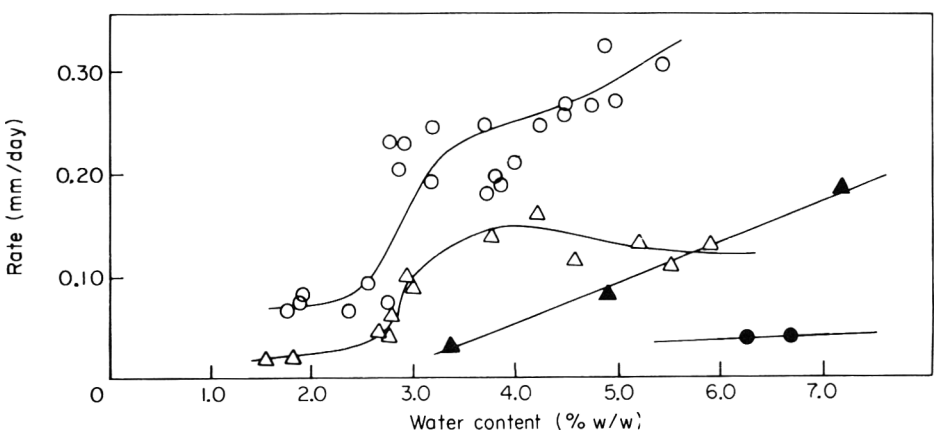

Figure 6. Rates of progress of the nucleation front of samples containing D-fructose or different proportions of dextrose at 20°C. ▲, 14% w/w D-fructose (mole ratio sucrose : fructose 3.24 : 1); O, 14% w/w dextrose (mole ratio sucrose : glucose 3.24 : 1); △, 20% w/w dedxtrose (mole ratio sucrose : glucose 2.11 : 1); ●, 30% w/w dextrose (mole ratio sucrose : glucose 1.22 : 1).

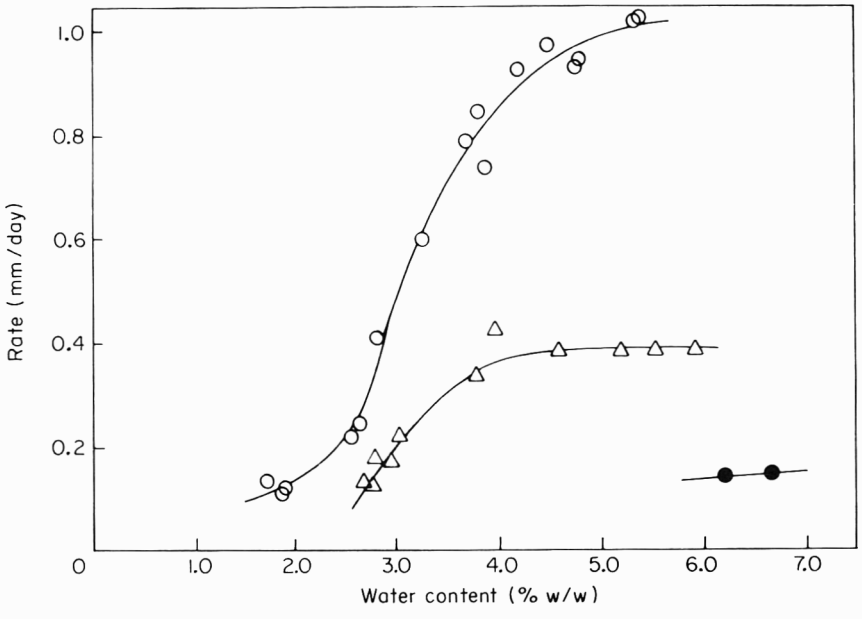

Figure 7. Rates of progress of the nucleation front at 30°C for samples containing different proportions of dextrose. ○, 14% w/w dextrose (mole ratio sucrose : glucose 3.24 : 1); △, 20% w/w dextrose (mole ratio sucrose : glucose 2.11:1); ●, 30% w/w dextrose (mole ratio sucrose : glucose 1.22:1).

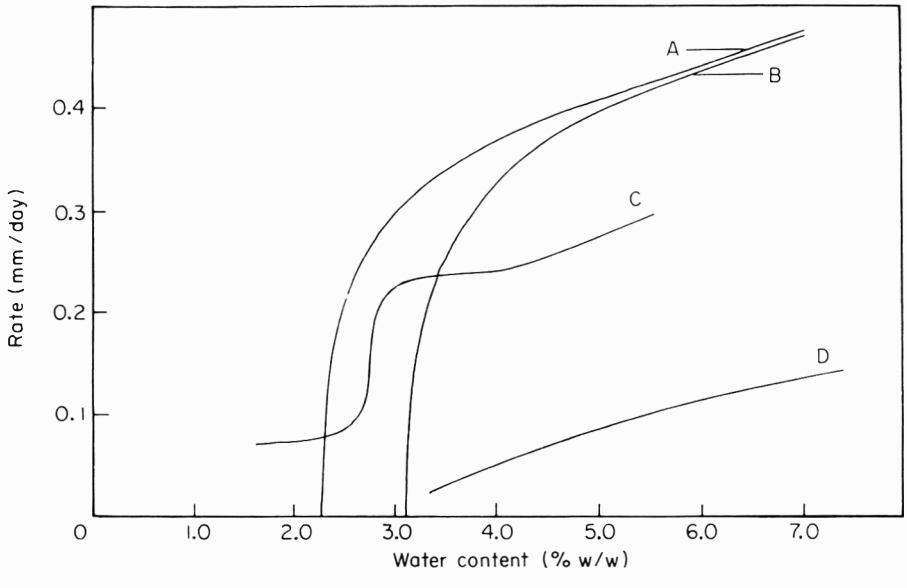

Figure 8. Rates of progress of the nucleation front at 20°C for samples containing 14% w/w of different components. A, confectioner's glucose (42% DE); B, confectioner's glucose (25% DE); C, dextrose; D, D-fructose.

Table 2. 'Threshold' water values (% w/w) at 20 and 30°C for sugar glasses of different compositions

T (°C)	% w/w	42% DE (high maltose)	25% DE	35% DE	42% DE (standard)
20			3.2 (±0.2)		2.3 (±0.1)
	14				
30			2.9* (±0.3)		2.2 (±0.1)
20					3.2 (±0.1)
	20				
30					2.7 (±0.1)
20		4.5 (±0.3)		4.6 (±0.3)	3.9 (±0.3)
	30				
30				4.0 (±0.3)	3.6* (±0.3)
20					5.8* (±0.4)
	40				
30					5.3* (±0.4)

*Value obtained by extrapolation.

'threshold' water content than the 42% DE confectioner's glucose; this is also seen by comparing Figs 4, 5 and 8. From Table 2 and Fig. 4 a similar stabilizing tendency is shown by the 'high maltose' confectioner's glucose. It would appear, therefore, that the lower DE confectioner's glucose which contain a great proportion of high oligomers confer extra stability on the sugar glasses at low water contents.

As can be seen from Figs 6 and 7, at low water contents in the pure dextrose samples the nucleation front progressed at a slow rate, which, over the moisture region studied, was not dependent on water content. In other words, threshold values were not obtained for samples using 14 and 20% w/w dextrose (equivalent to mole ratios sucrose : glucose of 3.24 : 1 and 2.11 : 1, respectively). These samples do not contain *any* dextrose polymers which supports our suggestion above that the amount of higher oligomers present is correlated with the threshold values.

The following facts are applicable to all our crystallization results: (i) A layer of viscous solution exists between crystals and glass. (ii) The water content of the crystalline layer equals the water content of the glass. (iii) The width of the viscous layer remains constant and, when a sample did not crystallize after initiation the viscous layer was still present. (iv) For any given solids composition there is a water content above which the rate increases rapidly. For the sucrose + glucose syrup glasses this is the 'threshold' water content, below which there is no measurable rate. For sucrose and dextrose glasses, this is the 'step' water content. (v) The 'threshold' water content is dependent on the dry solids composition. The 'step' water content is not so dependent. (vi) Both the 'threshold' and 'step' water contents are slightly temperature dependent, both decreasing with increasing temperature.

Discussion

Consider the general situation from the rate of progress of the nucleation front for the sucrose glasses containing the following components:

Dextrose: (i) Increasing the amount of dextrose *markedly* reduces the rate.

(ii) There are no 'threshold' values, but a fairly sudden drop in rates at lower water contents. (iii) The rate at low water contents tends to be independent of water content. The water content at which rates begin to increase is termed the 'step' water content. (iv) Above the 'step' water content the rates are lower than for similar weight ratios of confectioner's glucose to sucrose.

Fructose: This system gives a very slow rate.

Confectioner's glucose: (i) Increasing the quantity of confectioner's glucose reduces the rate. (ii) Increasing the quantity of confectioner's glucose increases the 'threshold' water content.

The work of Tammann (1926) considers the formation of crystals from a melt. They showed that the crystallization process occurred in two stages: first the crystal nuclei must form, and then these nuclei must grow. However, here the supercooled liquid or glass is not forming crystals directly but only through an intermediate phase—the viscous supersaturated solution. It will be assumed that only sucrose crystallizes out. The viscous solution accompanying the nucleation front is of constant width as it moves down the tube and the water content of the crystalline layer is equal to that of the glass; possible kinetic steps are: (i) supersaturated viscous solution → crystal nuclei + saturated aqueous solution; (ii) crystal nuclei + supersaturated viscous solution → crystals + saturated aqueous solution; and (iii) saturated solution + glass → supersaturated viscous solution. Any one or all of these steps may be rate determining depending on the water content.

Let us first consider step (i) which is the crystallization of a supersaturated solution and is similar to the formation of droplets from a supersaturated vapour. If we assume that step (i) is rate determining, then we are assuming that the rate determining step is the formation of crystal nuclei; once nuclei are formed, then crystallization is rapid. The rate of advancement of the nucleation front was determined in tubes of uniform bore, so that if x is the distance moved by the nucleation front, $dx/dt = \alpha J$ is measured, where α is a constant for all our measurements, since the rate of advancement of the nucleation front was dependent on the tube diameter. We found the opposite effect to that predicted by equation (2). The smaler the water content of the glass the lower the rate. As the water content of the crystalline layer is equal to that of the glass, this means that the smaller the water content of the glass the more supersaturated is the viscous phase. Thus here the more supersaturated the viscous phase, the smaller J, so that the Gibbs activation energy, G_D, and hence viscosity must be the predominating influence on J. The viscous phase was unstirred so that indeed it might be expected that diffusion would play a dominant role in nucleation and hence crystallization, if step (i) is rate determining.

However, nucleation theory does not take account of crystallization after nucleation and it may be that step (ii) is rate determining. The minimal concentration of sucrose in the aqueous layer at 25°C is the saturation concentration of 6.0 mol/kg water. A saturated solution of sucrose is extremely viscous and the water activity (or concentration) gradient resulting from crystallization may only be removed slowly by diffusion. Thus the activtion energy for water migration in the supersaturated solution, G_w, may be the rate determining parameter. The higher the water content of the glass, the more water is present in the viscous phase lowering its viscosity, so that the water can diffuse more easily, and the rate is determined by the activation energy for the diffusion of water through the viscous layer.

The rate may be determined by step (iii), the rate of solution of the glass by the

saturated aqueous solution. The driving force is determined by μ (sucrose in glass) $-\mu$ (sucrose in solution), but it is probably the rate of diffusion of water through the viscous solution immediately formed in the surface of the glass which is the dominant factor, so that the activation energy for water transport, G_w, is again rate determining.

Consider the crystallization of the 14% w/w dextrose glasses (mole ratio sucrose : dextrose 3.24 : 1) of varying water content (Fig. 6). Below 2.5 w/w of water the rate is almost constant, but at the 'step' water content, the rate increases rapidly before levelling off again. Several systems also showed a slight maximum in the rate at water contents above the 'step' value. This was found, for example, in the systems 20% w/w dextrose (mole ratio sucrose : dextrose 2.11 : 1) at 20°C (Fig. 6) and 30°C (Fig. 7). These sigmoidal curves imply that different steps may be rate determining depending on the water content. Below some critical value of the water content, all the water present in the viscous layer may be firmly bound as a dextrose hydrate so that the activation energy for water migration is rate determining. At higher water contents the diffusion of sucrose in the viscous layer to form crystal nuclei may determine the rate.

All the samples containing confectioner's glucose show a 'threshold' instead of a 'step' water content. If step (i) is rate determining at water contents above the 'threshold' values, then from Equation (1) it can be seen that a plot of $\log(J/T)$ against $1/T$ should be a straight line and the slope reflects how G_D changes with water content and glucose solids composition. In Figs 9 and 10 the logarithm of the rate divided by absolute temperature is plotted against reciprocal temperature for different water contents of samples of dry solids composition 14 and 20% w/w respectively of confectioner's glucose (42% DE). The rates were measured at 20, 30 and 50°C. The 2.5% w/w water content of the 14% w/w confectioner's glucose is almost the 'threshold' value at 50°C (Fig. 1); thus for both the 14 and 20% w/w confectioner's glucose at water contents well above 'threshold' straight lines are obtained within experimental error. The similarity in G_D for the different concentrations of confectioner's glucose at high water contents is most interesting as according to Equation (1) the pre-exponential factor must be doubled to be consistent with the rates shown in Fig. 2. Thus ρ (the number density) of sucrose molecules or 'clusters' about to nucleate in the viscous layer of the 14% w/w sample must be about twice that of the 20% w/w sample. Certainly the 14% w/w sample has a greater sucrose to glucose mole ratio. Thus these plots imply that at water contents well above the 'threshold', step (i) is rate determining and the diffusion of sucrose in the viscous supersaturated solution to form crystal nuclei is the crucial factor. Also the slopes are almost independent of water content, so that the diffusion coefficient of sucrose in these solutions should correlate with the rates.

There are not enough data at different temperatures to do a similar nucleation theory analysis for the dextrose glasses. However, as discussed earlier, it is probable that at high water contents, step (i) is rate determining. Comparison of the rate of progress of the nucleation front as a function of water content for systems containing 14% w/w of fructose, dextrose and confectioner's glucose are shown in Fig. 8. The dextrose and fructose glasses have smaller rates than the confectioners glucose at water contents greater than 4% w/w. The rates at 6% w/w for dextrose and confectioner's glucose at 20 and 30°C are shown in Fig. 11. This shows that not only are rates smaller for dextrose samples at this high water content but they are decreasing more rapidly, implying that G_D is larger for supersaturated sucrose solutions containing dextrose than it is for solutions containing dextrose polymers. Possibly the higher oligomers effect a solution of more open structure so that the sucrose molecules can diffuse more easily. The rate is even lower in fructose glasses and there is no 'step' water content; probably

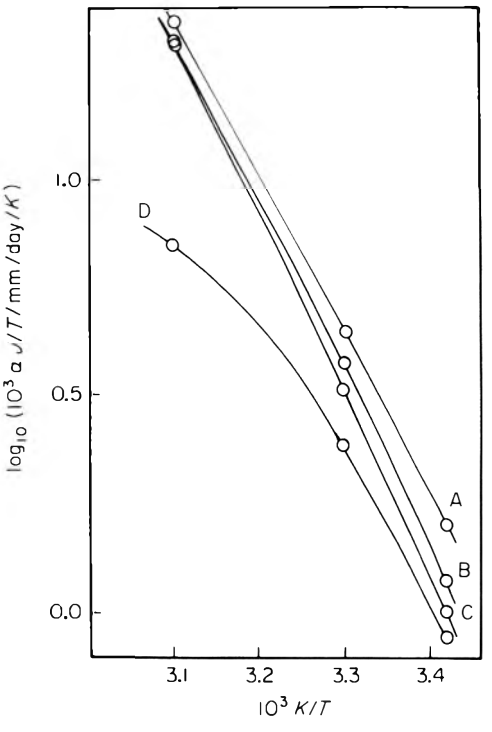

Figure 9. Variation of the logarithm of the rate divided by temperature against reciprocal temperature for confectioner's glucose (42% DE) 14% w/w. A, 6% w/w water; B, 3.5% w/w water; C, 3.0% w/w water; D, 2.5% w/w water.

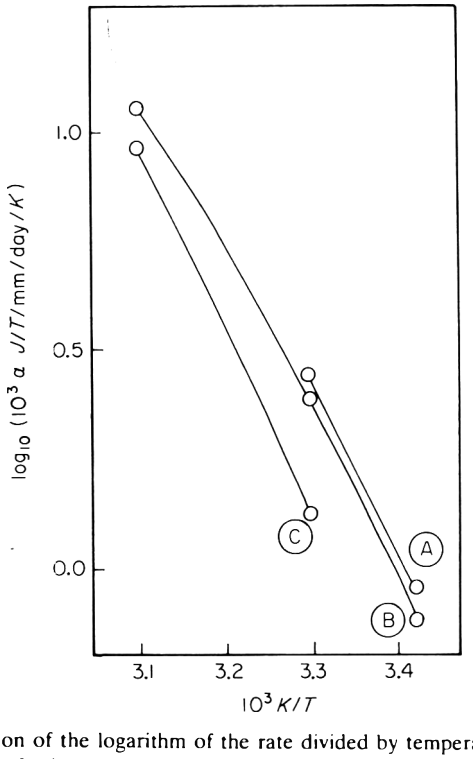

Figure 10. Variation of the logarithm of the rate divided by temperature against reciprocal temperature for confectioner's glucose (42% DE) 20% w/w. A, 6% w/w water; B, 4.5% water; C, 3.3% w/w water.

the same rate determining step is applicable at all water contents, namely the activation energy of migration of 'bound' water molecules.

The rate is effectively zero at low concentrations of water for the confectioner's glucose, whereas it is quite measurable for the dextrose samples (Fig. 8). It was suggested for the dextrose glasses that below the 'step' water content the water is firmly bound as a hydrate so that the activation energy of migration is large. Thus for the glasses containing confectioner's glucose the 'threshold' value of the water content probably relates to 'free' water rather than total water. The amount of 'bound' water will depend on the different sugars present, their concentration and the temperature. Figure 12 shows the effect of increasing the percentage of confectioner's glucose on the 'threshold' water content. Also shown in Fig. 12 are the 'step' water contents for

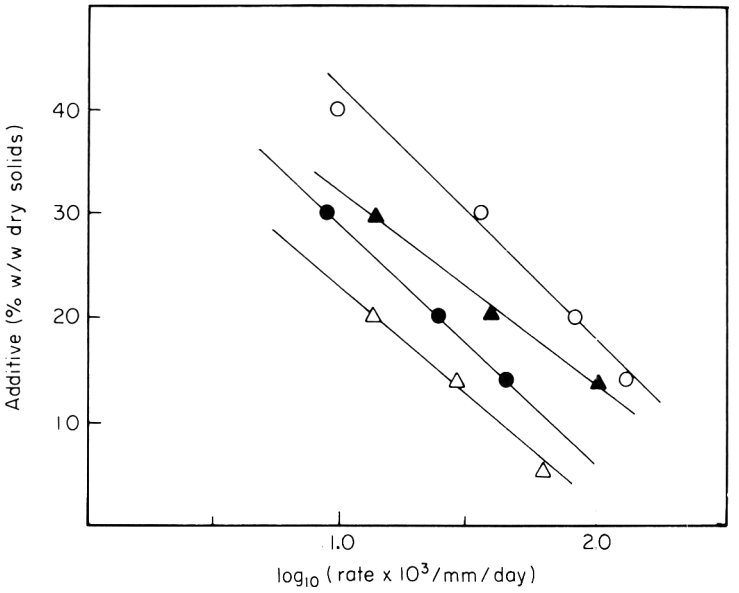

Figure 11. Comparison of rate with sugar composition at 6% w/w water content. The samples contain sucrose with the additives: ●, confectioner's glucose (42% DE) at 20°C; O, confectioner's glucose (42% DE) at 30°C; △, dextrose at 20°C; ▲, dextrose at 30°C.

dextrose glasses which increase slightly with increasing amounts of dextrose. The effect of temperature on the 'threshold' values is shown in Fig. 13; the 'threshold' value is lowered as would be expected if it were an effect determined by an activation energy for water migration G_w. It is suggested that the large dextrose polymers bind the water molecules even more firmly than dextrose itself. Possibly the 'threshold' relates to a transition from viscous to viscoelastic or even rigid behaviour when there is insufficient water to allow flow.

Crystallization from the viscose supersaturated layer and dissolution of the glass cannot be independent phenomena. This viscous phase positioned between the glassy and crystalline layers was always present in our samples. How does the nature of this viscous phase change with the inclusion of different components in varying proportions? Does the proportion of confectioner's glucose have the most marked effect on its viscosity? Also, the moisture content of this phase for samples of different initial moisture and solids content should be measured. With samples containing sucrose and

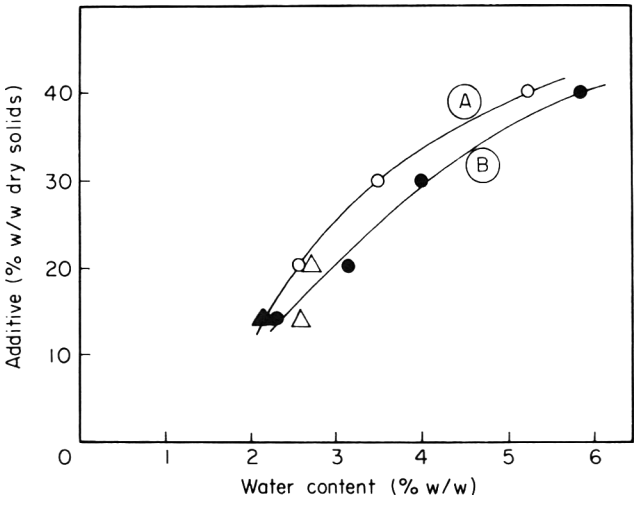

Figure 12. Variaton of 'threshold' and 'step' water contents with amount and type of additive at 20 and 30°C. A, threshold water content: ●, confectioner's glucose (42% DE) 20°C; B, threshold water content: O, confectioner's glucose (42% DE) 30°C. Step water content: △, dextrose 20°C; Step water content: ▲, dextrose 30°C.

large amounts of dextrose, possibly glucose as well as sucrose crystallizes—e.g. in a sample of solids composition 20% w/w dextrose, 80% w/w sucrose and 6% w/w water, the viscous phase could be supersaturated with respect to glucose—glucose crystallizing as the monohydrate would then remove water from the phase. Similarly, the remarkable doctoring effect of fructose may be due to the high total solids solubility of sucrose+fructose solutions (Kelly, 1954). More work needs to be carried out on the water activity and diffusion coefficients in supersaturated solutions of varying composition. A sample containing low DE confectioner's glucose with added quantities of fructose may combine the effects of high 'threshold' water content imparted by the low DE confectioner's glucose and low rate imparted by fructose.

The hypothesis that development of the crystal front involves dissolution of the glass as a rate determining step may be relevant to the 'threshold' or 'step' values. So far it has been considered that step (iii) is determined by water movement after dilution of the

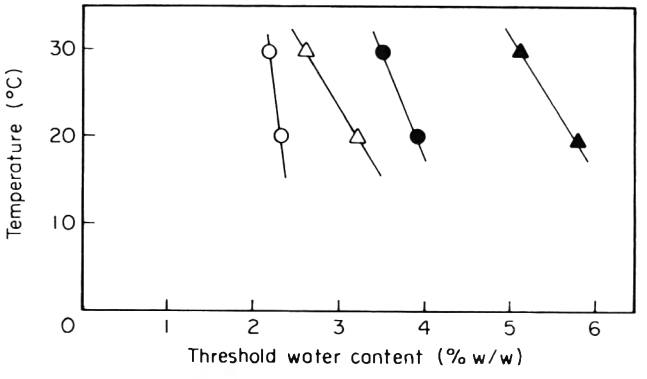

Figure 13. Variation of 'threshold' water content with temperature for samples containing different amounts of confectioner's glucose (42% DE). O, 14%, △, 20%, ●, 40% of confectioner's glucose on a dry solids basis.

supersaturated solution. However, does it depend on a structural property of the glass? Indeed are all the samples truly glasses or supercooled liquids? It has been suggested (Cakebread, 1969) that the greater stability of the low water content glasses may be due to the viscosity becoming greater than 10^{13} Pa s at the storage temperature resulting in the sample being in the glassy as opposed to the supercooled liquid state. The glass transition temperatures of these samples must therefore be higher than their storage temperatures. Are the dextrose and confectioner's glucose samples only glasses at low water contents? Are the fructose samples glasses at all of the water contents investigated? The view that passing from the supercooled liquid to the glassy state confers stability would appear to be worthy of consideration in relation to the 'threshold' and 'step' water contents. Investigation of this concept is presented in part II of this series of papers.

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Physico-chemical studies on sugar glasses. II. Glass transition temperature

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Summary

The glass transition temperature for sucrose glasses containing added dextrose or confectioner's glucose (42% DE) and varying water content has been determined by differential thermal analysis.

Introduction

The glass transformation temperature, T_g, locates the temperature region over which the transformation occurs from the glassy to the supercooled liquid state, or vice versa. Truly glassy materials exhibit the coincidence of changes in the coefficient of expansion, heat capacity and tensile behaviour at the mechanical glass transition (Miller, 1969). These changes occur over a broad temperature range as opposed to the narrow temperature range of first-order phase phenomena. Only below T_g is it correct to describe the material as a glass. Between T_g and the melting point the material is a supercooled liquid. T_g is not an accurately defined temperature; the value determined for a particular substance will depend on the method used and the time scale adopted. An aqueous sucrose glass may be crudely described as an undercooled liquid system that has assumed solid properties (Doremus, 1973). Detailed discussion of the nature of the glassy state appears in a review by Kauzmann (1948).

The Gibbs energy of a glassy state of a material is greater than that of its corresponding crystalline state. The difference between the free energy of glassy and crystalline dextrose has been measured by Parks & Rowe (1946). There must be a barrier to inhibit the formation of the crystalline state when the material is cooled below its freezing point. Experimental evidence shows that glass formers have high values of the activation energy for viscous flow in their liquid state (Pryde & Jones, 1952):

$$E(\text{visc}) = Rd\ln\eta/d(1/T), \tag{1}$$

where $E(\text{visc})$ is the activation energy for viscous flow, η is the viscosity and T the absolute temperature. This suggests that a high viscosity is intimately associated with the process that inhibits crystallization of sucrose glasses.

Cooling a supersaturated solution can lead to a dramatic increase in viscosity and effective cessation of diffusion. In forming a glass the viscosity increase may be supplemented by some configurational change, other than crystallization, at the molecular level. Differential thermal analysis (DTA) has been used to study such changes in inorganic and organic polymer glasses. Sestak (1974) has used DTA to study the crystallization kinetics of inorganic glasses: as the glass crystallizes a large exothermic

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peak is obtained on the differential temperature trace. Clinton, Mercer & Miller (1970) used the technique on lithium aluminium silicate glasses: the glass transition temperature, T_g, at which there are sharp changes in specific heat were indicated by a sharp decrease in the steady differential temperature baseline at temperatures several hundreds of degrees below the exothermic peaks marking crystallization. Methods previously employed by Parks, Huffmann & Cattoir (1928) and Nelson & Newton (1941) to determine glass transition temperatures for dextrose and organic liquids have involved direct measurement of the specific heat of a particular sample at different temperatures. This is a lengthy process, but by using DTA it was hoped that the transition temperatures of a large number of glasses of different chemical composition could be compared. This work aims to apply thermal analysis to sucrose glasses as one route to examining the mechanism of crystallization of these materials and the way it is affected by compositional variation.

Materials and methods

Materials

Sucrose, dextrose, confectioner's syrup (42% DE) and water were used in this work. Their exact characterization and analysis is given in part I of this series.

Differential thermal analysis (DTA)

The apparatus was designed to allow for selection of suitable sample sizes and to obtain a distinctive differential temperature peak. The apparatus is shown in Fig. 1. The sugar glass sample and an inert reference substance were contained in thin walled glass tubes. The main difference between this apparatus and standard differential analysis apparatus is in the use of mercury as a 'sample block'; this was used because it gave good thermal contact between the sample block and the sample tubes no matter what diameter sample tubes were used. Instead of a furnace, a water bath was used to heat the sample as at no time during an analysis did the temperature exceed 80°C. The water, being thoroughly stirred, created a more homogeneous temperature than that obtained by heating in an oven where the position of the heating element would be critical due to complex heating gradients.

Two thermocouples were used for temperature measurement, one to measure the actual temperature of the glass sample and the second to register the differential temperature between the sample and the inert material. The thermocouples were made of copper/eureka and sheathed in teflon. The response from both thermocouple circuits were registered on a two pen recorder. The thermocouple that measured temperature had one junction in the glass sample and the other in melting ice; the thermocouple was calibrated against a platinum resistance thermometer. The response from the thermocouple registering the differential temperature was amplified before input to the recorder; at maximum sensitivity full scale deflection for the pen recorder corresponded to approximately 1.2°C.

The sugar glass sample was prepared in a tube in exactly the same way as for the kinetic measurements described in part I. It was removed from the tube and slid directly into the thin glass sample holder, which has been coated internally with silicone fluid. This fluid ensured that the sample did not stick to the side of the tube and also provided good thermal contact between tube and sample.

It was necessary to anneal the samples if pronounced peaks were to be obtained on the differential trace. This also ensured that the glasses were in the same form for

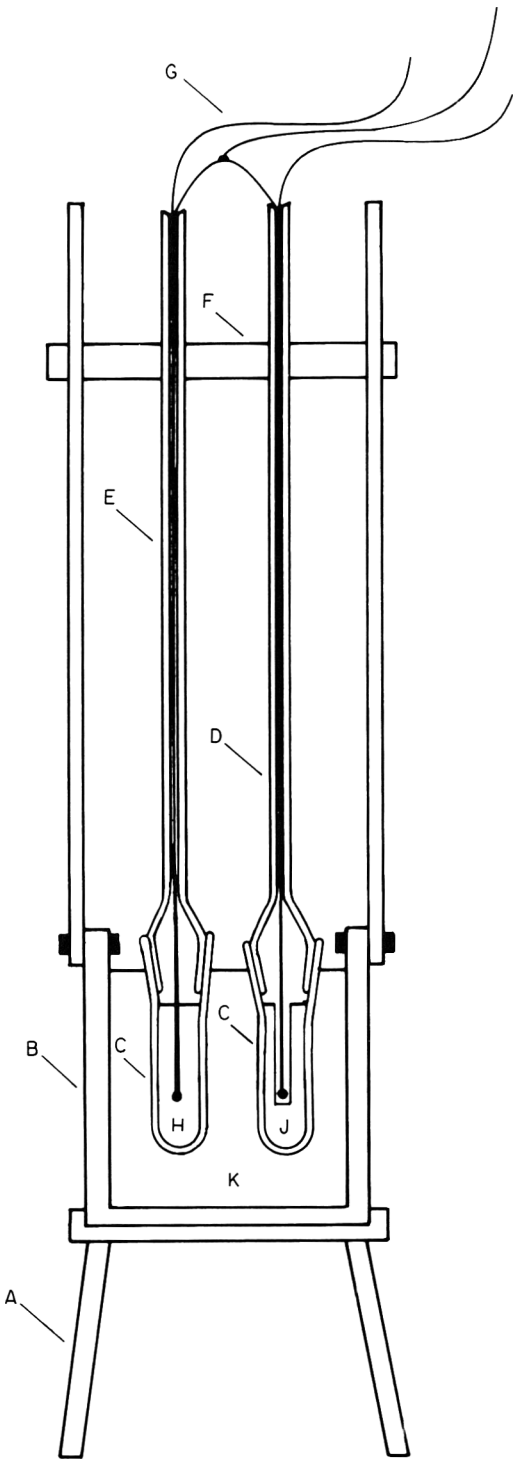

Figure 1. Differential thermal analysis apparatus. A, brass stand; B, stainless steel cup; C, thin walled glass sample holders; D, B5 quick fit joints; E, sample holder extension tubes; F, clamp; G, thermocouple leads (insulated); H, inert material; J, sugar glass sample; K, mercury.

comparative purposes. The sample was heated to a softening temperature in a glycerol bath and allowed to cool slowly to room temperature. The cooling time was of the order of 6 hr. A hole was prepared in the sample using a syringe needle when it became soft but not fluid and the thermocouple junction was inserted in the hole, after threading through the sample holder extension. As the sample flowed, so the thermocouple was effectively frozen into the glass. It was important to ensure that the thermocouple was mounted in the centre of the glass sample.

The inert material used for the second junction of the thermocouple was sodium chloride (100 mesh) with silicone releasing fluid added so that it just covered the surface of the sodium chloride. This fluid assured good thermal contact between the thermocouple junction and the inert materials and proved of sufficient consistency to hold the thermocouple junction in the centre of the tube. A differential thermal analysis between two reference junctions prepared this way showed no deviation from the steady state.

In order to obtain dynamic equilibrium during the heating process before the transition temperature region of the sample was reached, it was necessary to begin the thermal analysis at a temperature at least 15°C below the suspected transition temperature region. Accordingly, to allow this dynamic equilibrium to develop, the water bath was cooled to just above 0°C and the mercury cup cooled in ice before starting the analysis. The rapid cooling to 0°C did not affect the annealing of the majority of samples as they were below their glass transition temperature at room temperature. The few samples studied which had suspected transition temperatures near room temperature were kept in a cold environment after they had been slowly cooled to a low temperature during the annealing process.

A typical DTA trace showed a conical deflection from the baseline, the point of the cone or peak tip corresponding to the maximum differential temperature. This effect is produced by disturbance of equilibrium during a constant rate of heating due to changes in specific heat of the sample and is not related to endo- or exothermic effects as there is no enthalpy jump at a particular temperature. In order to decide whether the onset of the peak (T_I) or the peak tip (T_p) corresponded to the transition temperature, a study was made of the varying experimental conditions, such as heating rate, on the trace for anhydrous dextrose glass whose transition temperature had been obtained by other workers using different techniques (Parks *et al.*, 1928; Nelson & Newton, 1941; Parks & Thomas, 1934).

The T_I value was difficult to designate. It tended to occur between 12 and 15°C below T_p. It was found that T_p varied linearly with the heating rate. For anhydrous dextrose glass T_p was 4°C greater at a heating rate of 0.03 K/sec than the value of 37.5°C obtained by extrapolating to zero heating rate (Branfield, 1980). Parks & Thomas (1934) determined the specific heat of anhydrous dextrose glass using radiation calorimetry in which the sample was heated at 0.003 K/sec. They found a transition temperature in the range 28–38°C with a maximum in the specific heat at 34°C. A theoretical analysis (Branfield, 1980) shows that slow cooling followed by fast heating results in a maximum in C_p and this produces a peak in the DTA trace. The transition temperature depends on the thermal history of the sample. The Nernst method employed by Parks *et al.* (1928) and Nelson & Newton (1941) enabled the sample to be kept at the temperature of measurement for long periods. Parks *et al.* (1928) maintained samples at temperatures in the glass transition region for up to 48 hr and obtained low values for the transition range (2–14°C), which did not compare with the values they obtained by direct measurement of coefficients of expansion and refractive indices

(20–30°C). Nelson & Newton (1941) emphasized the importance of equilibration and kept the sample at the temperature of measurement for long periods, e.g. 5 days at 25°C; they found the glass transition temperature to be in the range 20–30°C. In our work a mixed sugar glass was studied to see if the variation of T_p with heating rate varied with composition; in all cases the variation was exactly the same as for dextrose glass. At very low heating rates the peaks in the DTA traces become indistinct and it was decided to standardize on a heating rate of 0.03 K/sec which gave reproducible results.

Results

A selection of sucrose glass systems were studied containing either dextrose or confectioner's glucose (42% DE). A typical trace is depicted in Fig. 2. This is reproduced directly from the recorder print out and shows the simultaneous measurement of differential and actual temperature against time. Because of the linear heating rates, the plots of differential temperature against actual temperature will be similar. In general the more pronounced peaks were obtained with samples containing dextrose instead of confectioner's glucose. The increased peak definition obtained by annealing the samples prior to analysis is demonstrated in Fig. 3.

As a result of the work on dextrose the results are presented in terms of the peak tip temperature (T_p) corresponding to a maximum differential temperature for a glass in the process of changing to a supercooled liquid when heated at a rate of 0.03 K/sec. Because the same heating rate is used throughout this provides a comparison between the glass forming temperatures of the systems studied. In Fig. 4 the temperature of the peak tip of the differential curve is plotted against water content for several samples composed of different proportions of sugar. Curve A is for sucrose glasses containing two different

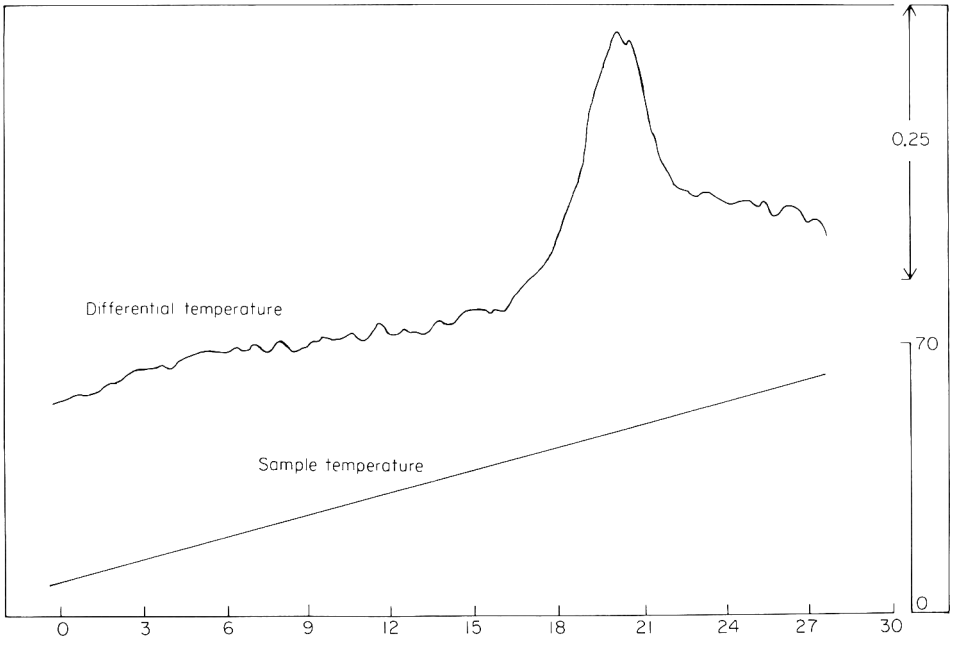

Figure 2. Typical thermal analysis trace. Glass composition: solids—86% sucrose, 14% dextrose; water 1.7%.

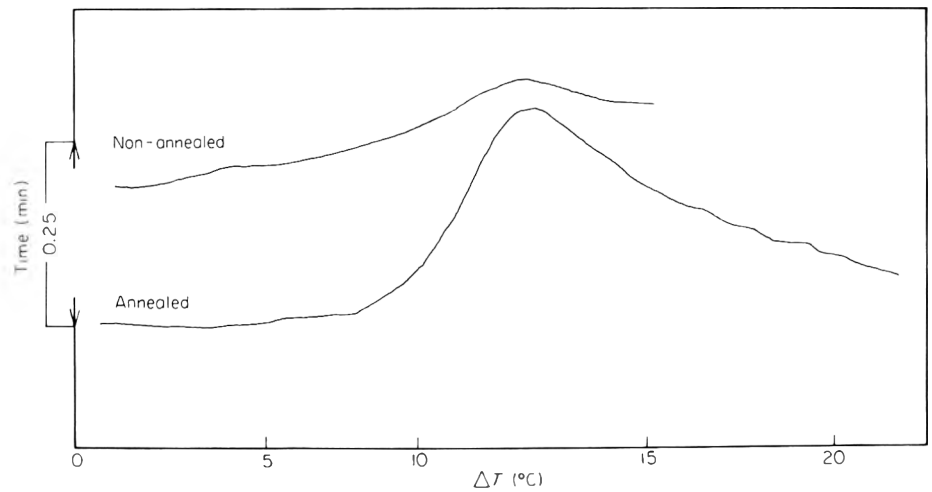

Figure 3. Differential thermal analysis of an annealed and a non-annealed sample.

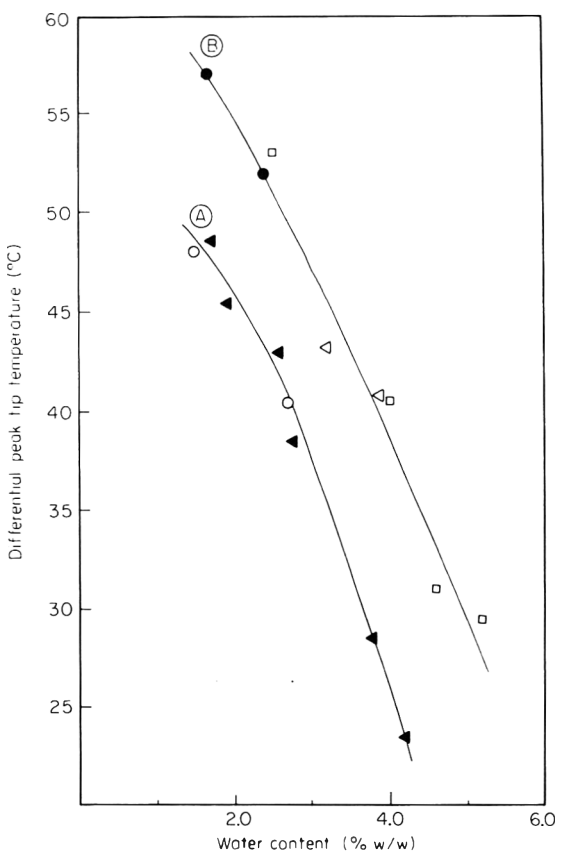

Figure 4. Temperature at differential peak tip against water content. Curve A: dextrose: ▲, 14% w/w (dry solids basis); O, 20% w/w (dry solids basis). Curve B: confectioner's glucose (42% DE), ●, 14% w/w (dry solids basis); △, 20% w/w (dry solids basis); □, 30% w/w (dry solids basis).

amounts of dextrose and curve B for sucrose glasses containing three different amounts of confectioners glucose.

Discussion

From the graph of T_p against water content (Fig. 4) it can be seen that, the higher the water content, the lower is the glass transition temperature. Also the samples prepared from confectioner's glucose have higher transition temperatures than the corresponding dextrose samples. In both the confectioner's glucose and the simple sugar samples, the reduction of transition temperature with increasing water content is very marked. What is most surprising is that the points for 14, 20 and 30% solids content of the (42% DE) confectioner's glucose all lie on the same curve within an experimental error of ±2%—i.e. the difference in glass transition temperature between samples containing 14 and 30% of this confectioner's glucose is negligible compared with that produced by a small change in water content. Thus it is the percentage of water present that is all important in determining T_p and *not* the ratio of glucose to sucrose either for confectioner's glucose or dextrose.

Shown in Fig. 5 are the measured 'threshold' water contents at 20°C for the different percentages of glucose solids for systems of the confectioner's glucose (42% DE). This demonstrates very clearly that variations in the proportions of confectioner's glucose have very little effect on T_p but have a large effect on the 'threshold' water content. In our crystallization measurements samples were held at particular temperatures for long periods thereby allowing lengthy times for 'equilibration' configurational changes to occur. The value of T_p measured in the differential thermal analysis will therefore be appreciably higher than the actual transition temperature range under the storage conditions. Comparison of our study of pure dextrose glass with the results of Nelson & Newton (1941), who took particular care over equilibration times, suggests that T_p-12 to T_p-22 represents the glass transition temperature range under normal storage conditions. If these adjustments are made then from Fig. 5 it can be seen that at 20°C, the 'threshold' water content samples for the 14 and 20% w/w confectioner's glucose systems would be in the glassy state, whereas the 30% w/w sample would be in its glass transition region which is then 17–27°C. However, the conclusion must remain that the 'threshold' values are determined by the amount of confectioner's glucose and the glass transition temperatures by the quantity of water present.

Our observations that the glass transition temperature is independent of the sucrose to dextrose ratio is in agreement with the work of McNulty & Flynn (1977). They studied aqueous sucrose glasses containing 35, 55, 70 and 100% w/w dextrose and 2.0–2.3% w/w water. Force–deformation tests revealed that the Young's modulus was independent of the amount of dextrose present. The Young's modulus decreased dramatically with temperature from 820 MN/m at 3°C to 30 MN/m at 30°C, and indicated a glass transition region between 22–28°C. The glass transition is not as abrupt as that found by Parks & Reagh (1937) for anhydrous dextrose glass. The sucrose+dextrose glasses studied by us in part I of this series contained a maximum of 30% w/w dextrose and no crystallization was observed at 20 or 30°C for less than 6% w/w of water. The DTA traces were determined for 14 and 20% w/w of dextrose with from 1.6% to 4.1% w/w of water. As can be seen from Fig. 4 at 2.0% w/w of water T_p is 46°C, so that as concluded above from comparison of our results with static specific heat data, T_g is given approximately by (T_p-20)°C.

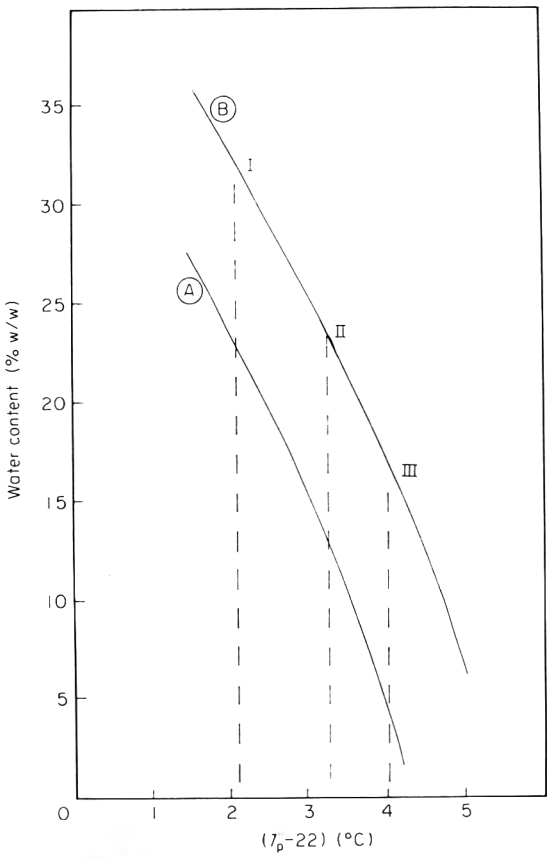

Figure 5. Variation of $(T_p - 22)$ with water content and comparison with 'threshold' water content at 20°C. $(T_p - 22)$ represents the temperature at which glass begins to change into supercooled liquid. A, sucrose glass containing dextrose; B, sucrose glass containing confectioner's glucose (42% DE). Threshold water contents at 20°C for I: 14% w/w, II. 10% w/w, and III: 30% w/w confectioner's glucose (dry solids).

McNulty & Flynn (1979) studied the stress relaxation behaviour of a sucrose glass containing 35% w/w of dextrose and 2.0–2.3% w/w of water. The system exhibited linear visco elastic behaviour enabling a glass transition temperature of 23°C to be calculated, consistent with their force–deformation studies. Analysis of their data gave a temperature variation of viscosity from 10^{12} to 1.2×10^{13} Pa s at 3°C to 5×10^{7} to 2×10^{8} Pa s at 25°C. Thus the viscosity at the glass transition is much lower than the 10^{13} Pa s often taken to define the glass transition temperature (Jones, 1971). If the viscosity measurements on soda-lime silica glass (Jones, 1971) are applicable to the lithium aluminium silicate glasses of Clinton, Mercer & Miller (1970), then at T_g the viscosity is 10^{13} Pa s but at the crystallization temperature the viscosity has dropped to 10^{7} Pa s. This implies that a viscosity of 10^{7} Pa s in these dextrose glasses would be low enough to allow rapid nucleation and crystal growth.

Conclusion

The rate of progress of the nucleation front of sugar glasses tends towards a constant value at high water contents. Increasing the quantity of glucose syrup decreases the

rate. At higher water contents pure dextrose inhibits the rate to a greater degree than the glucose syrup. Samples containing D-fructose have a lower rate than samples containing dextrose.

Sugar glasses containing confectioner's glucose exhibit a 'threshold' value of the water content below which crystallization does not occur. The lower the dextrose equivalent of the syrup, the higher the 'threshold' value for the same quality of glucose solids. 'Threshold' values decrease slightly with decreasing temperature. Samples prepared using pure dextrose do not show a 'threshold' value in the range of water contents investigated (lowest 1.5% w/w) but instead show a 'step' value.

The results obtained with fructose in this work suggest a more thorough investigation of sucrose glasses containing fructose, with or without confectioner's glucose, would be useful. Certainly a study of the rehology of these mixed sugar glasses and of their supersaturated solutions would be valuable.

Nucleation theory applied to our results suggests that the Gibbs function of activation for diffusion per molecule of sucrose plays the dominating role in crystallization at high water contents.

The glass transition temperature is determined by the percentage of water present and *not* the ratio of glucose to sucrose either from the glasses containing confectioner's glucose or dextrose.

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Heat processing of herring. I. Release of water and oil

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Summary

The release of water and oil, and changes in weight, during the heating and pressing of herring muscle have been studied, in the temperature range 35–112°C and for heating periods up to 60 min. Temperature had a significant effect on the changes, but heating periods up to 60 min did not. Water loss during cooking showed a maximum at 45°C, a minimum at 60°C, followed by a continuing rise to 112°C. There was an inverse relationship between the water loss during cooking and that during pressing, over most of the temperature range. Weight changes paralleled the changes in water content. Losses of oil were small, but varied with the initial oil content of the fish. Comparison is made with earlier work, and the technological implications are considered.

Introduction

Most fish receives some form of heat treatment before consumption, either by domestic cooking or in commercial processes such as drying, hot smoking, canning and fish meal manufacture. Nevertheless, cooking or, more generally, heat processing of fish has received relatively little scientific study. Cooking is not a simple process; many different physical and chemical changes occur simultaneously and successively when fish tissue is heated (Aitken & Connell, 1979). Perhaps the most important of these effects for the fish processing industry is the release of water and, in the case of oily fish, of oil. On a worldwide basis, most fish meal is made from oily species by successive cooking and pressing, before final drying. The efficient liberation of water and oil by cooking and pressing is important for a successful process. Again, precooking and draining of fish before canning is generally adopted, in order to reduce the water content and prevent an undue amount of liquor being cooked out of the fish in the can during sterilization.

The most comprehensive study of cooking losses remains that by McCance & Shipp (1933). They measured total weight loss, which in many foods is largely water loss, but did not undertake a systematic study of the factors affecting such loss. Ward, Wignall & Windsor (1977), studying the release of water and oil from fish during heating and pressing, showed that the release of liquor increased with temperature and that relatively low pressure was required to free most of the liquor.

A number of more limited studies of weight loss (or water loss) in fish are available (e.g. Tarr, 1941; Kushtalov & Saduakasov, 1971; Tulsner & Wagenknecht, 1976), while numerous papers have appeared on the effects of heat on separated components of fish muscle. Further references are to be found in Aitken & Connell (1979) and in Beraquet

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(1980). Work on meat is exemplified by the now classical contribution of Hamm & Deatherage (1960).

The work described in the present paper is a more detailed study than hitherto of the effects of heating temperature and time, and subsequent pressing, on the water and oil content of herring muscle. While it would have been simpler to study initially the behaviour of a species of low oil content, most commercial fish canning and fish meal processes are based on species of moderate or high oil content.

Materials and methods

Raw material

Herring (*Clupea harengus*) was chosen as the raw material for this work; more is known about the composition of this species than of other oily species, and, until recent limitations on catching as a result of overfishing, herring was the basis of the European fish meal industry and the most popular canned species in Europe.

The oil content of herring varies seasonally, and in order to study fish of differing oil contents two batches of fish were obtained, each from a single catch, one of fairly low average oil content (LF or 'low fat' fish) and one of moderately high oil content (HF or 'high fat' fish). It is impossible to measure oil content at all accurately in the whole herring and catches of fish are never of uniform oil content. Consequently, while the two batches were quite distinct, there were unavoidable variations in oil content within each batch. The two batches were frozen, glazed, stored at −30°C and thawed when required.

The oil content of herring varies not only between fish but also within each fish (Brandes & Dietrich, 1953). The influence of this variation on the measurement of oil and water release could have been minimized by mincing and mixing the fish to ensure a uniform oil content, either within a small group of measurements, or even, by mixing the entire batch, over all measurements. This simplification was rejected in favour of studying the heating of intact muscle as it was felt that the release of oil and water would be different in the intact tissue from that in minced tissue. Fish tissue remains intact during the canning process, during smoking, and, to a large extent, during cooking for fish meal. The effect of the unavoidable variability in oil content was minimized by the procedure described below.

Heating procedure

Six fish (either LF or HF) were thawed for each temperature/time combination. Single fillets were cut and skinned. Six fillets, one from each fish, were carefully trimmed to remove the belly flap which is particularly high in oil; the head and tail ends of the fillet were removed to give a roughly rectangular portion about 10 cm long and no more than 1 cm thick. Thermocouples made from 32 s.w.g. wire were inserted along the length of three of the portions, so that the junction was, as nearly as possible, in the centre of the portion. The portions were vacuum sealed in separate weighed polyamide bags which were reweighed. The thermocouples were brought through the bags by sealing them first with Araldite through short lengths of fine stainless steel tube, the latter passing through standard miniature thermocouple glands. For temperatures above 85°C, the bags containing the herring portions were put separately into cans filled with vegetable oil, which were vacuum seamed. The thermocouples were sealed through both the can and the bag.

The six bags, or cans, containing the six portions were distributed on a rack

immersed in a temperature controlled bath, filled with water for temperatures below 90°C, or with mineral oil for higher temperatures. The three thermocouple temperatures were read at 30 sec intervals with an electronic thermometer reading to 0.1°C. When three consecutive 30 sec readings in the slowest thermocouple were identical, the fish were judged to be at the desired temperature, and the duration of heating was measured from that point. After being heated for either 0, 15, 30 or 60 min the six bags were removed, dried and allowed to cool for 15 min, held vertically. The bottom of each bag was then punctured to allow the cook liquor to run off. After 45 min draining, the bags were reweighed.

The bags were cut open and a 25 mm diameter cork borer was used to cut two cylindrical pieces, one near the head end and one near the tail end of each portion. Two 'head' pieces and one 'tail' piece were combined to give one sample for analysis (after thorough mixing) the corresponding two 'tail' pieces and one 'head' piece being combined to give a second sample. The remaining six pieces were submitted to the pressing stage as described below.

From the six unheated fillets, from the original six fish, twelve pieces were taken by cork borer from the same 'head' and 'tail' positions; they were minced and mixed and two samples taken for analysis.

Pressing

Pressing was carried out in a stainless steel press of 25 mm diameter, the filter element consisting of four layers of polyamide mesh of 20 μm aperture supported on a perforated brass screen. The six pieces from each temperature/time combination were weighed individually, pressed for 3 min at 3×10^7 N/m^2 and reweighed. The six pieces were then combined in the same way as the heated pieces to give two pressed samples for analysis.

Analysis

Each sample, whether uncooked, cooked, or cooked and pressed, was dried at 105°C in air for 24 hr to determine moisture; the dried samples were extracted with diethyl ether in a Soxhlet apparatus for 6 hr, the extracts being freed of solvent and weighed to determine oil content. The analytical results from the two samples taken at each stage were averaged. From these analyses and the weights of the original and treated portions, the changes in weight, in moisture content and in oil content can be derived.

Results and discussion

Raw material

The average oil and moisture contents of the 'low fat' (LF) batch were 6 and 74%, and of the 'high fat' (HF) batch 16 and 65%, respectively.

Release of water

The amounts of water freed by heating alone in HF muscle are given in Table 1 as a function of heating temperature and duration of heating. The variance ratios derived by analysis of variance show that temperature had a highly significant effect on water loss, whereas duration of heating, up to 1 hr, had no significant effect. Exactly the same conclusion was reached for the heating loss from LF fish, for the pressing losses from both batches of fish and for the combined heating and pressing losses of both. The remaining data are not tabulated here; Table 1 is given only as an example.

Table 1. Influence of temperature and duration of heating on release of water by HF muscle as % of original water content

	Loss of water (%)				
Temperature (°C)	Duration of heating (min) 0	15	30	60	Mean
36.2	10.42	13.88	17.16	13.60	13.76
41.1	17.27	16.52	16.94	19.11	17.46
44.5	14.57	18.03	18.80	23.27	18.66
50.4	15.13	12.93	12.04	17.02	14.28
55.1	13.24	10.96	10.76	12.76	11.93
59.7	10.94	10.06	11.35	10.77	10.78
65.6	10.27	14.08	13.51	15.48	13.33
75.0	13.95	17.63	17.67	14.82	16.01
83.7	22.93	21.58	22.38	20.60	21.87
101.0	23.53	22.46	23.73	23.58	23.32
112.0	27.25	26.70	28.33	28.40	27.67

Factor	Variance ratio	Degrees of freedom	Significance level
Temperature	34.36	10, 30	0.001
Duration	2.15	3, 30	ns

The very rapid attainment of apparent equilibrium is in contrast to the slow continued loss of liquor by meat, observed by Hamm & Deatherage (1960), and similar effects in fish noted by McCance & Shipp (1933). Except at the highest temperatures, the time to reach thermal equilibrium in the present experiments (taken as zero time) was short, only a few minutes, because of the thinness of the portions used and the good thermal contact resulting from vacuum sealing. Indications of slow release of liquor in other work arise probably from slow attainment of thermal equilibrium, and other differences in the nature of their specimens and the technique used. The present work shows clearly that, in intact fish tissue, the reactions leading to release of liquor are rapid and are essentially complete by the time the fish reaches the desired temperature. (This does not, of course, imply that other reactions occurring during cooking—e.g. development of flavour or destruction of microorganisms—are equally rapid.)

The amounts of water liberated by cooking, by pressing, and by both are shown in Figs 1 and 2, for the LF and HF batches, respectively. The values are the averages over the four heating periods. It will be noted that the total losses of water, by cooking and pressing, calculated as percentages of the original weight of the fish are quite similar for the LF and HF batches.

As will be seen from Figs 1 and 2, the amount of water freed by cooking and draining, without pressing, was higher at the fixed heating temperature of about 45°C than at lower temperatures, lower again at about 60°C, then higher at successively higher temperatures up to the highest temperature reached. Over most of the temperature range, the water released by pressing was inversely related to the loss after cooking. The total loss, by cooking and pressing, increased rapidly to about 50°C, followed by a slower steady increase.

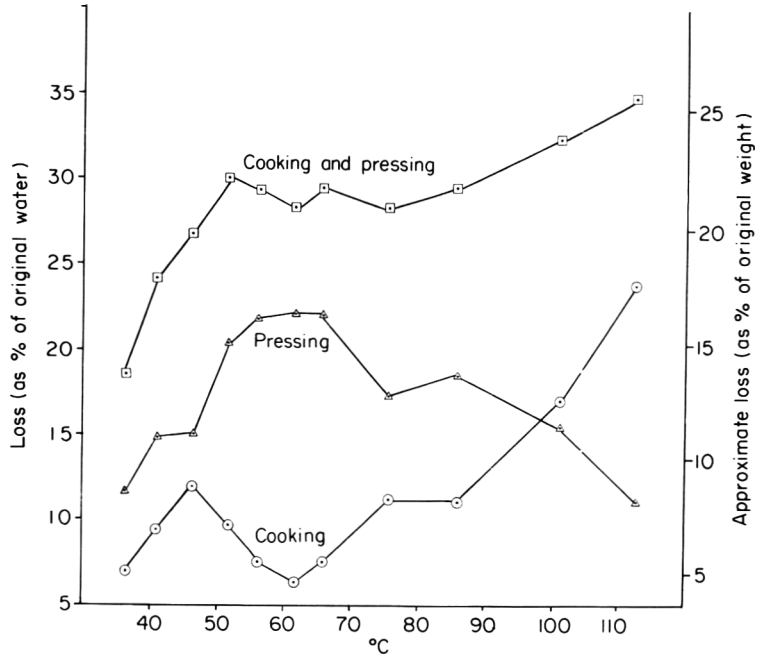

Figure 1. Loss of water from LF fish by cooking, by pressing and by both, at various fixed temperatures, expressed as % of original water and as *approximate* % of original weight. (Points are joined by straight lines to aid identification only.)

The inverse relationship between the amounts of water liberated by cooking and by pressing would appear to indicate that a certain amount of water becomes free at a particular temperature, the total loss shown in Figs 1 and 2; some of this water is able to flow out without pressure, while some is held in such a way as to require pressure for its

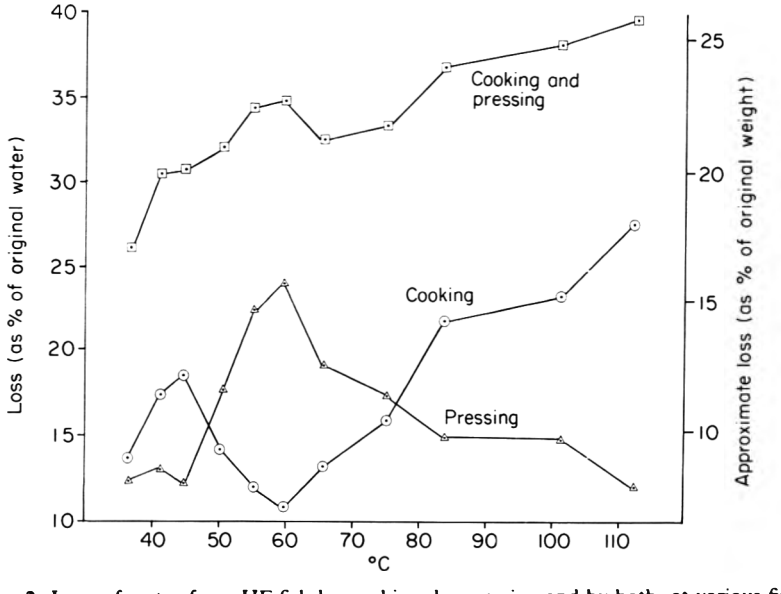

Figure 2. Loss of water from HF fish by cooking, by pressing and by both, at various fixed temperatures, expressed as % of original water and as *approximate* % of original weight. (Points are joined by straight lines to aid identification only.)

liberation. The amount requiring pressure for its liberation increases from about 45°C to about 60°C, then falls again. Kushtalov & Saduakasov (1971), who observed a similar effect in freshwater catfish, ascribed it to the reabsorption of water by collagen as it is converted to gelatin. Tulsner & Wagenknecht (1976) also detected a minimum in water holding at about 62°C in cod.

Comparison of Figs 1 and 2 shows that the HF fish lost a substantially higher proportion of their water than the LF fish during cooking, while during pressing the losses were similar for the two batches. Since the HF fish had a lower initial water content, one might expect them to lose less water than LF fish rather than more. As will be seen, the HF fish also lost considerably more oil than LF fish.

Release of oil

The losses of oil by cooking and pressing show a considerable degree of variability and so the results are given in tabulated rather than graphical form, in Table 2 for LF and in Table 3 for HF fish. Analysis of variance showed that, as for water release, time of heating after reaching bath temperature had no significant effect; the mean values for the four heating periods are given in the tables. (The negative values for oil loss in Table 2, implying a gain in oil content, arise from a relatively high variability in oil content between and within the paired fillets in this particular trial.)

Table 2. Influence of temperature on losses of oil during cooking and pressing of LF muscle in relation to original oil content

	Percentage losses*		
Temperature (°C)	Cooking	Pressing	Total
36.1	0.41	11.87	12.28
40.6	3.18	−4.88	−1.62
46.2	7.94	15.34	23.28
51.5	7.50	11.60	19.11
56.1	6.69	26.55	33.24
61.5	5.53	26.55	32.09
65.8	28.48	13.49	41.98
75.6	4.12	31.10	35.22
85.8	7.96	10.46	18.42
101.4	13.87	22.27	36.15
112.7	21.32	16.38	37.70

*Averaged over the 4 times studied.

Table 3. Influence of temperature on losses of oil during cooking and pressing of HF muscle in relation to original oil content

	Percentage losses*		
Temperature (°C)	Cooking	Pressing	Total
36.2	4.51	4.15	8.66
41.1	8.77	5.24	14.02
44.5	12.15	19.07	31.54
50.4	21.82	18.57	40.39
55.1	21.05	24.09	45.14
59.7	17.01	32.26	49.27
65.6	16.17	21.87	38.04
75.0	11.66	28.14	38.21
83.7	16.87	25.23	42.11
101.0	17.76	18.77	36.53
112.0	23.34	28.87	52.21

*Averaged over the 4 times studied.

Whereas in the case of water release there appeared, over most of the temperature range, to be a reciprocal relationship between the loss by heating and the loss by pressing, the two components of oil loss are generally parallel, the pressing loss being on average higher than the cooking loss. Again in contrast to the water loss behaviour, the HF fish lost more oil than the LF fish in relation to the original oil content, and also in proportion to the original weight of the fish. Since the location and mode of binding of the water and oil phases in herring are quite different, the water being largely associated with the proteins while the oil is mainly in discrete oil cells, one should not be surprised at the different behaviour of the two components. The loss of oil is generally simpler to explain. The losses of oil by the LF fish are rather variable for the reason already

mentioned; the oil loss by the HF fish increases with temperature, both in heating and in pressing, to about 50°C, then alters little above this temperature. Mohr (1979) showed that oil cell walls break down increasingly at temperatures up to 50°C. Some oil is expressed by the shrinkage of the tissue during heating, while the remainder of the available oil is freed by pressing. Although the cell walls are broken down at 50°C, a substantial proportion of the oil is not liberated by heating and pressing even at the highest temperatures.

Weight losses

From the losses of weight, and the water and oil changes already discussed, it is possible to estimate loss of solids, by difference. The total weight losses, partitioned into water, oil and solids losses are shown in Figs 3 and 4, for LF and HF fish. In these figures the sets of bars are centred on the temperatures of each trial (which are given in Tables 2 and 3).

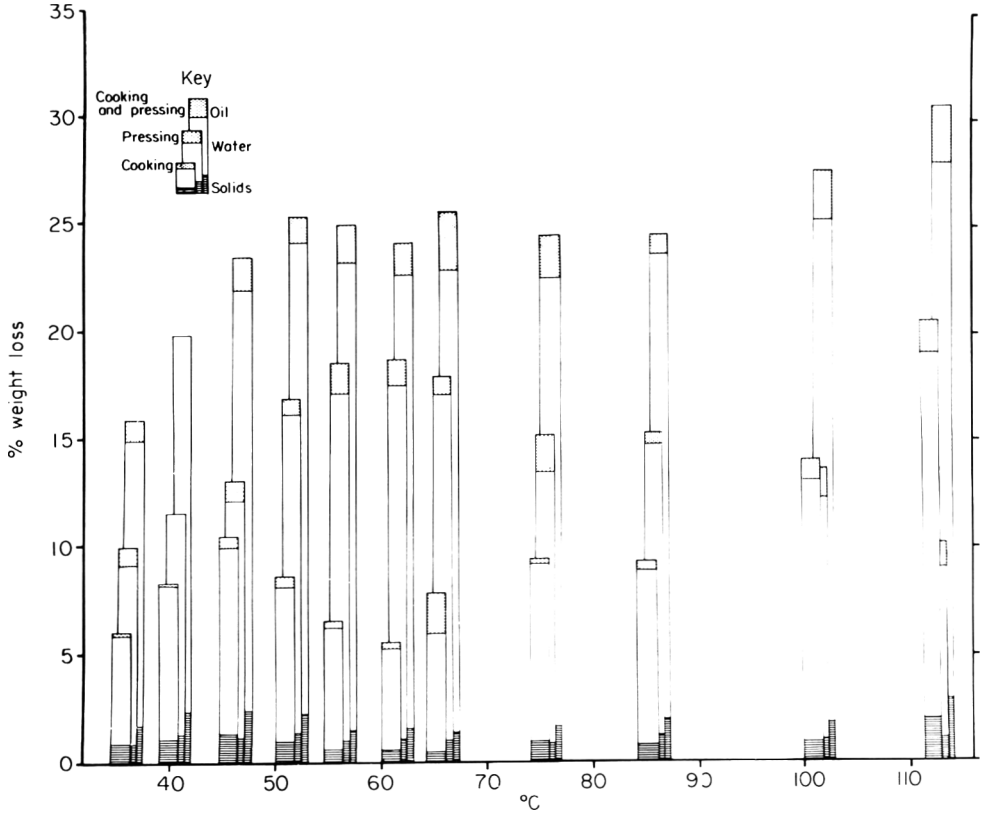

Figure 3. Total weight losses from LF fish partitioned into oil, water and solids. (The zero oil loss on pressing, and pressing plus cooking, at 40.6°C arises from the apparent gain of oil in Table 2, discussed earlier.)

Since much of the weight loss is due to water release, there is an inverse relation between the cooking and pressing weight losses. The total weight losses for HF fish are greater than for LF fish, the difference being partly accounted for by higher oil losses. Solids losses by the two batches did not differ significantly; losses were small and not obviously related to temperature. Much of the higher weight loss from the HF fish arose

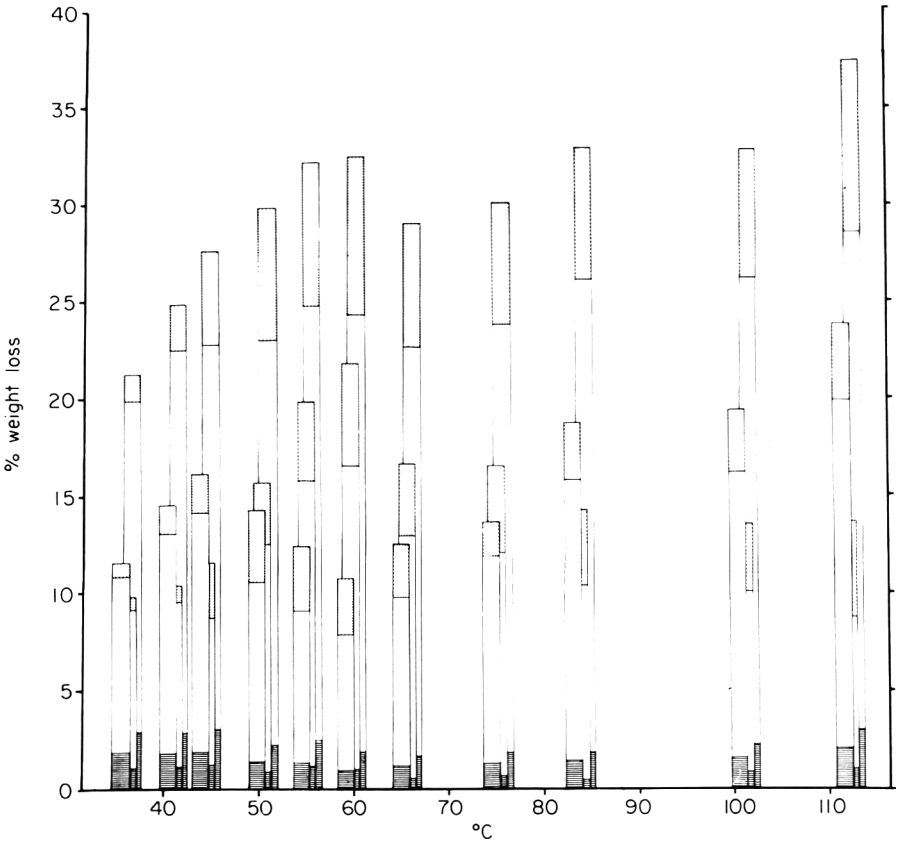

Figure 4. Total weight losses from HF fish partitioned into oil, water and solids.

during the heating period; weight losses by pressing were more similar for the two batches.

Since little or no evaporation occurred during heating and pressing, the left hand and middle bars in Figs 3 and 4 represent the amounts of the liquors released by cooking and pressing and their make-up in terms of water, oil and solids. Overall, the make-up of the cook and press liquors is the same. There is no consistent temperature effect on liquor make-up, apart from a relatively low proportion of oil in the liquors from HF fish at the two lowest temperatures. The mean solids contents of the combined cooking and pressing liquor are 9.7 and 8.1% for the LF and HF batches, respectively.

Comparison with other work

Because of the varied raw materials used, and the widely differing heating and pressing treatments applied to the fish, it is difficult to compare the present work with previous work by others. Most earlier work has reported weight losses; only Ward *et al.* (1977) measured water, oil and solids losses separately. These authors heated whole sprats, a species similar to herring, to mean temperatures of 60, 80 and 100°C, with continuous agitation. Temperature equilibrium was attained only at 100°C and comparison with our results will be confined to this temperature.

In Fig. 5, the water, oil and solids contents of the original fish are shown for both studies together with the amounts and composition of the total heating and pressing

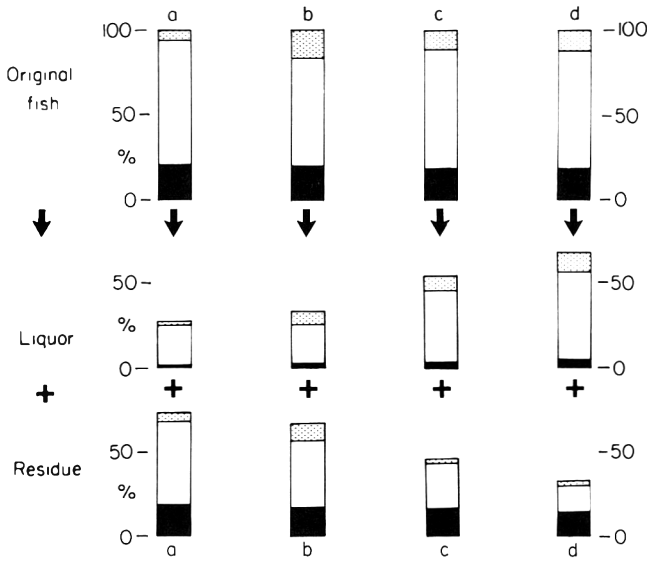

Figure 5. Comparison of effects of cooking and pressing in (a) LF herring at 101.4°C, (b) HF herring at 101.0°C, (c) sprats at 100°C (Ward *et al.*, 1977), and (d) oily fish meal process with steam heating (Windsor, 1971). (Partitioned from top into oil, water and solids.)

liquor, and of the pressed residue. Figures from Windsor (1971), for a typical fish meal process from oily fish, are included; although steam heating was used in this process it cannot be assumed that all the fish had reached 100°C. Not all the quantities in Fig. 5 were measured directly; the remainder were obtained by sum or difference from measured quantities. The biggest contrast between the two experimental studies is the much higher liquor loss from the sprats, 54.0% of the original weight, compared with 27.6 and 32.8% from LF and HF herring, respectively. The loss by sprats was higher than that by herring both during cooking and during pressing. The sprats were pressed at 10^7 N/m^2, a rather lower pressure than in the present work. In the commercial fish meal process, total losses by cooking and pressing are as high as 68%. A corresponding higher release of oil was achieved from the sprats by Ward *et al.* (1977), 80%, compared with an average of just over 40% of the original oil content by herring; in the commercial fish meal process, 92% of the oil is expressed. It is clear that a close relationship exists between the release of oil and water, and the loss of solids in the cooking and pressing liquor. An economic fish meal process aims to obtain maximum oil and water separation with minimum loss of solids. Neither the present work nor that of Ward *et al.* (1977) gives any clear indication of how this aim can be better achieved.

Weight losses by cooking alone, without pressing, have been more extensively reported. Thus, cooking losses by oily species, reported by McCance & Shipp (1933) averged 21% while other workers have noted losses up to 27%. Our mean weight loss of 16.6% for the two batches of fish is consistent with these earlier results.

Conclusions

The maximum release of water by cooking alone, occurring at about 45°C, and the inverse relation over most of the temperature range between water losses in cooking and pressing, are important to an understanding of the mechanism of water release by the

action of heat. Neither the present work nor any previous work has produced definite explanations of these two features. The possible role of the hydration of collagen, mentioned earlier, requires further investigation. It should also be pointed out that the literature on the effects of heat on separated components of muscle indicates that most changes in the protein fractions of muscle take place in the 40–60°C region.

The total loss of liquor is not significantly different at fixed temperatures of heating between about 50 and 85°C, nor does it increase with increased heating time. The implications for the fish meal industry are that lower controlled temperatures may be as efficient in expressing liquor as the higher temperatures used at present, with possible saving of energy and improved oil quality. Similarly in the precooking of herring for canning, the maximum weight loss by cooking at 45°C would suggest that a temperature lower than that applied at present might give the desired effect of reducing the water content before sterilization.

Acknowledgment

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Degradation of sorbic acid in fruit squashes and fish paste

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Summary

Degradation of sorbic acid (SA) in fruit squashes and fish paste has been found to be influenced by the nature of the food material and the packaging system. Losses in SA ranged from 60–90% in polypropylene and 41–65% in saran coated cellopoly pouches to 22–30% in paper—aluminium foil—polyethylene laminate pouches and glass bottles after 150–210 days at 37°C. The rate of degradation was significantly higher in fish paste than in fruit squashes.

The major portion of the added SO_2 in fruit squashes was lost during the initial stages of storage and the residual SO_2 (< 100 ppm) did not significantly influence the rate of degradation of SA. Browning intensity in fruit squashes and fish paste was also related to the oxygen permeability of the packaging materials. Addition of 0.1% SA did not significantly influence the rate of browning but at 0.2%, a slight increase in the rate was observed.

Introduction

Sorbic acid is permitted in many countries as an antimocrobial food additive and it is widely used in cheese, bakery products, fruit juices, wines and carbonated beverages. Whilst the literature on its physiological safety in foods is well documented, reports on stability during storage and processing and its effect on the sensory qualities of the product are at variance.

Arya (1980) reported that in aqueous solution, SA undergoes autoxidative degradation to form carbonyls. Degradation of SA followed a first order reaction kinetics and the rate of reaction decreased with rise in pH. The rate of reaction was also influenced by trace metal ions, sugar, salts, amino acids and antioxidants. Hildegard, Marx & Sabalitschka (1965) also reported that aqueous solution of SA stored in stoppered flasks underwent decomposition forming acrolein, crotonaldehyde and malonaldehyde. At room temperature about 90% of the SA was decomposed in 1 year and the rate of decomposition was accelerated by light but inhibited by propyl gallate. Steinbach & Franzke (1962) have reported that incorporation of SA in butter enhanced the rate of autoxidation. Bolin, King & Stafford (1980) have observed that losses of SA during storage of raisins were related to storage temperature and moisture content. Heintze (1971) has, however, reported that losses in SA were appreciable in fish sausage but insignificant in fruit juices. Losses in SA have also been reported during processing of mango beverage (Hamed, 1966). Anand, Soumitri & Johar (1958) reported that mango squash preserved with SA underwent intense browning during storage in glass bottles whereas Weaver, Robinson & Hills (1957) found that the storage life of fresh apple

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juice was greatly enhanced by incorporation of sodium sorbate in addition to heat treatment. Incorporation of SA in wines has been reported to result in off-odours during storage (Amerine, Berg & Cruess, 1967).

Besides the nature of food ingredients, packaging plays an important role on the rates of autoxidative degradations during storage. But surprisingly, in none of the previous studies has effect of packaging materials on the storage losses in SA been reported. In the present study the effect of various packaging materials on the stability of SA in fruit squashes and fish paste has been investigated.

Materials and methods

Mango squash

Ripe Badami (Alphonso) mangoes (*Mangifera indica*) were obtained from a local market. After washing and peeling, the flesh was separated from the stones using stainless steel knives and passed through a 2 mm mesh sieve in a stainless steel pulper. The squash was prepared from the pulp by mixing 3 kg of pulp, 2.4 l of water, 4 kg cane sugar and 1 g citric acid. The freshly prepared squash on analysis gave Brix 40°, pH 2.9 and total acidity 0.93%. The squash was pasteurized in a stainless steel vessel at 80°C for 10 min. Pasteurized squash was divided into four lots and each lot was separately treated with (i) 0.061% potassium metabisulphite (350 ppm SO_2), (ii) 0.268% potassium sorbate (0.2% SA), (iii) 0.134% potassium sorbate (0.1% SA), and (iv) 0.134% potassium sorbate (0.1% SA)+0.0175% potassium metabisulphite (100 ppm SO_2). The treated samples (50 ml) were packed in polypropylene (75 μm), saran coated cellopoly (75 μm) and paper (60 g/m^2) aluminium foil (40 μm) polyethylene (40 μm) laminate pouches (10×10 cm) and glass bottles (15 ml head space) and stored in the dark in an incubator maintained at 37±1°C.

Mosambi juice

Good quality mosambies (*Citrus sinesis*) obtained from a local market were thoroughly washed and hand peeled. The juice was extracted in a laboratory model stainless steel screw type juice extractor. Freshly extracted juice had Brix 9°, pH 4.5 and total acidity 0.54%; 8.5 kg of this juice was treated with 1.1 kg sugar and 39 g citric acid to obtain Brix 20°, pH 3.8 and total acidity 0.93%. The treated juice was pasteurized by heating in a steel vessel at 80°C for 10 min and divided into three lots. Each lot was treated respectively with (i) 0.134% potassium sorbate (0.1% SA), (ii) 0.067% potassium sorbate (0.05% SA), and (iii) 0.071% potassium benzoate (0.06% benzoic acid). The treated samples (50 ml) were stored in polypropylene, saran coated cellopoly and aluminium foil laminate pouches and glass bottles (15 ml head space) at 37±1°C as described for mango squash.

Fish paste

Ten kg of best quality Rahu fish (*L. Rohit* Ham) purchased from a local market were washed under running tap water, cleaned and cut into small pieces which were cooked in a pressure cooker at 15 lb pressure. The cooked fish was freed from bones and homogenized to obtain a paste (7.5 kg) which was divided into two equal lots with the pH adjusted to 3.5 and 4.2, respectively by the addition of lactic acid. Both lots were further treated with 0.268% potassium sorbate (0.2% SA) and 200 g samples were stored in sealed pouches of polypropylene and aluminium foil laminate pouches and glass bottles (15 ml head space) at 37±1°C.

Analysis

Sorbic acid (SA) was determined spectrophotometrically by the method of Alderton & Lewis (1958) with slight modifications. Samples containing 1–2 mg SA were treated with 50 ml of 1 N H_2SO_4 and 50 g magnesium sulphate and steam distilled in an all-glass steam distillation apparatus. About 350 ml of the distillates were collected, the pH of the distillate was adjusted to 4.7 and the volume made up to 500 ml. Absorbance was measured in a Perkin–Elmer UV spectrophotometer at 256 nm and the concentration of SA was calculated using $E^{1\%}_{256}$ of 2150. The values are the averages of two replicates and maximum variation did not exceed ±0.005.

Sulphur dioxide and total acidity were determined by the appropriate AOAC (1970) procedure. Brix readings were measured by using a hand refractometer at room temperature and browning intensity was measured by the procedure described by Mannheim & Havkin (1981). The TBA values of the fish paste were determined by the steam distillation procedure of Tarladgis *et al.* (1960) and total carotenoids were determined by the method described by Arya *et al.* (1979).

Microbiological analysis

Total aerobic count, total anaerobic count and yeast and mould counts in fresh and stored fish paste samples were measured as per APHA (1958). Total aerobic count was measured by the pour plate method using dextrose-tryptone agar medium. Plates were incubated at 37°C for 48 hr and counts recorded. Yeast and mould counts were determined on potato dextrose agar after incubation at 30°C for 96 hr.

Sensory evaluation

Acceptability of the fruit squashes was judged by a panel of ten judges on a nine point hedonic scale. During evaluation, samples were presented in 25 ml clear glass beakers under day light/fluorescent tube light. First, the undiluted samples were graded for colour and smell. Subsequently, the samples were diluted 3 times with water and graded for taste and aroma and overall acceptability. In all these tests, squash samples stored in glass bottles at −10°C served as control and samples receiving scores above 7 were rated as acceptable.

Results and discussion

The changes in the concentration of SA in mango squash and mosambi juice during storage at 37°C are shown in Tables 1 and 2, respectively, indicating that storage losses are mainly dependent on the type of packaging material. The losses were very high in samples stored in polypropylene and saran coated cellopoly pouches but only slight in laminate pouches and glass bottles. After 210 days, losses ranged from 85 to 90% in the mango squash samples stored in polypropylene and 63 to 65% in saran coated cellopoly pouches compared to 24.5 to 33% in laminate pouch and glass bottle samples. In Mosambi juice, the losses ranged from 64 to 67% in polypropylene, 41% in saran coated cellopoly, 22 to 31% in laminate and 28 to 31% in glass bottles after 150 days storage. In fish paste, losses in SA during storage were very high (60–80%) in polypropylene pouches compared to glass bottles and laminate pouches (10–30%) after 90 days storage at 37°C (Table 3). In particular, the rate of degradation of SA in fish paste in samples stored in polypropylene pouch was considerably higher than those mango squash or mosambi juice. This clearly shows that both packaging material and the nature of the food product influence the rate of degradation of SA during storage. This

Table 1. Changes in the concentration of sorbic acid in mango squash during storage at 37°C

Storage period (days)	Concentration of sorbic acid (%)											
	Paper—aluminium foil—polyethylene laminate			Saran coated cellopoly			Polypropylene			Glass bottles		
	(ii)	(iii)	(iv)	(ii)	(iii)	(iv)	(ii)	(iii)	(iv)	(ii)	(iii)	(iv)
0	0.200	0.100	0.100	0.200	0.100	0.100	0.200	0.100	0.100	0.200	0.100	0.100
30	0.190	0.095	0.090	0.182	0.085	0.081	0.176	0.081	0.076	0.190	0.095	0.089
90	0.178	0.087	0.079	0.144	0.057	0.054	0.105	0.040	0.037	0.162	0.082	0.081
	(11.0)	(13.0)	(21.0)	(28.0)	(43.0)	(46.0)	(47.5)	(60.0)	(63.0)	(19.0)	(18.0)	(19.0)
160	0.167	0.075	0.076	0.099	0.042	0.039	0.042	0.024	0.022	0.156	0.073	0.078
	(16.5)	(25.0)	(24.0)	(50.5)	(58.0)	(61.0)	(79.0)	(76.0)	(78.0)	(22.0)	(27.0)	(22.0)
210	0.151	0.070	0.069	0.071	0.037	0.037	0.020	0.015	0.014	0.151	0.067	0.070
	(24.5)	(30.0)	(31.0)	(64.5)	(63.0)	(63.0)	(90.0)	(85.0)	(86.0)	(24.5)	(33.0)	(30.0)

Figures in parentheses indicate percentage loss of sorbic acid.
*See Materials and methods (Mango squash section).

Table 2. Changes in the concentration of sorbic acid in mosambi juice during storage at 37°C

Storage period (days)	Concentration of sorbic acid (%)							
	Paper—aluminium foil—polyethylene laminate		Saran coated cellopoly		Polypropylene		Glass bottles	
	(i)	(ii)	(i)	(ii)	(i)	(ii)	(i)	(ii)
0	0.092	0.048	0.092	0.048	0.092	0.048	0.092	0.048
40	0.092	0.040	0.080	0.040	0.054	0.027	0.087	0.038
80	0.084	0.038	0.070	0.036	0.051	0.024	0.079	0.037
	(8.7)	(20.8)	(23.9)	(25.0)	(44.6)	(50.0)	(14.1)	(22.9)
120	0.078	0.036	0.059	0.033	0.037	0.020	0.070	0.034
	(15.2)	(25.0)	(35.9)	(31.2)	(59.8)	(58.3)	(23.9)	(29.2)
150	0.076	0.033	0.054	0.028	0.023	0.016	0.066	0.031
	(17.4)	(31.2)	(41.3)	(41.7)	(25.0)	(66.7)	(28.3)	(35.4)

Figures in parentheses indicate percentage loss of sorbic acid.

Table 3. Changes in the concentration of sorbic acid in fish paste during storage at 37°C

Packaging	Concentration of sorbic acid (%)							
	pH 3.5 Storage period (days)				pH 4.2 Storage period (days)			
	0	30	60	90	0	30	60	90
Paper—aluminium foil—polyethylene laminate	0.20	0.19	0.18	0.17	0.20	0.20	0.19	0.18
Polypropylene	0.20	0.08	0.05	0.04	0.20	0.10	0.07	0.06
Glass bottles	0.20	0.18	0.17	0.16	0.20	0.19	0.18	0.17

is not surprising because the diunsaturated SA would be expected to undergo autoxidation during storage as indicated by the formation of carbonyl compounds in aqueous solutions of SA. The rates of autoxidative reactions are mainly governed by the oxygen tension and the nature and concentration of catalysts or inhibitory substances present in the food systems. In sealed pouches and bottles, the oxygen tension in turn will be governed by the amount of head space, the dissolved oxygen and oxygen permeability of the packaging materials. Aluminium foil laminate pouches and glass bottles are impermeable to oxygen and provide maximum protection against autoxidative degradation of SA. Slight losses that have been observed during storage may have been brought about by the dissolved and head space oxygen in these packaging systems. On the other hand, because of the relatively higher oxygen permeabilities of polypropylene and saran coated cellopoly films—84–415 and 0.6 (ml/0.001 in/100 in^2/24 hr at atm. 73°F and 0% r.h.), respectively—autoxidative degradation proceeded rapidly resulting in very high losses of SA and total carotenoids. Losses in carotenoids during storage of mango squash were also found to be related to the oxygen permeability of the packaging materials. About 75–80% of the initial carotenoids was retained during storage in glass bottles and laminate pouches compared to 5–10% in polypropylene pouches and 30–

Table 4. Changes in SO_2 concentration (ppm) in mango squash during storage at 37°C

Storage period (days)	Concentration of SO_2 (ppm)							
	Paper—aluminium foil —polyethylene laminate		Saran coated cellopoly		Polypropylene		Glass bottles	
	(i)	(iv)	(i)	(iv)	(i)	(iv)	(i)	(iv)
0	332.0	90.8	332.0	90.8	332.0	90.8	332.0	90.8
30	173.0	54.2	135.0	21.8	71.7	12.2	184.0	49.8
60	96.2	23.8	32.1	3.2	16.8	ND	87.2	28.2
90	74.8	14.6	6.8	ND	2.4	ND	60.2	10.4
160	54.3	4.2	ND	ND	ND	ND	43.7	3.2
210	34.4	ND	ND	ND	ND	ND	28.4	ND

ND—not detectable.

35% in saran coated cellopoly pouches. The addition of SA did not significantly influence the rate of degradation of carotenoids in mango squash in any of the packaging systems.

Changes in added SO_2 in stored mango squash are shown in Table 4 and indicate that most of the added SO_2 was lost during the initial stages of storage in all the packaging systems. After 60 days of storage about 25% of the added SO_2 was retained in laminate pouches and glass bottles in comparison to 5 and 10% retention in polypropylene and saran coated cellopoly pouches, respectively. In these low concentrations (< 100 ppm), SO_2 did not significantly influence the rate of degradation of SA in mango squash (Table 1). Also, addition of 100 ppm of SO_2 did not significantly influence the rate of browning, but at a level of 350 ppm, it had an appreciable inhibitory effect especially in samples stored in polypropylene and saran coated cellopoly pouches (Table 5).

Table 5. Browning intensity in mango squash

Storage period (days)	Paper—aluminium foil —polyethylene laminate				Saran coated cellopoly				Polypropylene				Glass bottles			
	(i)	(ii)	(iii)	(iv)	(i)	(ii)	(iii)	(iv)	(i)	(ii)	(iii)	(iv)	(i)	(ii)	(iii)	(iv)
0	0.16	0.16	0.16	0.16	0.16	0.16	0.16	0.16	0.16	0.16	0.16	0.16	0.16	0.16	0.16	0.16
30	0.17	0.18	0.18	0.17	0.17	0.19	0.17	0.19	0.17	0.19	0.19	0.20	0.19	0.19	0.20	0.18
90	0.22	0.21	0.22	0.23	0.21	0.35	0.36	0.31	0.27	0.37	0.39	0.31	0.22	0.30	0.29	0.24
160	0.24	0.23	0.25	0.26	0.25	0.40	0.38	0.38	0.32	0.50	0.42	0.40	0.24	0.34	0.32	0.26
210	0.34	0.37	0.35	0.38	0.54	0.95	0.86	0.88	0.54	0.96	0.89	0.90	0.33	0.40	0.34	0.34

Browning intensity in stored mango squash and mosambi juice also seemed to be related to the permeabilities of the packaging materials. Though there was a gradual increase in the browning intensity of mango squash on storage in all the packaging materials, values were considerably higher in polypropylene and saran coated cellopoly pouches than in glass bottles and laminate pouches. Also, at 0.1% level, addition of SA did not significantly influence the development of browning, but at 0.2% level it tended

to slightly increase the rate of browning in stored mango squash, especially in polypropylene and cellopoly packs (Table 5). Even after 210 days samples of mango squash stored in glass bottles and laminate pouches at 37°C having 0.2% SA were acceptable in colour, taste and aroma to all the members of the taste panel. Anand *et al.* (1958), however, had reported that mango squash preserved with SA underwent intense browning and became unacceptable. In mosambi juice, browning intensity of the samples preserved with benzoic acid and SA were practically the same (Table 6).

Table 6. Browning intensity in mosambi juice

Storage period (days)	Paper—aluminium foil —polyethylene laminate			Polypropylene		
	(i)	(ii)	(iii)	(i)	(ii)	(iii)
0	0.24	0.24	0.24	0.24	0.24	0.24
40	0.25	0.25	0.26	0.43	0.46	0.34
80	0.25	0.27	—	0.56	0.57	—
120	0.30	0.30	0.32	0.68	0.64	0.61
150	0.40	0.35	0.39	0.74	0.75	0.68

In fish paste, the lead acetate precipitation method for measuring browning intensity could not be used because browning substances were mainly associated with the lipophilic fractions. However, visual examination showed that the samples of fish paste stored in polypropylene pouches had undergone intense browning during storage. On the other hand, samples stored in laminate pouches and sealed glass bottles had retained the original colour without significant browning. This suggests that the fish lipids which are most susceptible to autoxidative degradation are associated with the development of browning compounds. Though there was a gradual decrease in the TBA value of cooked fish paste during the storage period, samples stored in polypropylene pouches had relatively higher TBA values than in glass bottles and laminate pouches.

The antimicrobial action of organic acids is well known and both vinegar and acetic acid are widely used in the preparation of marinated fish. At pH values of 4.2 and below, all the pathogenic and majority of the food spoiling bacteria cease to proliferate and spoilage is mostly caused by yeasts and moulds which can grow even in highly acid products (pH < 2) (De Merindol, 1969). In the present study a combination of lactic acid and sorbic acid was used to preserve fish paste. The product kept well for more than 90 days and there were no signs of bacterial spoilage in stored fish paste samples treated with 0.2% sorbic acid and having pH < 4.2. After 90 days storage, total aerobic counts in treated samples were < 400/g whereas yeast and mould plate counts were < 50/g. In the samples preserved with lactic acid alone at pH 4.2 and 3.5, total aerobic count ranged between 25 000 and 30 000 and yeast and mould counts were < 300 after 90 days storage indicating the beneficial effect of sorbates in the preservation of fish producs in acidic medium. Tests for anaerobic bacteria were negative in 10 g samples and total titratable acidity remained practically unchanged indicating the absence or proliferation of acidophilic bacteria. This indicates a promising role that sorbic acid may have in the preservation of fish pickles and other marinated fish products, provided these are protected from autoxidative degradations with adequate packaging.

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Factors influencing the relationships between reducing sugars and fry colour of potato tubers of cv. Record

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Summary

The influence of sampling and sugar and colour assessment on the correlation between sugar content and fry colour of potatoes was investigated in cv. Record stored at 5 and 10°C (to produce a wide range of reducing sugars), and sampled at the basal, middle and apical region of the tuber.

When colour and reducing sugars from adjacent slices were compared excellent correlations were found between these two factors whether the colour was measured objectively, as reflectance density (RD) of the ground paste from fried disks ($r = 0.9550$) and optical density (OD) of extract from the paste ($r = 0.9507$), or subjectively against IBVL colour cards ($r = -0.9378$). Although good correlations were found for individual scorers, using matching colour cards, significantly different regression lines were found between individuals. Reducing sugar levels were generally higher at the basal end than at the apical end. Consequently, the correlations between fry colour and reducing sugars are much poorer if reducing sugar and colour are measured on different tissue in the same tuber and the variation in colour explained by variation in reducing sugar decreased from 90 to 50%.

Sampling within tubers thus appears to be a major factor determining the ability to accurately predict fry colour from reducing sugar content. It is suggested that if potatoes for processing are to be rejected on the colour of the darkest part of a tuber then a sample core for sugars should be taken from the basal region of the tuber.

Introduction

Frying of potatoes produces a brown colour due to the Maillard reaction between reducing sugars and amino acids. If sugar concentrations are high, an undesirable dark colour and bitter taste develop which lower the acceptability of fried potato products. Thus the concentration of reducing sugars is used by the crisp industry, often in conjunction with a fry test, for quality control at purchase and evaluating the suitability of material out of store for processing. Although the level of reducing sugars may explain the majority of the variation in colour, the correlations between reducing sugars and fry colour and slope and intercept of the regression lines vary considerably (Habib & Brown 1957; Schwimmer *et al.*, 1957; Shallenberger, Smith & Treadway, 1959; Glegg & Chapman, 1962; Hoover & Xander, 1963; Wünsch & Schaller, 1972). Moreover, the processors of crisps in the U.K. consider that the correlation between

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reducing sugars and fry colour is poorer than in the past (personal communication). Various reasons have been suggested by the industry for this poorer correlation including changes in husbandry (use of higher levels of nitrogen as a result of application of organic nitrogen from intensive animal and poultry farming) and improved seed (Potato Processors' Association, personal communications).

These differences in correlations and regression lines may be due to the interaction of two groups of factors, viz: (i) differences in methods of sampling, frying and estimation of sugars and colour, and (ii) differences in other tuber constituents—e.g. amino acids, organic acids—and pH that may influence colour formation (Habib & Brown, 1957); Fitzpatrick, Talley & Porter, 1965). Before the role of the second group of factors can be assessed, it is necessary to evaluate the first in order to devise a satisfactory standard test technique. This paper describes an experiment where the role of the first group of factors was assessed in potatoes showing the range of reducing sugars and colour that can be encountered during processing. The variety Record, the principal U.K. maincrop variety used by the crisp industry between October and July, was used to provide the experimental material.

Material and methods

Experimental material

The wide range of tubers varying in reducing sugars was selected by estimating glucose on the centre core of tubers of commercially grown Record which had been stored at 10 and at 5°C from harvest until the following February; 10°C is the storage temperature used commercially to minimize sugar accumulation, whilst at 5°C reducing sugars accumulate due to low temperature sweetening (Burton, 1966).

Sampling

Reducing sugars (Iritani, Weller & Russell, 1973; Hughes & Fuller, 1984) like other tuber constituents (Burton, 1966) are known to vary from basal to apical end. In order to assess the role that variations within a tuber play in influencing correlations between sugars and colour and in order also to maximize the variation in these factors, separate samples were taken from the basal end and apical end of the selected tubers. Cores 33 mm in diameter were taken transversely through the tubers. Skin and outer tissues of the tuber, including the vascular tissue, were removed from each end of the core. The remainder of the core was held within the core borer and accurately sliced into 1.5 mm disks (similar in thickness to those used by industry) until ten disks had been taken. They were then divided into two groups using alternate disks. One group was used for frying and the other group for sap extraction for estimation of sugars.

At the same time, using a sampling technique similar to that used by industry for estimating reducing sugar variation in potato samples, a core 8 mm in diameter was taken transversely from the centre of the tubers.

Sap extraction

Sap from the potato tissue of each sample from the basal, centre and apical area of each tuber was extracted under pressure, using a small hand screw press. The untreated sap from the centre sample was used for glucose analyses on the YSI glucose analyser. The sap from the basal and apical end samples was inactivated and deproteinized using Carrez I (potassium ferrocyanide) and Carrez II (zinc sulphate) and the clarified sample analysed for glucose, fructose and sucrose using automated enzymic methods (Anon., EAPR).

Sugar analysis

The straight sap was measured using a YSI Model 27 glucose analyser, which measures the hydrogen peroxide produced from the reaction of glucose with the immobilized glucose oxidase in the system.

The inactivated and deproteinized sap was analysed for glucose, fructose and sucrose using an automated Technicon system incorporating enzymic methods. Glucose and sucrose (after hydrolysis with invertase) were separately analysed using an automated method based on the glucose oxidase and peroxidase manual method (Werner, Rey & Wielinger, 1970). Fructose was calculated by subtracting glucose from the sum of glucose plus fructose estimated by an automated method based on the hexokinase glucose-6-phosphate dehydrogenase manual method (Schmidt, 1961).

Frying

Five disks for each sample, after rinsing in double distilled water to remove adhering starch and patting dry with filter paper, were placed in a wire mesh basket with a mesh lid to ensure that the disks were completely submerged during frying in a vessel containing 3 litres of fresh palm oil (Frytol) controlled at 180°C using a thermostatically controlled 3 kW capacity heating element.

The temperature was monitored using a thermocouple and digital thermometer. The disks were considered to be done when bubbling stopped and the temperature had returned to 180°C, which varied from 1.5 to 2.25 min between samples. The fried disks were removed from the basket and allowed to cool and drain on filter paper prior to colour observation.

Crisp colour measurement—subjective

Each disk from each sample for the basal and apical end of each tuber was matched against IBVL colour cards (Anon., EAPR) by five members of staff. The individual scores for each disk were measured to give an average score for each sample. The data for the mean score for the five members of staff are presented (1 = dark and 9 = light; 1–4 are unacceptable, 5–6 acceptable, 7–9 desirable coloured crisps).

Crisp colour measurement—objective

The five disks from each sample were ground in a pestle and mortar to a fine paste for measuring reflectance and for extraction of pigment.

Reflectance. The paste was placed in a reflectance holder covered with a glass plate and backed by aluminium foil (Little, 1964) and the reflectance spectrum measured using a diffuse reflectance head on the Unicam SP 800 spectrophotometer, zeroed with a magnesium oxide blank. The optical density scale was used and the results expressed as reflectance density (RD) at 650 nm after subtraction of the RD at 850 nm. Since a similar wavelength is recommended when using an Agtron (an abridged reflectance spectrophotometer), 650 nm was chosen for crisp colour measurement. The RD at 850 nm was subtracted since it was similar in dark and light crisps and was taken as a measure of the background colour of all the crisps.

Estimation of extracted colour. Approximately 0.5 g of ground crisp paste was refluxed for 1 hr with 55% ethyl alcohol. This extract was defatted using 40–60 boiling range petroleum ether and passed through glass paper to give a clear extract which was measured at 420 nm (Schwimmer *et al.*, 1957) and expressed as optical density/g ground crisp paste.

Statistical anlyses

The statistical relationships between various factors were investigated using the method of least squares for the production of regression lines, correlation coefficients (r) and coefficients of determination (r^2) which state the proportion of the variation explained by the regression line.

Results and discussion

Measurement of colour

Crisp colour measured subjectively, using the IBVL colour cards, which in these samples covered the range of quality from desirable to unacceptable, was highly correlated with colour measured objectively as RD of paste ($r = -0.9567$, $r^2 = 0.9153$) (Table 1, Fig. 1) and OD of extract ($r = 0.9551$, $r^2 = 0.9122$ (Table 1, Fig. 2). These two latter measurements which are different measurements of ground paste are naturally highly correlated ($r = 0.9872$, $r^2 = 0.9746$) (Table 1, Fig. 3).

Whilst these results suggest that mean crisp colour can be accurately judged by subjective means, variations between individuals (see Correlation between sugars and crisp colour) together with day to day variation could lead to error unless checks are carried out using known crisp or colour standards.

Sugar analysis

The ratio of glucose to fructose is roughly 1:1 in all tubers (Fig. 4) and there are consequently excellent correlations between individual reducing sugars and total reducing sugars. Glucose alone, even measured in the crude sap by the very rapid YSI method, (which is highly correlated with glucose estimated by the Technicon method $r = 0.9903$, Table 1, Fig. 5) would provide a very accurate indication of total reducing sugars. However, this would not be the case in all material since the ratio of glucose to fructose is known to alter, e.g. during storage and between varieties (Habib & Brown, 1957).

As shown by other workers there is no correlation between sucrose and reducing sugars (see Burton, 1966).

Correlation between sugars and crisp colour

Colour of fried products is thought to be determined by the total level of reducing sugars since both glucose and fructose are involved in the Maillard reaction. However, because of the very similar ratio of glucose to fructose in all samples, the correlations between crisp colour and these sugars and total reducing sugars are very similar (Table 1). Discussion of the relationship between reducing sugars and the different measurements of colour, will therefore be limited to total reducing sugars. The highest correlations are found between total reducing sugars and the objective measurement of colour as RD and OD (Table 1, Figs 6 and 7) and over 90% of the variation in colour is explained. The linear relationship between colour and the concentration of reducing sugars suggests, under these conditions, that this is a first order reaction with respect to reducing sugars. The lines may not pass through the origins possibly because of the background colour of natural pigments (e.g. carotenoids and flavanoids).

Although the relationship between reducing sugar content and colour estimated as RD or OD appears linear, the relationship between reducing sugar and crisp score appears curvilinear (Fig. 8). Nevertheless, even using a linear regression nearly 88% of

Table 1. Matrix of correlations* for colour and sugars in cv. Record

					Technicon			
	Crisp score	Reflectance density (650 nm)	Optical density (420 nm)	YSI glucose (mg/dl sap)	Glucose (mg/dl sap)	Fructose (mg/dl sap)	Total reducing sugar (mg/dl sap)	Sucrose (mg/dl sap)
Crisp score	1.0							
Reflectance Density (650 nm)	−0.9567	1.0						
Optical Density (420 nm)	−0.9551	0.9872	1.0					
YSI glucose (mg/dl sap)	−0.9319	0.9479	0.9512	1.0				
Technicon glucose (mg/dl sap)	−0.9227	0.9471	0.9425	0.9903	1.0			
Technicon fructose (mg/dl sap)	−0.9454	0.9554	0.9531	0.9906	0.9923	1.0		
Technicon total reducing sugars (mg/dl sap)	−0.9378	0.9550	0.9507	0.9914	0.9977	0.9982	1.0	
Technicon sucrose (mg/dl sap)	−0.2928	0.2670	0.3122	0.4295	0.4249	0.4165	0.4158	1.0

*All correlations are highly significant at $P = 0.001$, apart from those involving sucrose which are non-significant.

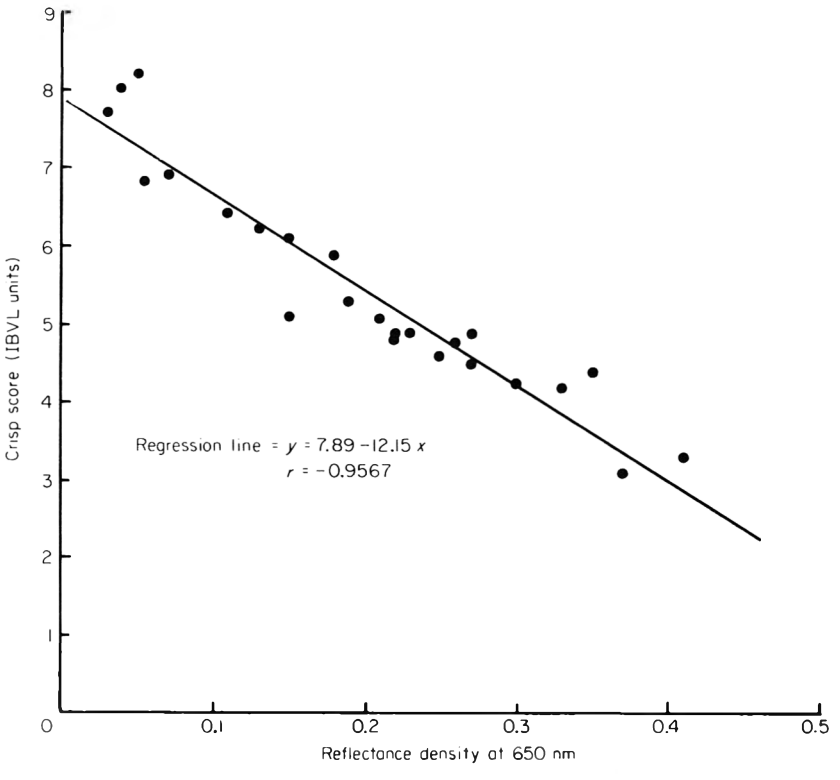

Figure 1. Relationships between crisp score and reflectance density of crisp paste.

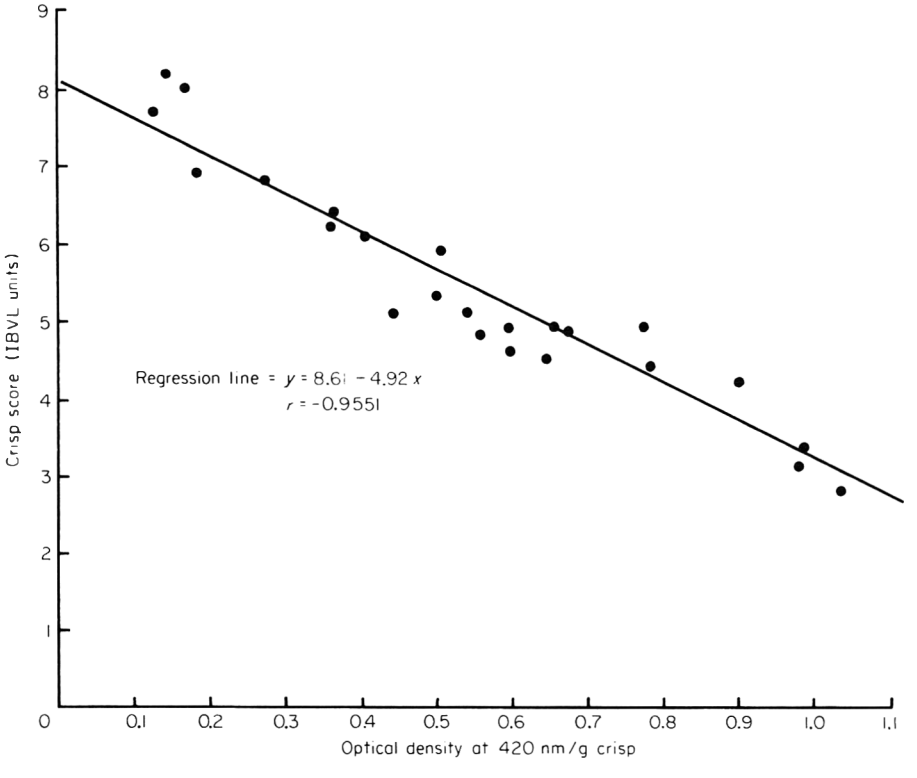

Figure 2. Relationship between crisp score and optical density of crisp extract.

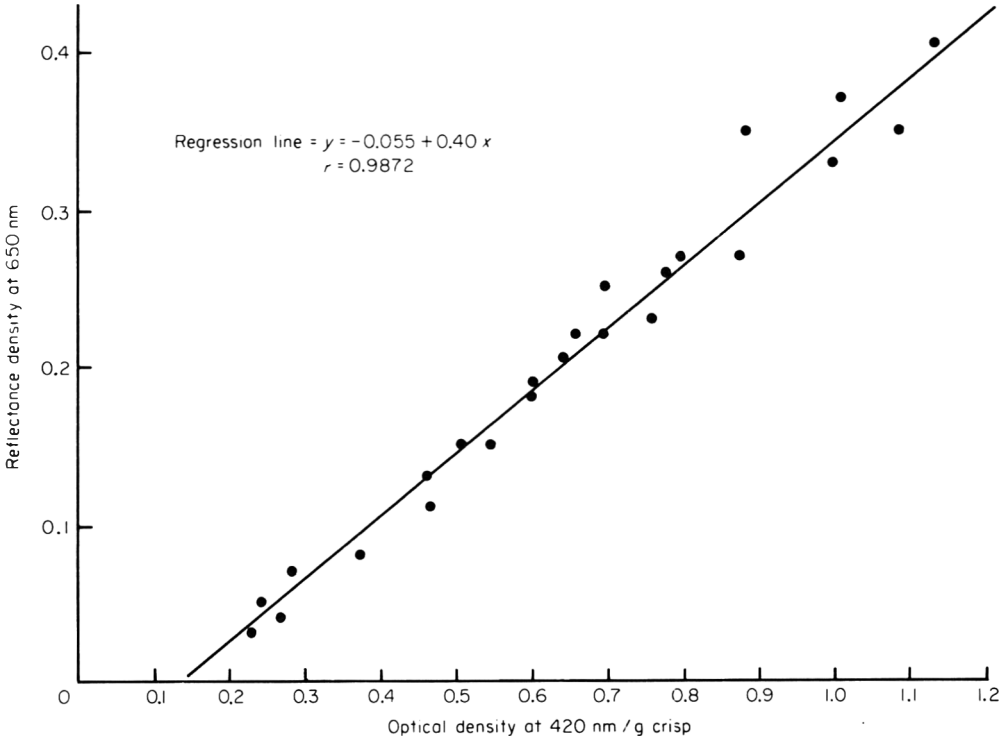

Figure 3. Relationship between reflectance density of crisp paste and optical density of crisp extract.

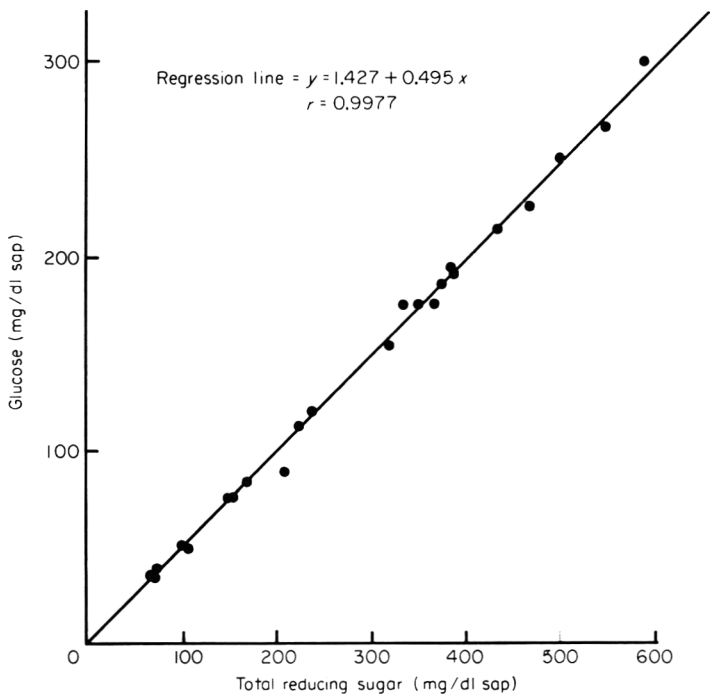

Figure 4. Relationship between glucose and total reducing sugar content of deproteinized sap.

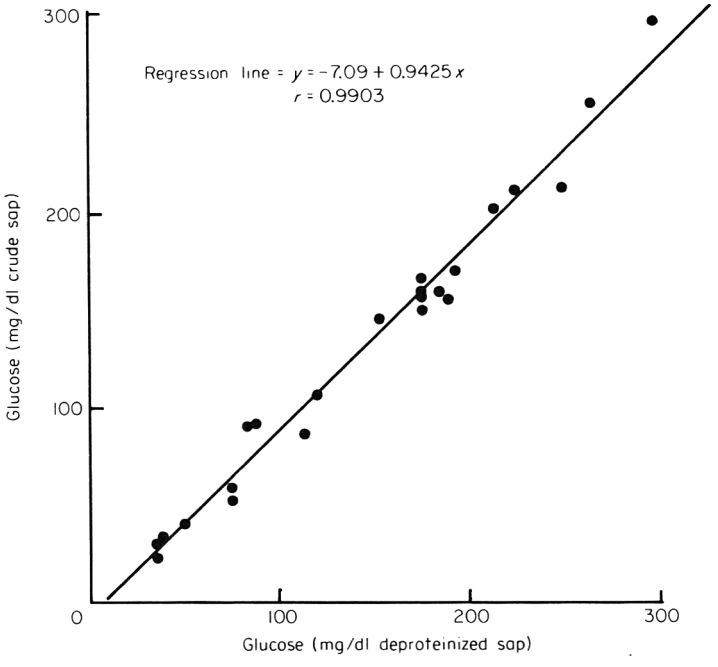

Figure 5. Relationship between glucose estimated by YSI glucose analyser on crude sap and glucose estimated by glucose oxidase—peroxidase method on deproteinized sap.

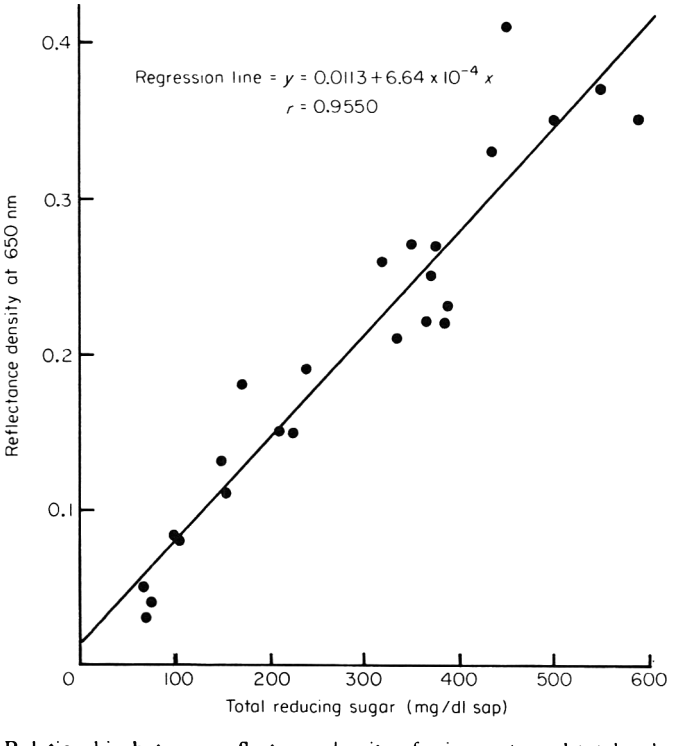

Figure 6. Relationship between reflectance density of crisp paste and total reducing sugar content of sap.

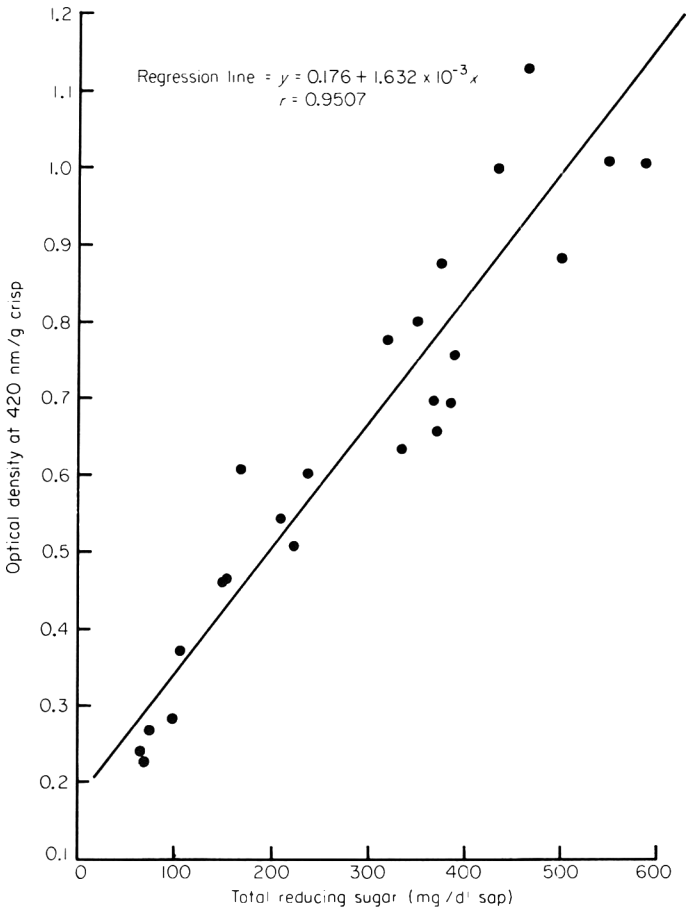

Figure 7. Relationship between optical density of crisp extract and total reducing sugar content of sap.

the variation in crisp score is explained by reducing sugar content of the samples. This relationship is possibly non-linear because of the scale used for the IBVL score cards. When reflectance densities were calculated from the % reflectance data for Agtron readings quoted for the scale units in the IBVL publication (Anon.) and were plotted against the IBVL scale units they gave a curvilinear relationship.

Good correlations were also found between reducing sugar and crisp score of individuals (Fig. 9). However, the variation in score between the most divergent individuals (A and B) was sufficiently great to give regression lines that were significantly different in slope ($P = 0.05$) when pairs of scores for A and B were compared. A scored crisps significantly lower than B both in the parametric test ($P = 0.001$) and non-parametric test ($P = 0.01$) (Armitage, 1980). This divergence was less in lighter crisps than in darker crisps, since the scoring difference, when the score was above 6, was significantly lower in both the parametric test ($P = 0.001$) and non-parametric test ($P = 0.05$).

Relationship between centre core glucose values and crisp colour

In order to predict the crisp colour of batches of potatoes to be used for processing, the central core plugs from a number of tubers are individually analysed for reducing

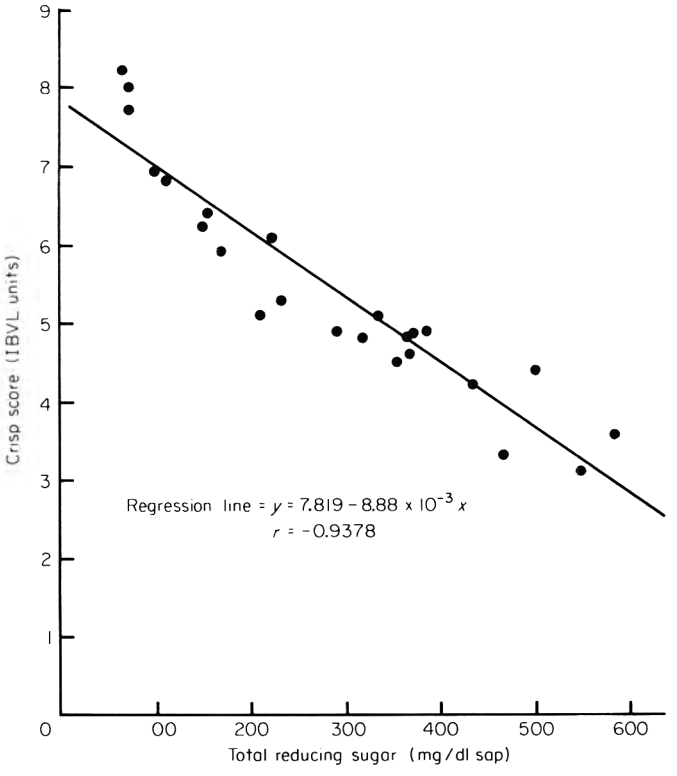

Figure 8. Relationship between crisp score and total reducing sugar content of sap.

sugar content by processors (Potato Processors' Association, personal communication). Because of the close correlation in this material between glucose and total reducing sugars it was considered worthwhile examining the data of this experiment to see how well the YSI glucose values predict crisp colour in the remainder of the tuber—even though data are not available for total reducing sugars on the centre core.

The individual centre core YSI glucose values have been correlated with crisp scores of disks taken from either basal end, apical end or mean of basal end and apical end of the same tubers from which the centre cores were taken (Table 2).

It can be seen that much poorer correlations are found between centre core glucose and crisp scores of the other sample sites than between the colour of thse disks and the glucose value of the appropriate basal or apical tissue, which is not surprising because of the variation in sugar along the tuber (Iritani *et al.*, 1973; Hughes & Fuller, 1984). Reducing sugar and crisp colour was higher at the basal end than the apical end in all tubers except two where the levels were very similar at both ends.

In fact only 54% of the variation ($r = 0.7365$) in colour of the disks from the basal end was explained by the variation in glucose from the centre core (Fig. 10) compared to 90% explained when basal end disks were correlated with basal end glucose values (Fig. 11). This indicates that if in practice centre core analyses are used to predict the colour of the darkest tissue found in the processed crisps (normally the basal end tissue) then a much poorer correlation will be found than in fact exists when like tissues are compared. If tubers are to be rejected on account of the score of the darkest part of the tuber and only one sugar analysis is to be made per tuber then the sugar sample core should be taken from near the basal region of the tuber.

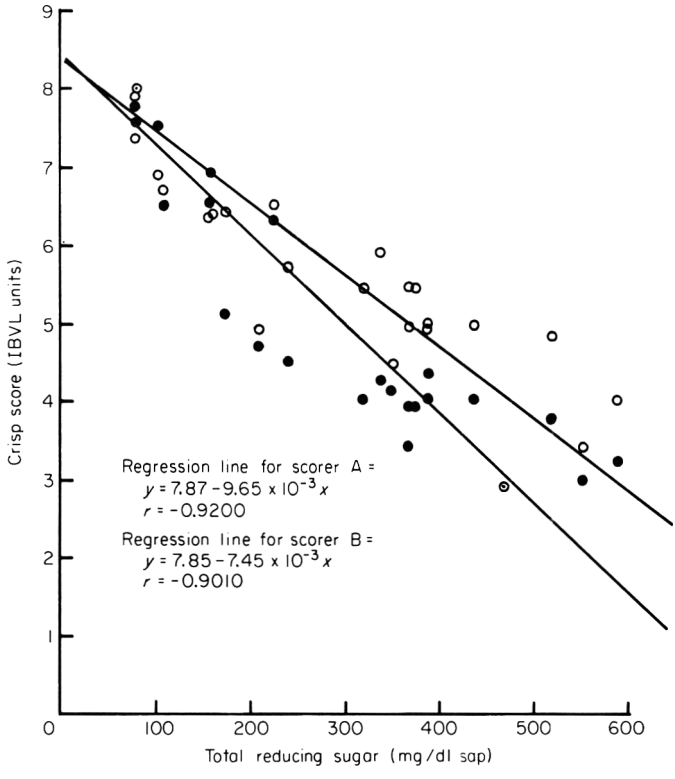

Figure 9. Relationship between crisp score of two individuals (A: ●; B: O) and total reducing sugar content of sap.

Table 2. Correlations between glucose content of central, basal, apical and mean of basal plus apical cores and crisp colour of basal, ap cal and mean of basal plus apical disks

	YSI glucose (mg/dl sap)			
	Centre	Basal	Apical	Mean basal + apical
Colour score				
Basal	−0.7365	−0.9512		
Apical	−0.8677		−0.9490	
Mean basal + apical	−0.8540			− 0.9740

Conclusions

These results show that when colour and reducing sugar from adjacent slices are compared excellent correlations are found between colour and either glucose, fructose or total reducing sugar, whether the colour is measured objectively or subjectively. However, the inherent dangers of the matching card system for colour score (e.g. differences between individuals) can led to significantly different regression lines. Correlations between crisp colour and sugar content immediately worsen if sugars and crisp colour are examined in different parts of the tuber and the variation explained can decrease from over 90% to about 50%.

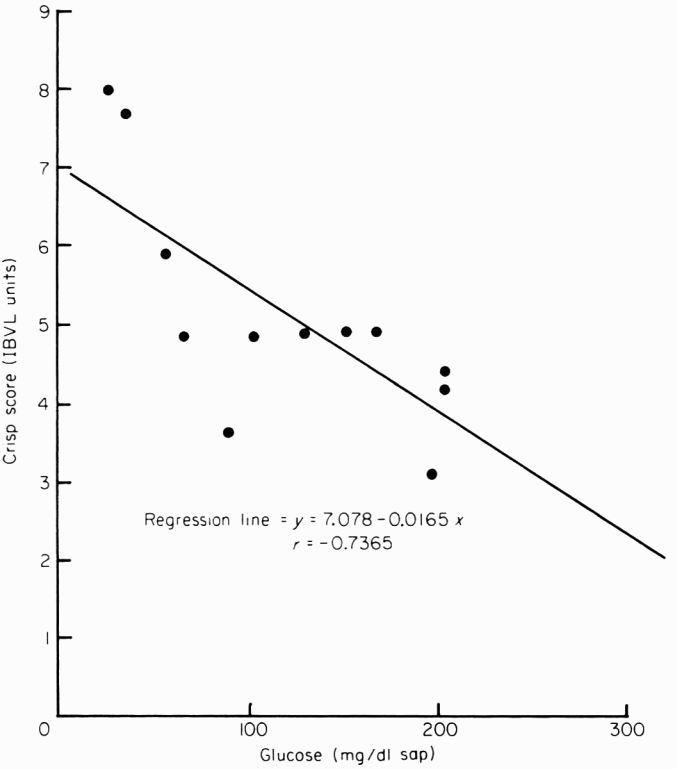

Figure 10. Relationship between crisp score of basal end disks and glucose of sap from centre core.

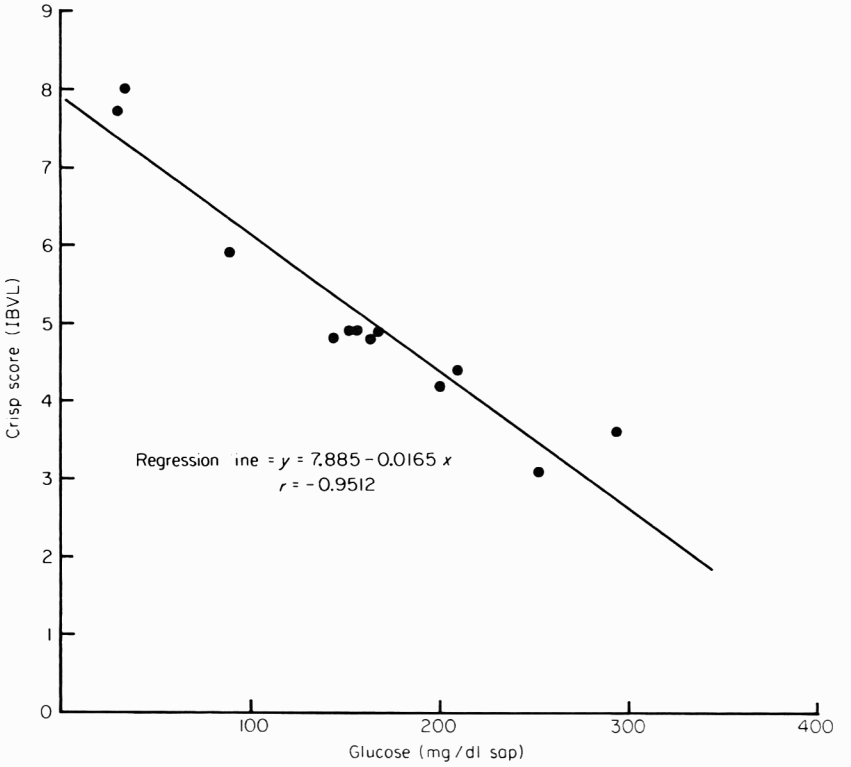

Figure 11. Relationship between crisp score of basal end disks and glucose of sap from basal end core.

In this experiment, where tubers having a very wide range of reducing sugar content and crisp colour have been examined using improved methods of measuring colour and reducing sugar, sampling appears to be the major factor determining the ability to predict accurately crisp colour from tuber reducing sugar analysis. The possible contribution of other tuber constituents to variation in colour between tubers of this batch of potatoes is small. However, between different batches of tubers the role of other tuber components may be greater and this will now be investigated using the improved technique developed in the course of the current work.

Acknowledgments

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Effect of type and level of added fat on heat induced binding in a fish loaf product*

Z. G. WEINBERG† AND S. ANGEL

Summary

The effect of addition of 2 and 5% solid and liquid fats on the binding properties of fish flesh was studied by a stress–relaxation test. Two percent added fat or oil had little effect on the binding properties, while the addition of 5% oil or solid fat reduced the compression forces and the relaxation times, depending on the original fat content of the fish. For lean fish, the addition of fat or oil reduced the compression forces and the relaxation times by *circa* 50%. For fatter fish, solid fat had a greater effect on these parameters. Moisture content of the fish flesh also seemed to affect the viscoelastic properties of the fish loaf product.

Introduction

The effects of type and level of fat on the emulsion stability of sausage products have been studied by many groups (e.g. Swift, Townsend & Witnauer, 1968; Baker, Darfler & Vadehra, 1969; Ackerman *et al.*, 1971; Townsend *et al.*, 1971; Deng, 1974; Brown & Toledo, 1975; Toledo, Cabot & Brown, 1977). In general, the type and level of fat, as well as the proximate composition of the raw material, chopping time and temperature, were shown to affect emulsion stability and the rheological properties of such products.

Very little work has been done on the effects of fat additions on heat induced binding properties of products formed from non-chopped batters. In such products the moisture content affects protein functionality, which plays an important role in stabilizing the texture (Weinberg, Regenstein & Baker, 1984). In a previous paper (Weinberg, 1983), the effect of species of fish on the heat induced binding in a fish product was described. In that work it was shown that fish containing 5% endogenous fat or above resulted in a product with poor binding properties. The purpose of the present work was to evaluate the effect of type and level of added fat on the binding properties of fish muscle.

Materials and methods

Preparation of loaves

Fresh whole silver carp (*Hypophthalmichtys molitrix*) was purchased from a local dealer and the fish was filleted. The fillets were cubed to *circa* 1 cm^3 and these were

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thoroughly mixed by hand with 1.5% NaCl and with or without added fat or oil. They were then placed in a paddle mixer and mixed again for 3 min. The treatments were: control (i.e. no fat or oil added), 2 and 5% (w/w) Crisco vegetable shortening, 2 and 5% (w/w) soybean oil. After mixing, the batters were packed into aluminium foil pans (23×7×4.5 cm) by hand. Care was taken to avoid the formation of air pockets. The pans were covered with aluminum foil, placed in an oven at 150°C, and baked to an internal temperature of 75°C. After cooling to room temperature, the loaves were stored overnight at 2°C. The experiments were repeated with fish bought on four different dates.

Moisture content

Moisture content of the raw fish of the cooked products was determined by the AOAC method (AOAC, 1975).

Fat content

Fat content of the raw fish and the cooked products was determined by a chloroform : methanol (2 : 1) extraction on the dried material.

Stress–relaxation test

The loaves were tempered to ambient temperature before being removed carefully from the aluminum pans and sliced into 30 mm thick rectangular shaped samples (60×45 mm), trimmed off the dry surface. The samples were tested in a compression cage of an Instron Universal testing machine (TM 1026). The lower part of the cage was raised at a constant speed of 50 cm/min until the samples were compressed to 50% of their original height (i.e. 50% deformation). The chart speed was also 50 cm/min. The compression forces were obtained from the peak heights. Relaxation times were obtained from the time needed for the peak to descend to its half height.

Statistical analysis

One-way analysis of variance and Duncan's multiple range test were performed with an SAS program using GLM procedure with an IBM 4341 computer.

Results and discussion

There was a marked difference between percent moisture and fat in the raw fish for the four experimental dates (Table 1), which represented shipments of fish of various sizes (the higher the fat and the lower the moisture content—the bigger were the fish). Such variability is a common phenomenon in fish (Weinberg, 1983). This variability in raw material was reflected in the proximate composition of the loaves and affected the compression forces and the relaxation times obtained with the Instron. The differences between the percent moisture in the control loaves and those to which oil or fat had been added were smaller than expected in some cases (e.g. experiment 4). The percent fat varied according to the additions made, approximately as expected. In some loaves (e.g. experiment 4) to which the higher percent fats were added, somewhat less oil or fat remained after cooking, and some oil or fat probably escaped due to saturation of the flesh.

The present method of testing the texture of the loaves was chosen because work by Weinberg and co-workers (Weinberg, 1983; Weinberg & Angel, 1984; Weinberg *et al.*,

Table 1. Moisture (M) and fat (F) contents of the raw fish and the cooked loaves (data are percentages ± s.e. of the mean)

	Experiment No.							
	1		2		3		4	
Treatment	% M	% F	% M	% F	% M	% F	% M	% F
Raw material	79.2±0.2	2.1±0.2	75.2±0.4	9.0±0.1	73.2±0.2	7.8±0.4	79.3±0.1	0.9±0.1
Control	76.9±0.5	2.3±0.2	75.0±2.0	7.2±0.3	71.1±0.1	8.0±0.2	76.6±0.1	2.4±0.1
2% added Crisco	75.6±0.5	4.9±0.4	67.5±1.3	9.8±0.1	69.9±0.1	9.9±0.2	75.4±0.3	2.9±0.3
5% added Crisco	71.6±0.5	8.2±0.8	68.6±0.6	13.0±0.2	65.1±0.1	4.7±0.1	74.1±0.1	5.8±0.3
2% added oil	74.9±0.1	3.3±0.5	71.5±2.0	8.5±0.1	70.6±0.1	8.9±0.1	74.6±0.3	4.2±0.4
5% added oil	74.0±0.4	6.5±0.6	68.7±1.5	12.3±0.9	68.5±0.2	2.2±0.8	75.1±0.1	4.6±0.3

1984) showed that tensile strength, while correlating well with compression forces, was not always in agreement with panelists' commments on binding quality, and was therefore not effective in reflecting the elastic properties accompanying binding in a fish loaf.

The stress–relaxation test yields information both as to compression force indicating hardness, and relaxation times indicating elastic properties. Thus, this test best elucidates the textural properties of the fish loaf.

The compression forces in Table 2 show that except for the fish from shipping date No. 2, which was relatively very fat, addition of either 2% fat or oil did not markedly alter the compression forces compared with the controls. On the other hand, addition of 5% Crisco or oil reduced the compression forces by about 50%. This indicates the addition of 5% fat, as either a solid or an oil, results in softening of the samples.

With regard to the relaxation times (Table 3), 2% added fat or oil resulted in almost no changes compared with the controls, corresponding to the compression force results. However, when the fish was lean (experiments 1 and 4), addition of 5% Crisco or oil reduced the relaxation times by *circa* 50% relative to the controls. It was observed that these samples were crumbly and softer than others. In fish or originally higher fat content (experiments 2 and 3) this effect was smaller, probably due to the effect of the original fat of the fish.

Table 2. The effect of fat additions on the compression forces (N ± s.e. of the mean) of the loaves*

	Experiment No.			
Treatment	1	2	3	4
Control	117.7 ± 5.9^{b}	95.2 ± 14.7^{a}	160.9 ± 4.9^{a}	121.6 ± 6.9^{a}
2% added Crisco	141.3 ± 3.9^{a}	36.3 ± 3.9^{c}	140.3 ± 5.9^{b}	121.6 ± 7.8^{a}
5% added Crisco	79.5 ± 5.9^{c}	33.4 ± 2.0^{c}	63.8 ± 2.9^{d}	78.5 ± 2.9^{b}
2% added oil	127.5 ± 3.9^{b}	$85.3 \pm 2.0^{a,b}$	101.0 ± 6.9^{c}	121.6 ± 8.8^{a}
5% added oil	71.6 ± 2.9^{c}	76.5 ± 2.9^{b}	91.2 ± 6.9^{c}	56.9 ± 2.9^{c}

*The dimensions of the samples were 60 × 45 × 30 mm.

Within a column, figures with different letters are significantly different at 0.05 level.

Table 3. The effect of fat additions on the relaxation times (sec ± s.e. of the mean) of the loaves*

Treatment	Experiment No.			
	1	2	3	4
Control	6.3 ± 0.3^{b}	3.9 ± 0.4^{a}	$4.9 \pm 0.3^{b,c}$	5.4 ± 0.5^{a}
2% added Crisco	7.9 ± 0.4^{a}	$3.4 \pm 0.7^{a,b}$	5.6 ± 0.1^{a}	4.6 ± 0.4^{a}
5% added Crisco	2.7 ± 0.1^{d}	2.8 ± 0.1^{b}	3.1 ± 0.7^{d}	3.2 ± 0.2^{b}
2% added oil	5.1 ± 0.2^{c}	$3.7 \pm 0.2^{a,b}$	$5.1 \pm 0.1^{a,b}$	4.9 ± 0.4^{a}
5% added oil	2.3 ± 0.1^{c}	$3.1 \pm 0.2^{a,b}$	$4.3 \pm 0.2^{a,b}$	2.5 ± 0.2^{a}

Within a column, figures with different letters are significantly different at 0.05 level.

In the control loaves, compression forces from fat (experiments 2 and 3) and lean (experiments 1 and 4) fish did not change in a consistent manner. That is, control loaves from fatter fish did not always have a lower compression force as compared with the lean (experiment 3). However, the moisture content of the raw fish and the control loaves in experiment 3 was lower than in the fish of the three other experiment dates (cf. Table 1). A lower moisture content might result in lesser hydration of the myofibrils, resulting in toughening, as expressed by a high compression force. With regard to relaxation times—which indicate viscoelastic properties—the control loaves from the lean fish had longer relaxation times than control loaves from the fatter fish. This indicates a higher degree of cohesiveness within the control samples of the lean fish. These results are consistent with the finding by Weinberg (1983) that fish containing 5% fat or above had poor binding properties.

With regard to the differences between the two types of fat, it appears from Tables 2 and 3 that for the leaner fish (experiments 1 and 4), the addition of either solid shortening or liquid oil did not yield a significantly different effect on the textural properties.

However, for the fatter fish (experiments 2 and 3), the solid shortening resulted in lower compression forces and relaxation times than the oil. This is consistent with the trend found by Ackerman *et al.* (1971) and Townsend *et al.* (1971) that beef fat separated from frankfurters more easily than did pork fat or vegetable oil in under-chopped emulsions. This was attributed to the melting characteristics of the added fat.

The mechanism by which fat or oil (present in the fish, or added) interferes with good binding in fish muscle is still a matter of speculation. One explanation might be that fat at high levels coats individual fish particles, hence presenting a physical barrier to the binding material. Another explanaton could be that during the blending of the fish with added salt plus fat, an oil-in-protein emulsion is formed. Added fat plus high levels of endogenous fat in the fish might result in loss of ability of the fish proteins to coat the fat. This could cause an emulsion breakdown with resultant crumbly texture in the cooked product.

Conclusions

The level of added fat and oil had a variable effect on the binding properties of the fish product. Addition of 2% fat or oil had little effect on the rheological properties of the loaves, while 5% added fat or oil reduced both the compression forces and the relaxation times, thus indicating poor binding.

The effect of added fat or oil on the texture of the product depended on the endogenous fat level of the fish flesh: with lean fish, the addition of either 5% Crisco vegetable shortening or oil reduced the compression forces and the relaxation times of the samples. When the fish was fatty, addition of liquid oil lowered these parameters only slightly, while solid fat had a marked effect.

The moisture content of the raw material and the loaf products also plays an important role in determining the textural properties, as evidenced by the case where the control samples of a fatty fish yielded high compression forces.

From this work it is clear that not only the added fat or oil affects the heat induced binding. The endogenous fat and moisture of the fish (varying within species) must be considered when preparing such products.

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Role of carbohydrates in soya extrusion

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Summary

When extruded under similar processing conditions, soya flour yielded a far more regular, honeycombed structure than soya isolate, though both had similar expansion ratios. At low concentrations both extrudates were almost totally soluble in solutions containing sodium dodecyl sulphate (SDS) plus 2-mercaptoethanol (ME), although in SDS or ME the extrudates were only partially soluble. These results suggest that, in both cases, the extrudates are primarily stabilized by disulphide bonds and hydrophobic interactions.

When rehydrated in water at temperatures in the range 20–120°C all the extrudates exhibited decreasing toughness and increasing protein solubility with increasing temperature. Also, the soya flour extrudates, but not those prepared from the isolate, exhibited a phenomenon at the lower temperatures characterized by minimum hydratability, pH and carbohydrate solubility at about 30–40°C. It is suggested that the soya flour extrudates are additionally stabilized, compared to the extrudates prepared from the isolate, by hydrophobic interactions involving the embedded carbohydrate.

Introduction

Because the substitution of textured plant proteins for meat has distinct advantages in terms of cost, soya protein texturized by extrusion has found extensive use as a meat-like ingredient in many processed meat products. Though texturised soya proteins have been produced since the early 1960s, the molecular changes which occur within the extruder are still largely unknown.

Solubility work directed at identifying the bonding forces responsible for the characteristic texture and microstructue of soya extrudates has given rise to widely varying conclusions. While some workers (Rhee, Kuo & Lusas, 1981; Jeuninck & Cheftel, 1979) have reported almost 100% solubility in a solvent containing 1% sodium dodecyl sulphate (SDS) and 1% 2-mercaptoethanol (ME), a solvent mixture in which all stabilizing forces except non-disulphide covalent bonds are broken, others (Burgess & Stanley, 1976; Simonsky & Stanley, 1982) have reported urea, SDS and ME to be largely ineffective in disrupting the bonding forces in texturized soya. These workers claim that isopeptide bonds are of importance.

While much research has been directed at the protein fraction, little attention has been given to the carbohydrate fraction, which typically accounts for 30% of the defatted soya products usually used in extrusion. There is evidence to suggest, however, that the carbohydrate fraction may play an active part in soya extrusion. Soya isolate (a

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high protein, low carbohydrate system), for instance, extrudes in a different way from soya flour (Smith, Mitchell & Ledward, 1982). Smith *et al.* (1982) also report that anionic polysaccharides included at the 1% level may exert significant effects on the extrusion behaviour of soy grits.

The work reported here was undertaken with a view to elucidating the role of the polysaccharides in soya extrusion.

Materials and methods

Defatted soya flour and isolated soya protein (purina protein 500E) were obtained from McAuley Edwards Ltd and approximate compositions are given in Table 1.

Table 1. Manufacturers analyses of soya flour and isolated soya protein

	Defatted soya flour (20 PDI)	Isolated soya protein (%)
Protein (N × 6.25)	50.0	91.0
Moisture	8.0	5.5
Fat	1.3	0.8
Fibre	3.5	0.1
Ash	6.5	3.8

The non-determined percentage was assumed to be carbohydrate.

The SDS, primar grade (S/5202), was obtained from Fisons Scientific Apparatus, and ME (No. M6250, type 1, lot No. 111F0272) was obtained from Sigma Chemical Co.

Extrusion

A Brabender laboratory extruder (model DN) was used. This was powered by a Docorder drive enabling torque to be continuously measured. Provision was made to record temperature, at the end of the screw, and pressure, at the die section. Feed, barrel and die temperatures, as determined by a Rosenbrock direct search procedure to give optimum expansion ratio (Smith *et al.*, 1982), were 127, 180 and 140°C, respectively. For all experiments, a 4 : 1 compression ratio screw was used at a speed of 250 rpm. The diameter of the die was 4 mm, and the moisture content of the feed was adjusted to 38 g water/100 g dry matter. The required amout of distilled water was mixed with the feed using a Kenwood mixer, and the moistened feed equilibrated overnight at 2–3°C prior to extrusion. A saturated solution of ninhydrin was also used to rehydrate some samples of soya flour and soya isolate to 38 g water/100 g dry matter prior to extrusion.

Protein solubility of the extrudates in SDS and ME

The extrudate was ground in a hammer mill, and a known weight (y) was added to the required solvent to give a total weight of 100 g. This suspension was stirred overnight and centrifuged at 40000 *g* for 20 min before filtering through Whatman No. 4 filter paper.

The protein concentration of the filtrate was determined, in duplicate, by a micro-Kjeldahl technique using 2 ml of the filtrate and calculated as:

$$\% \text{ protein} = \frac{A \times 100}{B \times y} \times 100\%,$$

where A = g protein/ml aliquot and B = % protein in extrudate.

Three solvents were used – 1% ME, which should rupture disulphide bonds, 1% SDS, which should rupture hydrogen bonds and hydrophobic interactions, and a solvent mixture containing 1% SDS and 1% ME. As soy proteins exhibit a steep salting out at low salt concentrations (Shen, 1981), the suspensions were not buffered.

Hydration and analysis of the hydrates extrudates

One hundred and seventy-five g of distilled water was added to 25 g of material in a 300 × 409 mm can, and the contents heated in a water bath or a steam retort for 1 hr. The heated samples were cooled and allowed to equilibrate for 16 hr at ambient temperature. The pH was measured with a combined glass electrode. The can contents were drained, the solid residue re-weighed, and water regain calculated as the percentage increase in weight. Texture measurements, using an Instron (model 1140) were made on the rehydrated material with an Ottawa Texture Measuring System (OTMS), having a nine wire grid and 30 cm^2 base. A crosshead speed of 50 mm/min and a chart speed of 100 mm/min were used. The peak force was recorded. The drained liquor was filtered through Whatman No. 4 filter paper, and the protein content of the filtrate determined by a micro-Kjeldahl technique.

Carbohydrate content of the filtered soya flour liquor was determined by the manual Klegg anthrone procedure (Osborne & Voogt, 1978). The original carbohydrate content was taken as 30% (Table 1) in the calculation of % solubilities:

$$\% \text{ carbohydrate} = \frac{A \times 200}{0.3 \times 25} \times 100\%,$$

Where A = g carbohydrate (as glucose)/ml filtrate.

Results

Extrusion data

Table 2 shows typical differences in the extrusion data for the two feed materials. Though the products had similar expansion ratios the honeycombed structure of the isolate was far more irregular (Fig. 1).

Table 2. Typical extrusion data for soya flour and soya isolate*

	Product temp. (°C)	Pressure (Pa)	Torque (Nm)	Expansion ratio	Mass flow (g/min)
Soya flour	166.0	1.90×10^6	16	1.92	96
Soya isolate	168.2	1.61×10^6	14	1.95	68

*Details in text. Though there was some variation in the results obtained from different 'runs', the same general trend was observed.

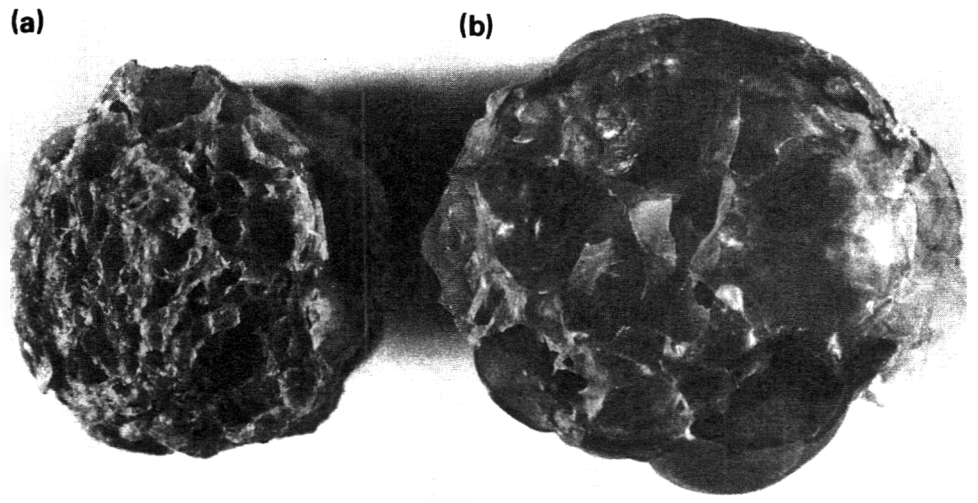

Figure 1. Typical structure of (a) extruded soya flour and (b) soya isolate.

Solubility studies

The solubility data for soya flour and soya isolate are shown in Figs 2 and 3. It is seen that the flour and isolate behave in much the same way with regard to solubility in the three solvents. When used together, SDS and ME have a synergistic effect on the solubility of extruded soy proteins, suggesting that both disulphide and hydrophobic interactions serve to stabilize the extrudates. Also, as the concentration of extrudate in the solvent increases, there is a noticeable decrease in the percentage of protein solubilized.

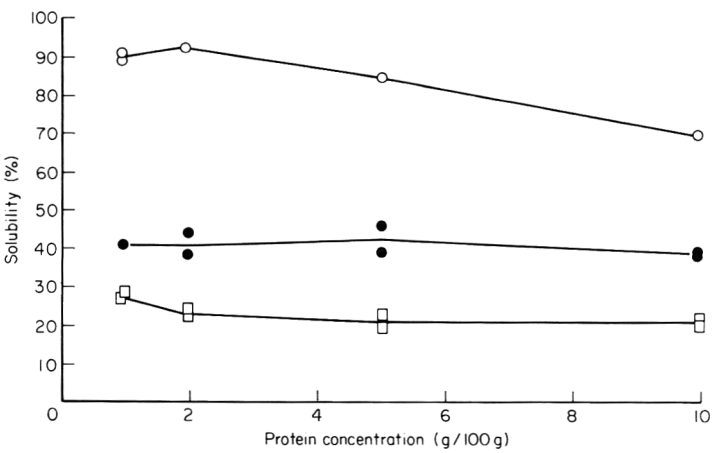

Figure 2. Percent protein solubilized by 1% SDS (●). 1% ME (□) and 1% SDS + 1% ME (○) in extruded soya flour as a function of the protein concentration.

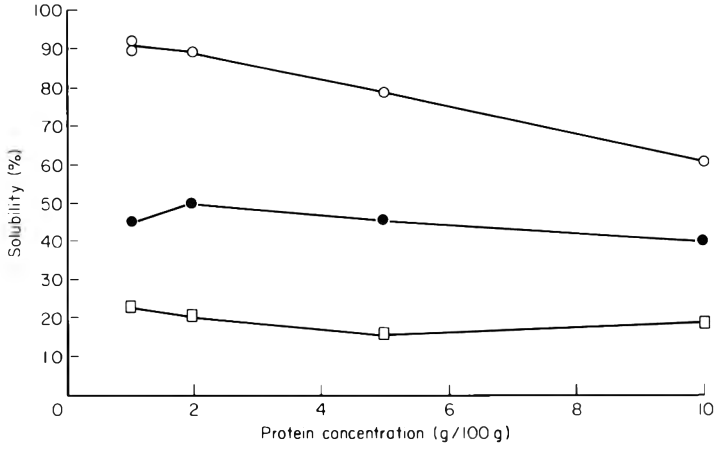

Figure 3. Percent protein solubilized by 1% SDS (●), 1% ME (■) and 1% SDS + 1% ME (O) in extruded soya isolate as a function of the protein concentration.

Analysis of the hydrates extrudates

Figures 4–8 show the variation of OTMS texture, soluble protein, soluble carbohydrate, water regain and pH with temperature of hydration, for the extrudates.

Below hydration temperatures of 100°C, it can be seen that soya flour has the lower peak force (Fig. 4), and a correspondingly higher protein solubility (Fig. 5), though the situation is reversed at higher hydration temperatures, with the isolate having the lower peak force and higher solubility. Correlation coefficients between texture and solubility were −0.97 for the flour and −0.98 for the isolate.

It is seen from Figs 6–8 that water regain, carbohydrate solubility and pH of the hydrated soy flour extrudates all show a marked minimum at hydration temperatures between 20 and 60°C. Above hydration temperatures of 60°C, water regain and carbohydrate solubility both increase with temperature whilst the pH steadily decreases. No such effects are apparent in the extruded soya isolate.

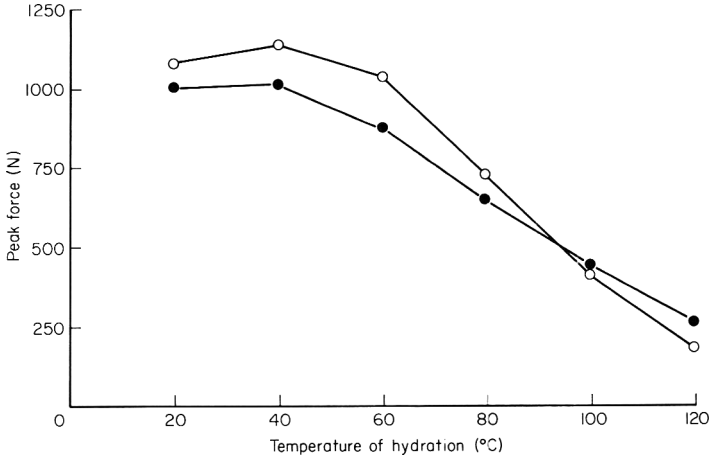

Figure 4. Variation of texture with temperature of hydration for extruded soya flour (●) and soya isolate (O).

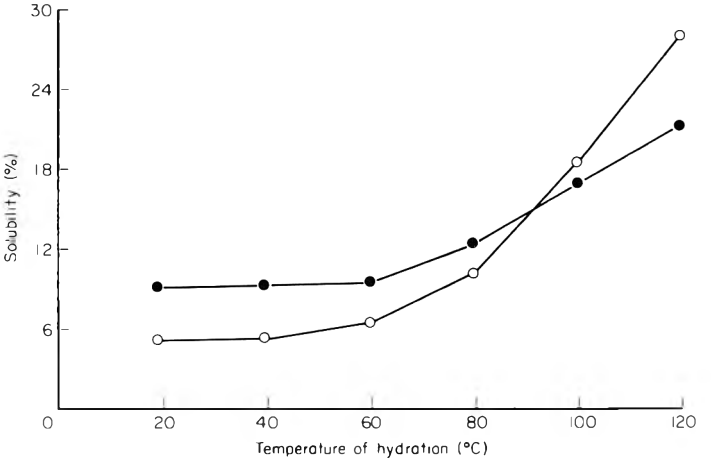

Figure 5. Percent protein solubilized for extruded soya flour (●) and soya isolate (O) hydrated at temperatures up to 120°C.

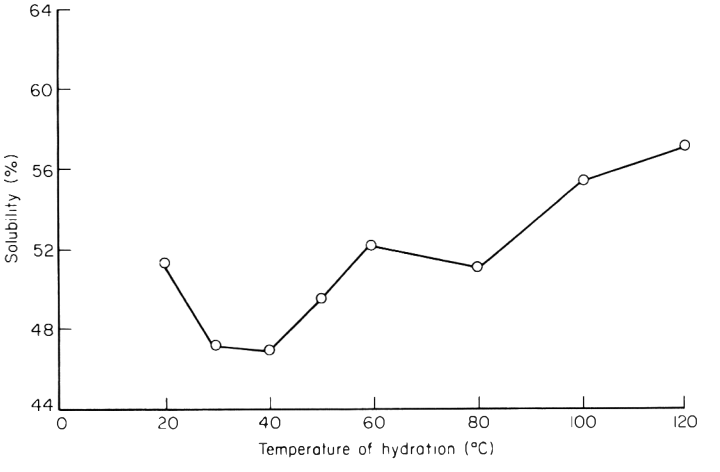

Figure 6. Percent carbohydrate solubilized for extruded soya flour hydrated at temperatures up to 120°C.

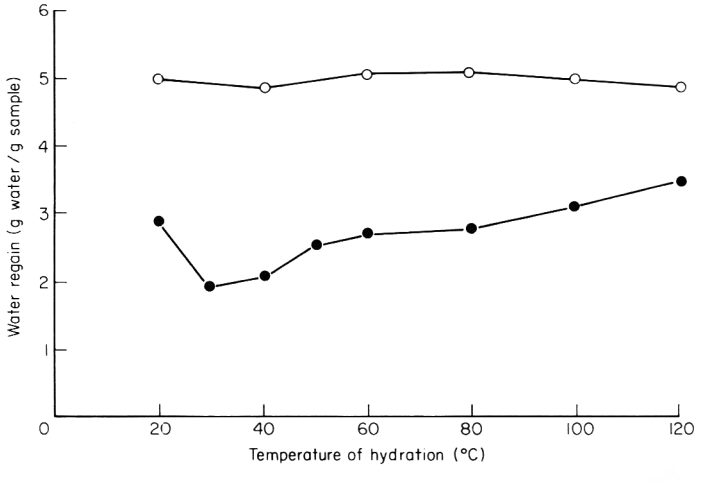

Figure 7. Water regain for extruded soya flour (●) and soya isolate (O) at hydration temperatures up to 120°C.

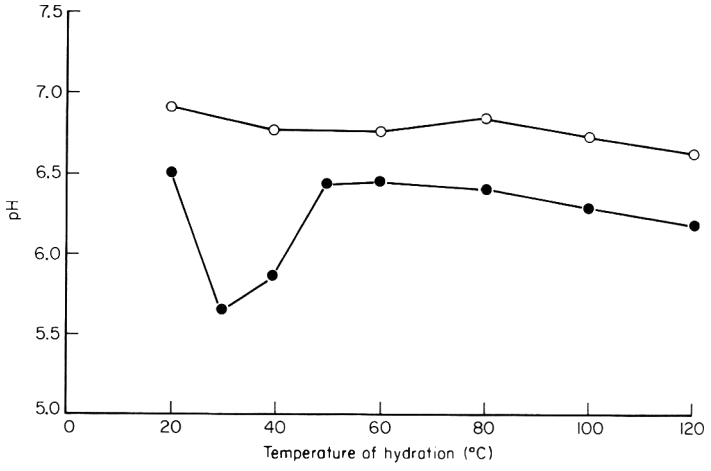

Figure 8. Variation of pH with hydration temperature for extruded soya flour (●) and soya isolate (O).

Effect of ninhydrin

Solubility in SDS and Me, of extrudates prepared from soya flour and soya isolate moistened with ninhydrin solution prior to extrusion, is shown in Table 3. It is seen that the solubility in all three solvents is decreased compared to control samples moistened with distilled water.

Table 3. Percent protein solubility of soya flour and soya isolate extrudates moistened with ninhydrin prior to extrusion*

Solvent	Extruded flour	'Ninhydrin' flour	Extruded isolate	'Ninhydrin' isolate
% SDS	44	28	50	24
1% ME	24	20	20	15
1% SDS + 1% ME	92	66	89	61

*Protein solubilities were obtained with 2 g of extrudate in a total weight of 100 g.

Discussion

Though there are clear differences between extruded soya flour and soya isolate in terms of their morphology (Fig. 1) and the extrusion behaviour (Table 2), little can be deduced from this information concerning the molecular changs that occur within the extruder. The differences are presumably due to the carbohydrate component present in the flour but not the isolate, though there are other differences between the two starting materials, such as protein solubility, which could conceivably affect extrusion behaviour and morphology.

The solubility data show subtle, but not major differences between the two extrudates. They are alike in having about 20% of the total protein soluble in ME, 40–50% soluble in SDS, and 70 to about 90% (depending on the total protein concentration) soluble in the combined solvents. It is also readily apparent that percentage solubility depend on the amount of protein added to the solvent. Shen (1981) explains,

in terms of the thermodrnamic requirements for solubility, the difficulties in comparing results obtained by different methods. This concentration dependence of solubility may be a significant cause of confusion in the literature regarding the effectiveness of different solvents in solubilizing soya extrudates.

However, the present results do show that there is a synergistic effect between SDS and ME, suggesting that both disulphide and hydrophobic interactions play an important role in stabilizing the extrudate. It may well be that disulphide interchange initially orientates and aggregates the protein in the extruder and the hydrophobic interactions form later and further stabilize the extrudate.

It also seems unlikely that covalent linkages (other than disulphide bonds) are involved in the stabilizing of soy proteins texturized by extrusion, since almost 100% solubility can be obtained by dissolving 1 g of sample in 99 g of solvent containing 1% SDS and 1% ME.

This conclusion refutes the idea—proposed initially by Burgess & Stanley (1976) and more recently by Simonsky & Stanley (1982)—that intermolecular peptide bonds are involved in the stabilization of extruded soy protein. Because ninhydrin resulted in a product lacking in alveolate morphology, these authors proposed that ninhydrin was successful in competing with potential peptide forming groups. However, the reduced solubility found for extrudates prepared from ninhydrin treated feeds (Table 3) argues against the involvement of peptide linkages, as the presence of ninhydrin should inhibit the formation of such bonds in the products. It seems more likely that ninhydrin affects the molecular changes that occur within the extruder, by modifying the charge distribution, and this in some way results in a product which is less soluble in SDS and ME than the untreated samples.

It is apparent from Fig. 4 that the 'texture' of the extrudate becomes less tough with increasing temperature of hydration. The decrease in toughness is mirrored by an increase in the amount of protein solubilized during hydration (Fig. 5). Although relatively stable at the lower temperatures the solubilization of the protein in hot ($> 60°C$) water suggests that some protein–protein interactions must be broken. It is believed that the strength of hydrophobic interactions decreases at temperatures above 50°C (Kinsella, 1982) and thus the temperature dependence of protein solubility supports the importance of these forces in maintaining the integrity of the extrudates. It is readily apparent that the carbohydrate containing extrudates are less sensitive to hydration temperature than those containing no carbohydrate (Figs 4 and 5). It may be that, in some way, the embedded carbohydrate effectively stabilizes the more labile hydrophobic interactions or gives rise to additional stabilizing forces. Microscopic work shows this carbohydrate to be embedded in a matrix of protein (Coomaraswamy & Flint, 1973). Taranto, Kuo & Rhee (1981), using transmission light microscopy and transmission electron microscopy, have shown that the bulk of the soluble carbohydrate material can be removed by aqueous extraction with little effect on morphology, whilst the insoluble carbohydrate appears to be an integral part of the microstructure.

Tentative support for the hypothesis that the carbohydrate increases the hydrophobic stabilization of extrudates is afforded by the observation that soya flour extrudates exhibit a phenomenon between 20 and 60°C, characterized by minimum hydratability, pH and carbohydrate solubility. This phenomenon is not shown by extruded soya isolate. The protein in the extrudates must already be denatured and, thus, the effect of temperature of rehydration on their properties must relate to the protein–solvent and protein–protein interactions in the swollen matrix and not to any major conformational change. Most bonds will become weaker with increasing tem-

perature, whereas up to 60°C hydrophobic interactions become stronger, and thus, if hydrophobic interactions are of major importance in the extrudate, the minimum in water uptake at 40–50°C is not unexpected. If the above suggestion is valid, the virtual absence of these minima in the extrudates prepared from the soya isolate, indicates that the presence of the carbohydrate must be a key factor in their formation. It may be that on raising the temperature, the carbohydrate serves to further 'cement' the protein chains together by hydrophobic forces, leading to decreased water uptake and carbohydrate solubility as the temperature is increased to 50°C. At higher temperatures as the hydrophobic interactions and, possibly, other interactions become weaker the expected increase in these properties will occur.

The marked changes in pH observed in these systems indicate that the charge on the protein is modified as these interactions increase (and decrease) in strength, but the reason for this must await further study.

In the light of these differences between soya flour and soya insolate, it is envisaged that the carbohydrate components in soya flour modify the properties of the proteinaceous melt within the extruder. The resulting product consists of carbohydrate material embedded in a matrix of protein, morphologically dissimilar from soya isolate in having a more uniform distribution of air cells.

Acknowledgments

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Effect of heat treatment on the dietary fibre contents of potato and tomato

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Summary

The effects of autoclaving at 100, 120 and 130°C, baking in an oven, and microwave heating on the dietary fibre (DF) content and composition of potato and tomato were studied at normal pH and after acidification. The fibres were fractionated by sequential hydrolysis, and the sugar compositions were determined by gas chromatography (a modification of Englyst's method). All heat treatments appeared to increase the total DF content of the potato; the fraction analysing as 'cellulose' showed the major change, which was probably due to the retrogradation of starch. Autoclaving, especially at 130°C, reduced the total DF of tomato, while baking increased it. Excessive autoclaving may have hydrolysed some of the water soluble non-cellulosic polysaccharides (w.s. NCP), and solubilized a part of the water insoluble (w.i.s.) NCP. Baking increased the w.i.s. NCP and cellulose fractions, in particular. Slight acidification caused only minor additional changes in the fibre fractions.

Introduction

The physiological effects of dietary fibre are probably closely related to the physico-chemical properties of this heterogeneous group of compounds. Food processing operations, such as heat treatment and adjustment of pH may change the chemical characteristics and solubility of indigestible polysaccharides in foods. Consequently, detailed knowledge of these changes is required when estimating the effects of fibre in prepared foods and diets.

In potato, both neutral and acid detergent fibres are known to increase on cooking (Johnston & Oliver, 1982). Boiling increases the solubility of pectic substances of potato by degrading galacturonan chains (Hughes, Faulks & Grant, 1975; Keijbets, Pilnik & Vaal, 1976). Cooking also decreases the quantity of water insoluble fibre substances in various other vegetables (Ooraikul, Packer & Hadziyev, 1974; Hughes *et al.*, 1975; Schrumpf & Charley, 1975). The proportions of neutral and acid detergent fibres and cellulose in the dry matter of carrots, cabbage and broccoli increase with cooking time (not incuding the substances dissolved in the cooking water) (Mattheè Appledorf, 1978). However, no great losses of fruit or vegetable fibre are evident in household food preparation or in commercial processing (Zyren *et al.*, 1983).

In this study, the effects of different heat treatments at normal and low pH on the dietary fibre (DF) composition of potato and tomato were analysed in detail using a modification of Englyst's (1981) sequential hydrolysis method.

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Materials and methods

Random 20 kg samples of potatoes (cv. Rekord) and tomatoes (cv. Sonato) were purchased from a local retail market. The heat treatments (Table 1) were autoclaving under three different sets of conditions (corresponding to those of normal boiling, normal pressure cooking and excessive pressure cooking), baking in an oven, and a microwave treatment. All three autoclaving treatments were done at the normal pH of the sample materials (potato 6.0 and tomato 4.2) and at a lowered pH (potato 4.2, and tomato 3.0).

Table 1. Heat treatment of potato and tomato

	Temperature (°C)	Time (min)	
		Potato	Tomato
Autoclaving 1*	100	35	20
Autoclaving 2	120	15	25
Autoclaving 3	130	100	100
Baking (oven)	200	50	50
Microwave oven†	(2450 Hz)	9‡	4

*Santasalo-Sohlberg 1–32 food processing autoclave.
†Bauknecht-Termidor, 650 W.
‡Potatoes immersed in water.

Precooking operations

Potatoes were washed but not peeled. Tomatoes were homogenized in a disintegrator (Rietz RP-6) using a 1.3 mm sieve. The slurry was steam blanched for 3 min to inactivate the enzymes. The unblanched control slurry was quickly frozen and stored at −40°C.

Cooking

Potatoes were autoclaved in airtight tins (400 ml) in distilled water (normal pH) or in buffer solution (lowered pH), baked uncovered on aluminium foil, or microwave treated in beakers. Tomato slurry was autoclaved in airtight tins (200 ml), baked in uncovered square pans, or microwave treated in beakers.

Postcooking operations

The unopened potato and tomato tins were stored at 4°C, while the baked and microwave treated samples were stored in polyethylene bags at −20°C until analysed (2–7 weeks). The potatoes were peeled and mashed in a blender (Bamix) for analysis.

Fibre analysis

Extractions and hydrolyses. The analytical method followed that published by Englyst (1981) with minor modifications (Laine, Varo & Koivistoinen, 1981). Available carbohydrates were not analysed. The sample, containing about 200 mg dry matter, was extracted with sodium acetate buffer (pH 5, 5 hr, 90°C, 25 ml), hydrolysed with amyloglucosidase (16 hr, 45°C), and centrifuged. Water soluble non-cellulosic poly-

saccharides (w.s. NCP) were precipitated from the supernatant (5 ml) with ethanol (20 ml) and hydrolysed with H_2SO_4 (0.5 M). The original water insoluble (w.i.s.) precipitate was sequentially hydrolysed with 0.5 M H_2SO_4 (2.5 hr) and cold 72% H_2SO_4 (24 hr) to dissolve w.i.s. NCP and cellulose, respectively. The residue, Klason lignin, was determined gravimetrically.

Sugar compostions. The sugar composition of w.s. and w.i.s. NCP were determined by gas chromatography (glc) from the freeze-dried hydrolysates as aldonitrilo acetates on 3% OV-225 (Morrison, 1975). A quantitative mixture of rhamnose, arabinose, xylose, mannose, glucose, galactose and inositol was used as an external standard, and myo-inosital as an internal standard. Cellulose was determined photometrically as hexoses using anthrone-thiourea reagent (Roe, 1955).

Uronic acids. The uronic acids were determined colorimetrically from the hydrolysates of w.s. and w.i.s. NCP using the carbazole method of Bitter & Muir (1962). The error caused by hexoses was corrected by subtracting an empirical term (0.16 times the amount of hexoses) from the experimental value.

Reporting the results. The average number of replicate extractions and analyses was six per sample, and the values reported are means of these determinations. Sugar compositions are reported on the anhydro basis, and fibre values as polysaccharides.

Results

The influence of thermal treatment at the two pH levels, normal and acidified, on the fibre composition of potato is given in Table 2 and that of tomato in Table 3. Total DF in untreated potato was 6.8% of dry matter. All treatments increased total DF, most changes being statistically significant. The maximum value was 10.9% (130°C, pH 4.2). Total DF in untreated tomato was 23.2%, and autoclaving reduced it, the minimum being 18.6% (130°C, pH 4.2). Baking in an oven increased the total DF in tomato to 26.0% d.m., while microwave treatment did not cause significant changes.

Table 2. The effect of heat treatment on the dietary fibre composition* of potato (% of dry matter as polymers; s.d. in parentheses)

	Normal pH (6.0)					Lowered pH (4.2)				
	NCP					NCP				
Treatment	*n*	w.s.	w.i.s.	Cellulose	Total DF	*n*	w.s.	w.i.s.	Cellulose	Total DF
Raw	9	1.3 (0.1)	3.6 (0.7)	1.9 (0.1)	6.8 (0.9)					
100°C	7	2.3 (0.2)‡	3.5 (0.2)	3.5 (0.1)‡	9.3 (0.5)‡	4	2.0 (0.2)‡	2.9 (1.1)	3.6 (0.1)‡	8.5 (1.3)†
120°C	6	1.9 (0.1)‡	3.8 (0.4)	3.2 (0.1)‡	8.9 (0.6)‡	4	1.2 (0.1)†	2.2 (0.2)‡	3.4 (0.1)‡	6.8 (0.4)
130°C	4	1.5 (0.1)‡	4.5 (0.1)‡	4.3 (0.1)‡	10.3 (0.4)‡	2	1.4 (—)	4.6 (—)	4.9 (—)‡	10.9 (—)‡
Baking	5	1.6 (0.2)‡	2.8 (0.3)‡	3.4 (0.1)‡	7.8 (0.6)†					
Microwave	5	1.5 (0.2)	4.0 (0.1)	3.2 (0.1)‡	8.7 (0.4)‡					

*Lignin was detected only in trace amounts.
†Significantly different ($P < 0.05$) from raw potato.
‡Significantly different ($P < 0.01$) from raw potato.
NCP = non-cellulosic polysaccharides, w.s. = water soluble, w.i.s. = water insoluble, DF = dietary fibre.

Table 3. The effect of heat treatment on the dietary fibre composition of tomato (% of dry matter as polymers; s.d. in parentheses)

	Normal pH (4.2)						Lowered pH (3.0)					
	NCP						NCP					
Treatment	*n*	w.s.	w.i.s.	Cellulose	Lignin	Total DF	*n*	w.s.	w.i.s.	Cellulose	Lignin	Total DF
Raw	6	9.8 (0.8)	3.1 (0.2)	7.1 (0.5)	3.2 (0.8)	23.2 (2.3)						
100°C	5	10.9 (0.5)†	3.4 (0.4)	6.3 (0.1)†	2.3 (0.7)	22.9 (1.7)	5	10.1 (0.6)	3.0 (0.2)	6.3 (0.1)†	2.6 (0.5)	22.0 (1.4)
120°C	8	10.4 (0.5)†	2.8 (0.2)*	6.8 (0.2)	2.3 (0.8)	22.3 (1.7)	9	9.8 (0.5)	2.6 (0.2)†	6.7 (0.1)	2.8 (0.9)	21.9 (1.7)
130°C	3	8.0 (0.3)†	2.2 (0.2)†	6.5 (0.0)*	1.9 (0.6)	18.6 (1.1)†	7	7.3 (0.6)†	2.1 (0.1)†	7.0 (0.3)	2.9 (0.7)	19.3 (1.7)†
Baking	8	10.3 (0.5)†	4.1 (0.5)†	8.0 (0.4)†	3.6 (0.6)	26.0 (2.0)*						
Microwave	4	10.2 (0.2)*	3.8 (0.2)†	7.2 (0.2)	2.7 (0.8)	23.9 (1.4)						

*Significantly different ($P < 0.05$) from raw tomato.
†Significantly different ($P < 0.01$) from raw tomato.
NCP = non-cellulosic polysaccharides, w.s. = water soluble, w.i.s. = water insoluble, DF = dietary fibre.

Table 4. The effect of heat treatment on the composition* of potato w.s. NCP (% of dry matter as anhydrosugars)

	Normal pH (6.0)						Lowered pH (4.2)					
Treatment	*n*	ara	glu	gal	uro	total (s.d.)	*n*	ara	glu	gal	uro	total (s.d.)
Raw	9	0.1	0.2	0.5	0.5	1.3 (0.1)						
100°C	7	0.2	0.2	1.2	0.7	2.3 (0.2)	4	0.2	0.1	1.1	0.6	2.0 (1.3)
120°C	6	0.2	0.2	1.3	0.3	1.9 (0.1)	4	0.1	0.1	0.6	0.4	1.2 (0.4)
130°C	4	0.1	0.1	1.2	0.2	1.5 (0.1)	2	0.1	tr	1.1	0.2	1.4 (—)
Baking	5	0.1	0.1	0.8	0.6	1.6 (0.2)						
Microwave	5	0.1	0.1	0.7	0.5	1.5 (0.2)						

*Xylose and mannose were detected only in trace amounts.

ara = arabinose, xyl = xylose, man = mannose, glu = glucose, gal = galactose, uro = uronic acids, tr = traces.

Table 5. The effect of heat treatment on the composition* of tomato w.s. NCP (% of dry matter as anhydrosugars)

	Normal pH (4.2)							Lowered pH (3.0)						
Treatment	*n*	ara	man	glu	gal	uro	total (s.d.)	*n*	ara	man	glu	gal	uro	total (s.d.)
Raw	6	0.7	tr	0.3	2.2	6.6	9.8 (0.8)							
100°C	5	0.7	tr	0.2	2.0	8.0	10.9 (0.5)	5	0.5	tr	tr	1.5	8.1	10.1 (0.6)
120°C	8	0.5	0.1	0.2	2.0	7.4	10.4 (0.5)	9	0.3	tr	tr	1.8	7.7	9.8 (0.5)
130°C	3	0.2	0.1	0.1	2.3	5.3	8.0 (0.3)	7	0.3	tr	0.2	1.8	5.0	7.3 (0.6)
Baking	8	0.6	0.2	0.2	1.6	7.7	10.3 (0.5)							
Microwave	4	0.6	tr	0.2	2.0	7.4	10.2 (0.2)							

*Xylose was detected only in trace amounts.
See Table 4 for abbreviations.

Lignin was not observed in any of the potato samples. Potato cellulose increased very significantly in all treatments, and most in the excessive autoclaving at 130°C. Water insoluble NCP was distinctly increased only in the excessive autoclaving, while w.s. NCP increased during boiling and returned to the original level with the excessive autoclaving. Baking and microwave treatment of potato seemed to cause fewer changes than autoclaving.

Table 6. The effect of heat treatments on the composition* of potato w.i.s. NCP (% of dry matter as anhydrosugars)

	Normal pH (6.0)							Lowered pH (4.2)						
Treatment	*n*	ara	xyl	glu	gal	uro	total (s.d.)	*n*	ara	xyl	glu	gal	uro	total (s.d.)
Raw	9	0.2	0.1	2.0	1.2	0.1	3.6 (0.7)							
100°C	7	0.1	0.1	2.8	0.5	tr	3.5 (0.2)	4	0.1	tr	2.5	0.3	tr	2.9 (1.3)
120°C	6	0.1	0.1	3.4	0.3	tr	3.8 (0.4)	4	0.1	tr	1.9	0.3	tr	2.2 (0.4)
130°C	4	0.1	tr	4.1	0.2	tr	4.5 (0.1)	2	0.1	0.1	4.3	0.1	tr	4.6 (—)
Baking	5	0.1	tr	1.9	0.7	0.1	2.8 (0.3)							
Microwave	5	0.2	0.1	2.7	1.0	tr	4.0 (0.1)							

*Mannose was detected only in trace amounts.
See Table 4 for abbreviations.

Table 7. The effect of heat treatment on the composition of tomato w.i.s. NCP (% of dry matter as anhydrosugars)

	Normal pH (4.2)								Lowered pH (3.0)							
Treatment	*n*	ara	xyl	man	glu	gal	uro	total (s.d.)	*n*	ara	xyl	man	glu	gal	uro	total (s.d.)
Raw	6	0.4	0.6	0.5	0.7	0.7	0.1	3.1 (0.2)								
100°C	5	0.4	0.6	0.7	1.0	0.7	0.1	3.4 (0.4)	5	0.3	0.5	0.5	0.9	0.6	0.2	0.3 (0.2)
120°C	8	0.3	0.4	0.5	0.8	0.6	0.2	2.8 (0.2)	9	0.2	0.4	0.5	0.9	0.5	0.2	2.6 (0.2)
130°C	3	0.2	0.4	0.5	0.7	0.4	0.1	2.2 (0.2)	7	tr	0.3	0.3	1.1	0.3	0.1	2.1 (0.1)
Baking	8	0.5	0.5	0.5	1.5	0.8	0.3	4.1 (0.5)								
Microwve	4	0.5	0.5	0.6	1.3	0.8	0.2	3.8 (0.2)								

See Table 4 for abbreviations.

Lignin and cellulose contents of autoclaved tomato samples were smaller than those of untreated tomato. Water insoluble NCP fell following treatment at 120 and 130°C. Water soluble NCP was higher at 100 and 120°C, but at 130°C it was very significantly lower than in the untreated tomato. Baking increased the quantities of all constituents. Microwave treatment also significantly increased the NCP values of tomato.

Acidification of the cooking water of potato or the tomato slurry did not have a clear effect of DF. It tended to reduce the NCP values of both potato and tomato, but the differences were generally not statistically significant. No changes in cellulose were observed.

The sugar compositions of potato w.s. NCP are given in Table 4, and that of tomato w.s. NCP in Table 5. It can be seen that galactose increased in all heat treated potato samples, while changes were small in tomato. The concentration of uronic acids in tomato was much higher than that in potato, but the pattern of changes is similar: uronic acid concentration was lowest in the samples autoclaved at 130°C.

Glucose was the main sugar constituent of potato w.i.s. NCP, while the same fraction in tomato was a mixture of nearly equal amounts of several hexoses and pentoses (Tables 6 and 7). In the case of potato, autoclaving increased the amount of glucose and reduced the amount of galactose very significantly. Baking in an oven and the microwave treatment caused only minor changes in the amounts of these sugars. All sugars of tomato w.i.s. NCP were slightly affected by autoclaving. The concentration of w.i.s. uronic acids was very low in both the potato and tomato samples.

Discussion

The total DF content of untreated potato was slightly higher than the mean of a recent collaborative study (Varo, Laine & Koivistoinen 1983), but lower than that reported by Englyst (1981) using the same methodology as in the present study. The effect of heat treatment was also similar to those reported earlier (Englyst, 1981; Johnston & Oliver, 1982; Varo *et al.*, 1983). Dietary fibre was increased more by boiling and pressure cooking than by baking or microwave treatment. The increment in the total DF was due to the increases in both w.i.s. NCP and cellulose. This was evidently caused by retrograded starch, which seems to be partially insoluble in dilute acid.

Autoclaving at lowered pH seemed to cause smaller changes in w.i.s. NCP glucose than autoclaving at normal pH (temperatures 100 and 120°C).The changes in cellulose were nearly the same at both pH values. Different autoclaving conditions tended to cause slight differences in the amounts of potato dry matter but this explains only a small fraction of the observed changes.

The total DF of tomato in the present study was 23.2% d.m. This is within the range reported for tomato in the literature (Salo, 1967; Paul & Southgate, 1979; Englyst, 1981). All the autoclave treatments lowered total DF. However, only the changes at 130°C were statistically significant. Baking increased total DF significantly. This treatment caused considerable drying and scorching of the product, increasing not only the lignin, but also all other fractions. In this study the NCP fractions were of about the same magnitude as those reported by Englyst (1981) or Salo (1967). The changes in the tomato w.s. NCP closely followed those of uronic acid. The amounts of neutral sugars were low, and the trends cannot be seen clearly. The same pattern of changes as seen in the total w.i.s. NCP is also evident in all individual sugars. This suggests that the thermal effect was not selective, but all different molecular species of polysaccharide in this fraction have been affected equally. Tomatoes were treated as a slurry. Thus, there

was no cooking water to be discarded, and the changes are not due to losses of soluble solids.

In potato the character of the changes was different. The increments in w.i.s. DF were mainly due to the increased amounts of glucose from starch. Autoclaving reduced both galactose and arabinose contents in the potato w.i.s. NCP, while the contents were distinctly increased in the w.s. NCP fraction. This suggests that cooking slightly increases the solubility of hemicellulose. A similar phenomenon is indicated in the results for the tomatoes. Drastic autoclaving may also hydrolyse some of the w.s. NCP, as suggested by the downward trend in this fraction with increasing temperature.

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Technical note: Cyanide elimination, chemical composition and evaluation in breadmaking of oven dried cassava peeled root chips or slices

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Introduction

Previous reports have shown that it is possible to prepare acceptable bread containing up to 20% of either fresh cassava (Crabtree, Kramer & Baldry, 1978a,b) or dried cassava flour (Dendy, Clarke & James, 1970; Crabtree, Kramer & Baldry, 1978b). Higher levels of wheat flour substitution could be obtained by using cassava starch rather than flour (Kim & De Ruiter, 1968; Pringle, Williams & Hulse, 1969; Dendy *et al.*, 1970).

In most of these reports little attention has been paid to some factors such as the cassava cultivar used, the effect of plant age on root quality, the loading rate of cassava root pieces or chips per unit of drying surface area and its effects on cyanide losses, etc., which may affect the quality of the cassava product(s) and henceforth the results of the breadmaking evaluations.

The present note describes some preliminary observations on the effect of oven drying at 60°C on cyanide elimination from peeled root thin chips or thick slices, the chemical composition including the starch and sugar contents of the resulting cassava flour, and its evaluation in breadmaking. In addition, a few observations on the chemical composition and cyanide content of root peel, a by-product of the cassava flour processing, were also obtained.

Materials and methods

Processing for cassava flour preparation

Cassava roots from 8 month old plants of a local cultivar (M Col 113) which is classified as a low cyanide containing variety (Gómez *et al.*, 1980) were used in this study. The roots were washed and peeled by hand wth a knife. Peeled roots were immersed in water for approximately 30 min prior to being either cut with a machete into transverse slices of about 1 cm thickness or chipped in a Thai-type chipping machine (Thanh *et al.*, 1979). The dimensions of the chips were not regular and no attempt was made to select them by size. The length, width and thickness of the irregular chips varied from 5 to 10, 2 to 4 and 0.3 to 0.6 cm, respectively.

Fresh peeled root slices or chips were immediately weighed on to load wired-bottom trays, each with an area of 0.54 m^2, with 10.8 kg/tray so that a loading rate of 20 kg/m^2

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was obtained. Four trays with fresh slices and four with chips were intercalated within the oven's cabinet and dried in the forced air electrically heated oven (Despatch Model V-31, Despatch Industries, Minneapolis, Minnesota); a temperature control thermostat was standardized and set at 60°C as the operating temperature. In addition, two trays with irregular root peel pieces, obtained by breaking the peels by hand, were also included in each drying and placed at the lower positions of the oven cabinet. The exact weight of root peel per tray was not measured, but since root peel represented approximately 18% of total root fresh weight, the estimated load per tray was around 7.5–8 kg of fresh root peel giving a loading rate of about 14–15 kg/m^2.

Immediately after spreading the fresh slices, chips and peel pieces onto the trays, samples from each tray were taken for dry matter (DM), cyanide, starch and sugar analyses. Dry matter content was determined by drying the samples to constant weight at 60°C; total and free cyanide were analysed using the enzymic assay (Cooke, 1978) and bound or glycosidic cyanide was estimated by difference. Aliquots of each sample were freeze dried (Model SB5 Chem-lab Instruments Ltd, Hornchurch, Essex) for subsequent analyses of total and reducing sugars by the method described by Cronin & Smith (1979) and starch by the acid hydrolysis method (Blake & Coveney, 1978). Samples of dried slices, chips and root peel were separately ground through a laboratory mill (Cyclone Sample Mill, UD Corporation, Boulder, Colorado) using a 0.5 mm steel screen. Dried ground samples were analysed for the parameters which were determined in the fresh samples using the same methods as previously described. In addition, for each two trays a sample of the dried products was also analysed for its proximate chemical composition by the AOAC (1970) methods.

Each tray was considered as an experimental unit and experimental data were compared using the *t*-test (Steel & Torrie, 1960). Two dryings were performed so that eight values of each parameter for either peeled root slices or chips were statistically analysed.

Breadmaking

Dried peeled root slices and chips were ground and the resulting flour used for breadmaking. The levels of substitution of wheat flour by cassava flour were 10, 15, 20 and 25%. The baker's flour used was about 78% extraction and 12% protein content. The breadmaking formula for 100 g of wheat/cassava flour blend included 6 g sugar, 4 g shortening, 4 g pressed yeast and 2 g salt. The volume of water to be added to the flour blend was increased as the ratio cassava flour/wheat flour increased, and varied between 63 and 65 g. The water addition was controlled so as to give a dough of suitable consistency.

Bread was baked from the wheat/cassava flour blends using a laboratory-type Hobart mixer equipped with a hook blender, by a straight dough method with 90 min fermentation at 30°C and 80% relative humidity. Then the dough was maintained at room temperature for 15 min, moulded mechanically into loaves of 370 g and allowed to ferment for approximately 55 min. The loaves were baked for 25 min at 195°C in a stationary cabinet oven with thermostats for controlling both top and bottom temperatures. The loaf height, weight and volume were measured 24 hr after breadmaking. The specific volumes of the baked loaves were determined by seed displacement. The loaves were scored, using a scale from 0 to 10, for shape, crust appearance and crumb texture.

A few bread samples, one for each of the cassava flour levels at 0, 15 and 20% were analysed for their cyanide (Cooke, 1978) content.

Results and discussion

The proximate chemical composition, the starch and sugar contents of cassava flour prepared by oven drying (60°C) peeled root slices and chips is summarized in Table 1. The moisture, starch, crude fibre and ash contents found in the cassava flour samples analysed fell within the range of specifications for commercial cassava flour following official standards (Ingram, 1975). The crude protein content of cassava flour obtained in this study is slightly higher than values reported for parenchyma (peeled root) tissue of roots of most of the known cassava cultivars (Barrios & Bressani, 1967; Gómez & Valdivieso, 1983; Gómez, unpublished observation). Generally, cassava flour tends to have similar protein content than that of sweet potato flour (De Carvalho *et al.*, 1981) but lower than potato flour (Yañez *et al.*, 1981).

Table 1. Composition of cassava (peeled root) flour

Constituent	%
	on a DM basis
Dry matter	98.2±1.3
Crude protein	4.8±1.3
Ether extract	1.2±0.2
Crude fibre	3.1±0.4
Ash	3.0±0.2
Starch*	78.7±2.4
Reducing sugars*	1.4±0.4
Total sugars*	4.9±1.0

*Each value is the mean of sixteen samples ±s.e., and each remainder value is the mean of eight samples ±s.e.

The peeled roots of the local cultivar M Col 113 contained low cyanide levels (135±29 mg/kg DM; Table 2) confirming previous results (Gómez *et al.*, 1980); most of the cyanide was present as bound cyanide and only 12±4% was found as free cyanide. Drying of cassava slices and chips considerably reduced the cyanide content present in the fresh material, but at the same drying temperature (60°C), loading rate (20 kg/m^2) and drying period (20–22 hr), the cyanide losses were affected by the geometry and size of the cassava peeled root pieces. Thus, oven drying of chips allowed a 72±7% elimination of either total or bound cyanide, whereas in 1 cm thick slices only 49±16% of the initial cyanide content was lost. These results clearly demonstrate the effect of cassava root piece shape and size on cyanide elimination. However, dried slices and chips showed cyanide levels which were low enough to be acceptable as a human food. The amount of total cyanide eliminated was almost entirely accounted for by the hydrolysis of the cyanogenic glucoside, as has also been observed in some drying experiments with whole root chips (Gómez, unpublished observation).

The results of the breadmaking evaluations are summarized in Table 3. The inclusion of cassava flour at levels of 10 and 15% of the wheat/cassava flour blends resulted in bread quality similar to that of the wheat flour. Higher levels (20 and 25%) of cassava flour inclusion led to a slight increase in water absorption but notably to lower

Table 2. The effects of cassava peeled root piece shape on cyanide elimination by oven drying at 60°C and at a loading of 20 kg/m²

Parameter	Slices		Chips
	—	on a DM basis	—
Cyanide in fresh chips†			
Total (mg/kg)	—	135±29	—
Bound (mg/kg)	—	118±26	—
Free (% of total)	—	12± 4	—
Cyanide in dried chips‡			
Total (mg/kg)	61± 5		39±10**§
Bound (mg/kg)	53± 5		33± 9**
Free (% of total)	12± 2		14± 2*
Cyanide losses as % of initial contents			
Total	49±16		72± 7**
Bound	49±16		72± 7**

†Each value is the mean of sixteen samples ±s.e.
‡Each value is the mean of eight samples ±s.e.
§Values were different at $*P < 0.05$ or $**P < 0.01$.

loaf specific volumes and loaf scores as compared to the results with levels of substitution of 10 and 15%. The level of 15% cassava flour inclusion gave a bread-quality which was the closest to that obtained with the wheat flour. These results indicate that cassava flour prepared as described in this study could be incorporated in wheat/cassava flour blends at levels of 10 and 15% and satisfactory bread quality could be obtained.

Only three samples of bread (0, 15 and 20% cassava flour) were analysed for their cyanide content and the results showed total cyanide values of 3.5, 2.5 and 1.9 mg/kg DM, respectively. The free cyanide proportions of the three bread samples were 53, 74 and 92%, respectively. The total cyanide concentrations in bread samples were not significantly different, and even normal bread without cassava flour showed small amounts of cyanide-like reacting components. These low cyanide levels suggest that elimination of the residual cyanide of cassava flour may continue further under the moisture and temperature conditions of the fermentation process used. Since most of

Table 3. Bread assessment of wheat/cassava flour blends

	Cassava flour level (%)				
Parameter	0	10	15	20	25
Water absorption (%)	63	63	63	65	65
Loaf characteristics					
Height (cm)	12.3	12.3	13.5	12.2	11.2
Volume (ml)	1593	1523	1535	1480	1435
Weight (g)	319	320	311	327	325
Loaf specific volume (ml/g)	5.0	4.8	4.9	4.6	4.4
As % of control	100	96	98	92	88
Loaf score					
0–10 scale	9	8	8.5	7.5	6
As % of control	100	89	94	83	67

the promising cultivars produce roots with higher cyanide concentrations than those of roots of local cultivars, research on cyanide elimination and the effects of residual cyanide content in cassava flours on bred quality and nutritional aspects merits special attention.

Table 4 summarizes the chemical proximate composition, the starch and sugar contents as well as the cyanide concentration of dried root peel pieces. Dried peel contained higher levels of crude protein, crude fibre and cyanide than the corresponding cassava flour (Gómez & Valdivieso, 1983; Gómez *et al.*, 1980). Root peel contains a sizeable amount of starch (58.3±2.9% on a DM basis) and sugar levels slightly higher than those of the corresponding root parenchyma tissue. Root peel however, constitutes only 15–20% of the total root fresh weight.

Table 4. Chemical composition and cyanide contents of dried cassava (cv. M Col 113) root peel*

Component	%	
	on a DM basis	
Dry matter	94.2± 0.8	
Crude protein	9.1± 1.9	
Ether extract	2.0± 0.6	
Crude fibre	12.0± 2.1	
Ash	5.0± 0.4	
Starch	58.3± 2.9	
Reducing sugars	2.3± 0.4	
Total sugars	6.8± 1.8	
Cyanide in dried chips		
Total (mg/kg)	444 ±39	(1273±308)†
Bound (mg/kg)	273 ±29	(998±248)
Free (% of total)	39 ± 3	(22± 2)
Cyanide losses as % of initial contents		
Total	64 ± 8	
Bound	72 ± 5	

*Each value is the mean of four samples ±s.e m.

†Values in parentheses correspond to fresh root peel samples.

The cyanide concentration of root peels was higher than that of the parenchyma (Cómez *et al.*, 1980) and oven drying eliminated approximately two-thirds of total and bound cyanide. However, the final cyanide content of dried peel was 4 times the maximum permissible hydrocyanic acid level set by the European Economic Community (cited by Ingram, 1975) as a quality standard for cassava products to be used as animal feeds. The chemical composition and notably the cyanide content of dried peels suggest that further research is needed to ascertain their potential nutritional value as animal feed. This is of special relevance because the root peel of most of the promising cassava cultivars contains considerably higher cyanide levels than the parenchyma (Gómez *et al.*, 1980).

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Technical note: Microbiology of oriental shrimp paste

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Introduction

Traditional oriental methods of preserving fish and other aquatic animals make use of various combinations of salting, drying and microbial fermentation. Those involving some period of anaerobic storage are almost invariable referred to as 'fermentations' in the literature, regardless of whether or not microbial action is known to be implicated. Since improvement and standardization of these products rests upon a thorough understanding of the processes concerned, it is important to distinguish the microbial from the non-microbial ones.

It is well established that many of the fish sauces are primarily autolytic products (e.g. Amano, 1962), and Orejana & Liston (1979) showed that microorganisms play no essential role in the production of Philippine fish sauce. Other products clearly do depend upon microbial acid production for their preservation (e.g. Orillo & Pederson, 1968).

Belacan is a Malaysian preserved shrimp paste, and similar products are made in other South-east Asian countries. Its method of preparation and some properties are described in Steinkraus *et al.* (1983). Ch'ng & Seow (1972) suggested, without experimental evidence, that a mixed bacterial fermentation probably occurred. Steinkraus *et al.* (1983) postulated that the tissues largely undergo enzymatic breakdown, with or without bacterial assistance, and that bacteria play an important role in flavour development. The aim of this work was to examine the properties and microbial flora of belacan in order to identify the role played by microorganisms and the factors important in its preservation. The results suggest that rather than being a product of bacterial fermentation, belacan might better be viewed as a high salt intermediate moisture food.

Materials and methods

Samples

The samples of shrimp paste were obtained from two commercial manufacturers in Malaysia and stored at 5°C until required. The following process descriptions are based on conversations with these manufacturers.

Shrimp paste 1 (wet belacan). The small shrimps (*Acetes* spp.) were caught by local fishermen who mixed the fresh shrimps with salt (information on the exact proportions was not obtained) and packed the mixture in cotton sacks which were hung up to allow excess liquid to drain. The shrimps were then pounded and sold to the belacan

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manufacturer. He sorted the material to remove any foreign matter and small fishes and then packed the partially ground shrimp into a wooden tub, using a pestle to secure tight packing and the elimination of air. The tub was covered with a plastic sheet and stored at ambient temperature (approximately 28–30°C) until further processed for sale (4–5 months in the case of this sample). The plastic sheeting was used without weights to force it into uniform contact with the belacan and consequently surface spoilage is common and results in some surface material being later discarded. When required, paste was scooped out and dried in the sun in thin layers for 2–3 hr, cooled in the shade, pounded further to produce a finer product, pressed into shape and wrapped in polythene film. This type of product is known as wet belacan as only one sun drying is used and the final product is relatively moist.

Shrimp paste 2 (belacan). The manufacturer of this product purchased semi-dried salted shrimps (*Acetes* spp.) from Singapore. No specific information was obtained on their preparation. but the general procedure involves mixing fresh shrimps with approximately 10% (w/w) finely ground salt and drying the mixture in the sun. The period of drying is weather dependent but ranges from 4–5 hr to a few days and is continued until the moisture content is reduced to about 50% w/w. The belacan processor began by mincing the shrimps, with the additon of some water to moisten the slightly overdried shrimps and produce a product of the desired consistency. The minced shrimps were tightly packed into wooden tubs, covered with plastic sheeting and stored for 7 days at ambient temperature. The paste was then taken out and dried in the sun for about 3 hr, after which it was minced again and repacked in tubs. This sequence of anaerobic storage, drying, mincing and anaerobic storage was repeated a number of times (sometimes up to 7) to obtain a product with the desired fine texture. The period of anaerobic storage between dryings did not exceed 3 months to avoid spoilage (presumably due to excessive accumulation of liquid products of autolysis). Once the desired texture was achieved the belacan was pressed and wrapped in polythene for sale.

Shrimp paste 3 (immature belacan). This was sample 2 but had been stored for only 2 weeks.

Chemical and physical methods

Moisture content was determined by drying at 100°C and sodium chloride by ashing at 500°C and titration with 0.1 M silver nitrate (Pearson, 1976). The water activity of samples was measured with a Novasina meter (type DAL20, Novasina, Zurich, Switzerland).

Microbiological methods

Samples of paste were added to 0.1% peptone water diluent (Oxoid L37) and blended in a Colworth stomacher. Further dilutions were prepared in 0.1% peptone water. General viable counts of bacteria were made on yeast glucose lemco agar (Harrigan & McCance, 1976) plus 6% (w/v) sodium chloride. Preliminary trials showed that this concentration of salt yielded higher colony counts than either medium without added salt or medium with 12% salt. Lactic acid bacteria were enumerated on MRS agar (Oxoid) and on Keddie's acetate-free Tween agar (Varnam & Grainger, 1973). Malt extract agar (Oxoid CM59), without added salt, was used for fungi. Cultures were

incubated in air at 30°C except for the Tween agar cultures which were incubated anaerobically (Oxoid gas generating system). Total microscopic counts of bacteria were done by Breed's smear method (Harrigan & McCance, 1976).

Results and discussion

The results of the analyses made are shown in Table 1. The values for moisture content, salt content and microbial flora are in the ranges reported in Steinkraus *et al.* (1983). A brief examination of the colonies obtained indicated that a diversity of bacterial types was present—also a feature noted in Steinkraus *et al.* (1983). The numbers of viable bacteria were very low in all the samples in comparison with the numbers encountered in truly bacterial food fermentations, where populations of the order of 10^8–10^9 CFU/g are normal (e.g. Orillo & Pederson, 1968). That these microbes did not merely represent the survivors of an earlier much higher population is shown by the microscopic counts of bacterial cells, which, though higher than the viable counts, are not sufficiently high to suggest the previous existence of a vigorous bacterial fermentation. Merrican (cited in Steinkraus *et al.* (1983) reported viable bacterial counts for semi-dried shrimps that are similar to those obtained here for immature and mature belacan. The near neutral pH values of the pastes, which are little changed from those of the starting materials, shows that no significant amount of acid had been formed during the process. It is, therefore, hard to escape the conclusion that the bacteria present in belacan are more likely to be survivors of the natural flora of the shrimps, or contaminants that grew up before the shrimps were dried and salted, than to have grown in the shrimp paste.

Table 1. Characteristics and microbial flora of shrimp pastes

Analysis	Wet belacan	Immature belacan	Mature belacan
Moisture (%)	47	51.5	33.3
Sodium Chloride (%)	13	ND*	20.2
pH value	6.8	7.5	7.0
Water activity	0.71	0.73	0.67
General viable count (CFU/g)	8.0×10^4	5.0×10^5	3.6×10^4
Lactic acid bacteria (CFU/g)			
on MRS medium	< 10	< 10	< 10
on Tween medium	3.5×10^2	4.5×10^2	2.5×10^3
Moulds (CFU/g)	8.0×10^1	1.1×10^2	6.0×10^1
Microscopical bacterial count (cell/g)	5.3×10^6	5.3×10^6	4.2×10^6

*Not determined.

The water activities of the wet belacan and belacan samples were in the range where no bacteria are able to grow, though there are some fungi that can grow at these low values (Nickerson & Sinskey, 1972). However, only very low numbers of fungal propagules were detected in plate counts and none were seen in the microscopic examinations. Since the dried shrimps starting material for the belacan also offers an unfavourable environment for bacterial growth, it is evident that, so long as the mixture remains homogeneous, bacteria cannot play a significant role in the conversion of shrimps into belacan. In the case of the wet belacan sample, differences in the method

of preparation and the lower salt content might suggest the possibility of greater microbial development, but the results show that this had not, in fact, occurred.

It is unfortunate and quite misleading, therefore, to refer, as is commonly done (e.g. Steinkraus *et al.*, 1983), to the process as a fermentation. The manufacture of belacan is almost certainly a purely enzymatic process where the product is maintained in a paste consistency by periods of sun drying to evaporate water produced from the autolysis of shrimp tissues. Thus, shrimp or fish pastes of the belacan type are better categorized as high salt intermediate moisture foods and the use of the term 'fermentation' should be avoided. This would encourage future research to be directed to understanding the enzymatic processes rather than towards futile searches for roles for microorganisms.

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Technical note: Correlation of BET monolayer moisture content in foods with temperature

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Introduction

It is well known that despite the theoretical limitations of the BET adsorption analysis, the BET monolayer concept is a reasonably correct guide with respect to various aspects of interest in dried foods. Among these, the mobility of small molecules in food systems, the correlation of BET monolayer with the total number of polar groups binding water, and the correlation with the physical and chemical stability of dried items (Karel, 1973; Almási, 1979) are of particular importance. Several authors (Kumar, 1974; Almási, 1979) but mainly Iglesias & Chirife (1976) noted that the monolayer values in foods and food systems decrease significantly with increasing temperature. It is the purpose of the present communication to show that a simple equation may be used to quantitatively correlate such dependence of BET values with temperatures.

Villota, Saguy & Karel (1980) recently developed an equation correlating shelf life of dehydrated vegetable products with temperature and used a function in which the BET monolayer moisture content was taken into account. The model postulated was

$$\ln t_f = a_0 + a_1(1/T) + a_2(m - X_m), \quad (1)$$

where t_f = time of failure; T = temperature of storage; m = moisture; X_m = monolayer moisture content; a_0, a_1, a_2 = constants. Villota *et al.* (1980) recognized that BET values are temperature dependent and consequently the value to be used in equation (1) should be that corresponding to the storage temperature (T). This temperature correction for the BET monolayer can be easily performed with the equation developed in the present work.

Results and discussion

The BET values for different food systems at various temperatures were taken from the literature, as indicated. The mathematical model postulated to correlate BET values with temperature was:

$$\ln X_m = \beta + \alpha T, \quad (2)$$

where, X_m is BET monolayer moisture content (g water/100 g dry solid), T is temperature (°C), and β and α are constants. A plot of $\ln X_m$ *versus* T should be a straight line from which the parameters β and α may be calculated. A least squares analysis was used to obtain the values of the parameters β and α which are shown in Table 1 for various foods and food systems. Table 1 also indicates the range of

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Table 1. Application of equation (1) to various food materials

	Temperature range (°C)	α	β	r^*	$n^\dagger$	$(\epsilon\%)_{av.}$	Ref.
Starchy foods							
Corn (D)	4.5–60	−0.0086	2.18	0.9789	6	2.9	(a)
Potato (A & D)	10–80	−0.0042	1.91	0.9919	4	2.4	(b)
Sorghum (A)	4.2–32.2	−0.0052	2.11	0.9965	3	0.5	(c)
Starch gel (A)	0–50	−0.0091	2.41	0.9926	6	1.7	(d)
Wheat flour (A)	20.2–50.2	−0.0056	1.98	0.9987	4	0.4	(e)
Wheat starch (A)	20.2–40.8	−0.0028	2.00	0.9561	3	0.7	(e)
Proteins and protein foods							
Beef, raw (A)	30–50	−0.0176	2.39	0.9968	3	1.1	(d)
Chicken, cooked (A)	5–60	−0.0137	2.08	0.9813	3	5.7	(f)
Chicken, cooked (D)	5–60	−0.0145	2.21	0.9945	3	3.2	(f)
Chicken, raw (A)	5–60	−0.0143	2.20	0.9939	3	3.3	(f)
Chicken, raw (D)	5–60	−0.0142	2.23	0.9916	3	3.9	(f)
Eggs, dried (A)	17.1–70	−0.0021	1.34	0.9882	4	0.53	(g)
Fish protein conc. (A)	25–42	−0.0042	1.77	0.9936	3	0.21	(h)
Gelatin gel (A)	10–40	−0.0200	3.0	0.9995	5	0.63	(d)
Trout, cooked (A)	5–60	−0.0174	2.24	0.9999	3	0.14	(f)
Trout, raw (A)	5–60	−0.0149	2.14	0.9998	3	0.68	(f)
Turkey (D)	0–22	−0.0138	2.18	0.9979	3	0.76	(i)
Fruits							
Banana (A)	25–60	−0.0181	1.87	0.9796	3	5.0	(f)
Peach (A)	30–50	−0.0229	2.85	0.9999	3	0.11	(d)
Pineapple (A)	25–60	−0.0282	3.67	0.9994	3	1.4	(f)
Vegetables and spices							
Anise (A)	5–45	−0.0072	1.61	0.9991	3	0.45	(f)
Cardamom (A)	5–60	−0.0114	2.05	0.9995	3	0.77	(f)
Celery (A)	5–60	−0.0042	1.77	0.9828	3	0.21	(f)
Chamomile tea (A)	25–60	−0.0217	2.37	0.9995	3	0.85	(f)
Cinnamon (A)	5–45	−0.0133	2.14	0.9999	3	0.23	(f)
Cinnamon (D)	5–45	−0.0161	2.39	0.9936	3	2.8	(f)
Coriander (D)	5–45	−0.0122	2.04	0.9699	3	4.7	(f)
Ginger (D)	5–45	−0.0139	2.20	0.9826	3	4.0	(f)
Laurel (A)	5–60	−0.0164	1.91	0.9971	4	2.0	(f)
Nutmeg (A)	5–60	−0.0121	1.78	0.9793	4	4.8	(f)
Nutmeg (D)	5–45	−0.0128	1.91	0.9881	3	3.1	(f)
Onion (A)	10–45	−0.0185	2.06	0.9999	3	0.12	(j)
Paranut (A)	5–60	−0.0128	0.8736	0.9966	3	2.2	(f)
Peppermint tea (A)	25–60	−0.0214	2.47	0.9956	3	2.7	(f)
Horse radish (A)	5–60	−0.0124	2.11	0.9647	4	5.7	(f)
Sweet marjoram (A)	5–60	−0.0200	1.98	0.9961	4	3.6	(f)
Sweet marjoram (D)	5–45	−0.0218	2.14	0.9941	3	3.6	(f)
Thyme (A)	5–60	−0.0112	1.79	0.9936	4	2.4	(f)
Thyme (D)	5–45	−0.0166	2.02	0.9991	3	1.1	(f)
Various							
Dextrin (A)	10.7–39.7	−0.0076	2.04	0.9999	3	0.14	(k)
Yoghurt (A)	5–45	−0.0138	1.73	0.9969	3	1.6	(f)

(A): adsorption; (D): desorption.

*Correlation coefficient.

†Number of observations

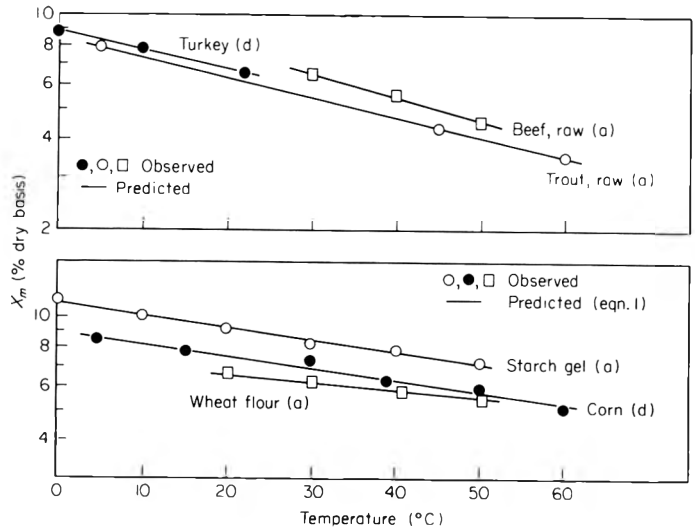

Figure 1. Predicted and observed BET values at different temperatures for some selected foods: (a) adsorption; (d) desorption.

temperatures over which equation (1) was applied as well as the correlation coefficient (r) and the average percent error—$(\epsilon\%)_{av.}$—defined as:

$$(\epsilon\%)_{av.} = \left[\sum_{i=1}^{n} \frac{|(X_m)_{pred.} - (X_m)_{obs.}|}{(X_m)_{obs.}} \right] \times \frac{100}{n}. \quad (3)$$

It can be seen that equation (1) describes very well the temperature dependence of BET monolayer moisture contents—$(\epsilon\%)_{av.}$ is mostly below 5%—for a large variety of foods in the approximate temperature range of 5–60°C (depending on the product tested). The food materials studied comprised thirty-seven different items including starchy foods, proteins and protein foods, some fruits, vegetables and spices. The results obtained suggest that the proposed equation (1) may be a useful tool for studies requiring estimation/correlation of BET values with temperature. It is to be noted that the relative effect of temperature on BET values is very different for different foods. For example BET values in some fruits (banana, pineapple, peach) decrease by about 21–35% between 25 and 40°C, while in eggs the decrease is only 3% over the same temperature interval. Fruits, however, have type-III isotherms for which the determination of BET values may be somewhat uncertain (Iglesias & Chirife, 1976). The relative variation of BET values with temperature depends on the physico-chemical nature of the food (Iglesias & Chirife, 1976); however, the time needed to reach sorption equilibrium may also have affected the results. In turn, the equilibrium–time dependence is determined by the experimental device utilized to determine the isotherm. In some cases equation (1) failed to reproduce the behaviour of BET values with temperature. These cases included sugar beet root, avocado, egg plant, radish,

References:
(a) Chen & Clayton (1971).
(b) Gane (1950).
(c) Chen (1971).
(d) Saravacos & Stinchfield (1965).
(e) Bushuk & Winkler (1957).
(f) Wolf, Spiess & Jung (1973).
(g) Makower (1945).
(h) Rasekh, Stilling & Dubrow (1971).
(i) Kirg, Lam & Sandall (1968).
(j) Mazza & Le Maguer (1978).
(k) Volman *et al.* (1960).

active dried yeast, lentil, mushrooms and some spices. Most of these items have type-III isotherms.

Figure 1 shows a plot of predicted *versus* observed BET values at different temperatures for some meats and starchy foods. It seems that the relative effect of temperature in BET values for the foods within each group (meats or starchy) is approximately the same.

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Book Reviews

The Psychobiology of Human Food Selection. Edited by Lewis M. Barker. Chichester: Ellis Horwood, 1982. Pp. xviii+262. ISBN 0 85312 542 2. £18.00.

The psychobiology of human food selection is a bewilderingly complex subject and there is a genuine need for a text which provides a broad overview. Although this compilation volume gives a detailed insight into some of the multitude of factors that interact to determine human food choice, it does not provide an overview, and therefore may only be of limited interest to a general food science and technology readership. There are thirteen chapters which are organized into three sub-sections as follows: Part 1. Biological aspects of human food selection: (1) biological basis of food selection (L. M. Beidler, 13 pp.); (2) diet, performance and their interaction (P. O. Åstrand, 16 pp.); (3) brain mechanisms involved in feeding (E. T. Rolls & B. J. Rolls, 30 pp.). Part 2. Psychological determinants of food choices: (4) how nutritional effects of foods can influence people's dietary choices (D. A. Booth, 18 pp.); (5) building memories for foods (L. M. Barker, 16 pp.); (6) the influence of variety on human food selection and intake (B. K. Rolls, E. T. Rolls & E. A. Rowe, 22 pp.); (7) the synergistic properties of pairs of sweeteners (J. C. Smith, D. F. Foster & L. M. Bartoshuk, 16 pp.); and (8) social determinants in human food selection (M. Krondl & D. Lau, 14 pp.). Part 3. Sociocultural factors in human feeding behavior: (9) choice and occasion: sweet moments (S. W. Mintz, 13 pp.); (10) food behavior and biocultural evolution (S. H. Katz, 18 pp.); (11) the structure of cuisine (E. Rozin, 15 pp.); (12) geography and genetics as factors in the psychobiology of human food selection (F. J. Simoons, 20 pp.); and (13) human food selection: the interaction of biology, culture and individual experience (P. Rozin, 30 pp.).

Each of the three sub-sections begins with a brief introduction which helps to orientate the reader. In Part 1, Chapter 1 describes the innate attraction between some animals and sweet tasting molecules. Chapter 3 is particularly valuable in that it provides a comprehensive treatise of the complex brain mechanisms involved in feeding. However, the sheer weight of information contained in this chapter, combined with rather specialist vocabulary, make it difficult to assimilate in one sitting. Chapters 4, 5 and 6 in Part 2 lucidly describe a very important role for flavour in food selection; it is seemingly the medium through which an organism remembers and hence predicts the metabolic consequences of ingesting a particular food. A chapter dealing specifically with hunger, appetite and satiety would have complemented this section of the book. In Part 3, Chapters 10 and 12 provide a fascinating insight into the origins of cultural food habits. Chapters 9, 11 and 13 contribute something to the general theme, but all seemed unnecessarily protracted.

Although the general theme is evident throughout most of the chapters, some of the authors seem to digress onto marginal issues. Indeed, Chapter 7 is almost entirely at a tangent to the main theme.

The book is attractively presented, the typeface is bold and legible and there are few typographical errors. Diagrams and tables abound and are generally well produced,

although some of the legends could have been more precise. Most of the chapters are well documented and include up to date references. The index is adequate.

This book is unique and, if only for this reason, is of intrinsic value to those interested in food acceptability and choice.

David M. H. Thomson

Chemistry and Biochemistry of Legumes. Edited by S. K. Arora. London: Edward Arnold, 1983. Pp. ix+359. ISBN 0 7131 2854 2. £19.50.

Starchy legumes have an important role in human nutrition, particularly in the less developed countries of the world, where diets are largely vegetarian. However, even in the developed world, legumes are being advocated for consumption as part of a 'healthful diet'. Increasing the intake of these foods, at the expense of other high protein components of the diet, such as meat and dairy produce, would increase the amount of dietary fibre and, at the same time, reduce fat intake.

In the past, much research has been carried out on the leguminous oilseeds, particularly soyabean, and several excellent books have been written on this subject. There is now a considerable literature related to the composition and nutritional value of raw and processed starchy legumes. However, to date few reviewers have been published on this topic, so from this point of view the publication of this book is timely.

The book contains eight chapters dealing with starchy legumes, with only a brief reference to soyabeans. Each chapter is written by a specialist in the field and the following topics are covered: carbohydrates, lipids, storage proteins, non-protein nitrogeneous compounds, toxic constituents, minerals, nutritive value and genetic improvement. Each topic is dealt with in depth as would be expected for an intended readership of research workers and postgraduate students.

On the whole, each topic has been treated comprehensively. However, in the chapter on carbohydrates by Dr Arora considerably space is devoted to the industrial application to guar gum, with perhaps too little attention to starch. Although specific dietary fibre components are all dealt with, the term dietary fibre is not used, and no reference is made to current medical interest in this area.

In the chapter on lipids by Dr Salunkhe and his colleagues there are comprehensive tables on the lipid content and composition of a wide range of food legumes. However, as so often happens when dealing with species of the *Leguminoseae* family, some confusion has arisen over nomenclature. For example, in one table, both cowpea and black-eye bean are given as separate species (showing different values for fatty acid composition), when they are both common names for *Vigna unguiculata* (L.) Walp. Perhaps a summary table of common and botanical names at the beginning or end of the book would have improved this aspect.

The chapter on storage proteins by Drs Mossé and Pernollet gives detailed descriptions of all aspects of the protein composition of legumes, together with some excellent, rarely published scanning electron micrographs of the cotyledons of starchy grain legumes. However, this chapter would have benefited from firmer editing of the English, a second language of the authors.

The book is well laid out, clearly printed and well referenced, with titles of articles included, which greatly increases their usefulness. However, in some chapters the

references are not as up to date as might be expected for a book published in 1983. In addition, the index would have been easier to use if subjects had not been grouped under major headings, which can make them difficult to find. Despite these minor points, the book is a useful, if not unique, reference source for all those concerned with the composition of grain legumes.

Ann F. Walker

Milk and Dairy Products in Human Nutrition, 4th ed. By E. Renner. München: Volkswirtschaftlicher Verlag, 1983. Pp. 450. ISBN 3 87875 011 0.

To say that this book is an excellent source of references would be an understatement. Not only is the text crammed with names and dates, but around 168 of 450 pages are devoted entirely to reference lists at the ends of the ten chapters.

The author has certainly been thorough and efficient in the collection of information about milk and dairy products in human nutrition. What is lacking in the style of writing (or more likely the vagaries of the translation), is more than compensated for by the factual material extracted from the thousands of papers which the author had to consult to compose the lectures on which his book is based.

The book was first published in 1974 in German, and this fourth edition, translated into English, has been completely revised and updated to include many of the controversial debates concerning milk and milk products. The ten chapters include comprehensive reviews of the nutritional properties of the constituents of milk; milk protein; lactose; minerals and trace elements in milk; vitamins in milk; enzymes, hormones and organic acids in milk; the role of milk products in nutrition; cultured milk products and butter; cheese, and evaporated, condensed and dried milks.

Milks from different species of mammals occupy unique positions among all the foods that are consumed because they are the sole source of energy and nutrients during the early part of life.

The production of cow's milk is vitally important throughout the world, not only as a major source of nutrients in the diet of man, but because of its economic, political and social significance. The book explores these issues in depth in terms of the contribution of milk to growth and development in man, in addition to providing a balanced account of the links between the various milk components and milk consumption and the aetiology of the degenerative diseases. The modifications of cows' milk to resemble mothers' milk, and the use of modern technology in the processing of milk and the manufacture of milk products are also discussed.

There is an extensive index enabling the reader to find what he requires quickly, and the text and figures are clear and precise. The hardback book will be extremely useful to students and professional scientists, as well as those engaged in production, marketing and distribution. Food scientists, technologists and nutritionists will find this text invaluable, and the book will appeal to agricultural scientists, paediatricians and doctors concerned with nutrition.

The stated aim of the book is to outline the role that milk and milk products play in a complete and balanced diet. The author has succeeded in achieving his objectives, and the review chapters in the book fill a necessary gap in the already extensive literature. In conclusion, the book is highly recommended as a key source of information.

D. P. Richardson

Hydrogenation of Fats and Oils. By H. B. W. Patterson.
Barking, Essex: Applied Science, 1983. Pp. xv+310. ISBN 0 85334 201 6. £38.00.

This book offers a thorough coverage of the chemical and technological aspects of the subject, dealing with the reactions, process data, hydrogen and catalysts, safety and quality control. A valuable major section also details the procedures used in the hydrogenation of specific oils and fats and the applications for the products.

Process operators and research and development scientists and engineers in this field, as well as food technologists working with the products in food formulation or processing, will find this a welcome text and a good source of reference. Its appeal should extend well beyond the U.K. as there are very few texts of this kind in this field. Perhaps that is partly because the author's experience as a plant manager handling a very diverse range of raw matrials must be almost unique.

The book is written in a clear, attractive style, which makes it difficult to put down—one wishes that this could be said of more technical material nowadays! It is packed with numerical data and process detail including carefully compiled information on chemical compositions and physical characteristics of the products. There is a good reference list but it might have been more up to date in some areas. For example, the author still quotes the third edition (1964) of 'Bailey', though the fourth edition (1979–1982) has been around for some time.

At the risk of exposing a special interest, this reviewer wonders why the author has so little to say about the nutritional, and possibly toxicological, aspects of hydrogenated oils and fats. Essential fatty acids do get a cursory mention (pp. 279–280) but recent work implicating *trans* fatty acids as prostaglandin antagonists, and linolenic acid as a true essential fatty acid (to say nothing of the long chain polyunsaturated acids in marine oils), calls for more comment. In view of the enormous research effort that has gone into improvement of selectivity it is disappointing that such substantial amounts of isomerized polyunsaturated fatty acids still turn up in products.

These, however, are minor comments on what, by any standards, is a timely and valuable text.

B. J. F. Hudson

Sanitation in Food Processing. By John A. Troller.
New York: Academic Press, 1983. Pp. xiii+456. ISBN 0 12 700660 5. U.S. $34.50.

This book is intended as a guide to food process sanitation (i.e. food processing hygiene) for food scientists working in this area, and as a primary text for university and other courses which include food hygiene in their curricula. It is based on the author's extensive experience in industrial food sanitation.

There are nineteen chapters. After a short introduction, five chapters are devoted to food plant sanitation programs, food plant design and construction, process equipment, and cleaning. Aspects such as design for hygiene, CIP systems, criteria for choosing

detergents and sanitizers are briefly covered in this section. There is one chapter on microbial growth in foods, in which there is an attempt in twenty pages to give an elementary account of the morphological, biochemical and ecological characteristics of micro-organisms. The next two chapters are concerned with food borne diseases and their prevention, and personal hygiene. Chapters 9–12 cover pests—insects, rodents and birds. Chapters 13–16 deal with packaging, food storage, transportation, and water. Chapter 17 looks at the opportunities for airborne contamination, and Chapter 18 deals with raw materials, their specifications, inspection and storage. The final chapter discusses U.S. food laws and regulations. There are four short appendices listing such things as the addresses of U.S.F.D.A. district offices and, U.S.F.D.A. factory inspection forms. There is also a twenty-four page index and a short list of references provided at the end of each chapter.

The chapter on microbial growth in foods is perhaps the least satisfactory feature of the book, and contains a number of errors of commission and omission. For example, in commenting that 'from the food sanitarian's point of view, the lag, or resting, phase . . . and the logarithmic phase . . . are the primary determinants of the number of organisms present', reference is made to a figure purporting to show a bacterial growth curve, but in which the lag phase is not shown, and the logarithmic, stationary and decline phases are labelled 'resting phase', 'logarithmic phase' and 'maximum stationary phase' respectively! Spores of bacteria and of moulds are referred to, but there is no mention of the differences in their responses to heat, drying, chemical disinfectants, etc., which one would have thought to be of great importance in food hygiene. After commenting that "traditional" total counting procedures for bacteria are unsatisfactory for the enumeration of moulds; consequently, this subject is treated separately', only twelve lines of text on this topic follow with merely brief mention of the enumeration of moulds by plate counts using acidified agar media and of the Howard mould count, without any reference to the problems of correlating a plate count of moulds with cell mass when a colony may result from a conidiospore, a small hyphal fragment or a much larger hyphal fragment, and the consequent problems of interpreting data obtained by preparing homogenized suspensions and dilutions of foods carrying fungal colonies.

There is an uneasy literary style which on occasions makes it difficult for the reader to follow the author's line of argument. For example, the introductory section of the chapter on food borne diseases appears to be both self-contradictory and at odds with the later material in the chapter. I was surprised by this, since a previous work by the author and J. H. B. Christian (*Water Activity and Food*, also in Academic Press's *Food Science and Technology Series of Monographs*) was a model of clarity and concise writing. Occasional typing and editorial errors occur (e.g. on page 289 — 'automatic chlorination of can-cooling water is required to prevent bacterial buildings'), and the word 'cidal' is coined when lethal would have been adequate.

However, very many worthwhile points are made in the book which one hopes will stay in the memories of students using the book. For example, comments are made on the inadvisability of using hot air hand driers in food process areas because of the possibility of contaminating food with dust blown off the floor, and on the tendency for the wearing of gloves by food handlers to promote 'a kind of complacency that is not conducive to good hygienic habits'. Furthermore, there are relatively few books comprehensively covering all the aspects of food hygiene found in this book, so its publication is to be welcomed.

W. F. Harrigan

Quality Control in Foodservice, revised edition. By Marvin E. Thorner and Peter B. Manning.
Westport, Conn.: AVI, 1983. Pp. xi+366. ISBN 0 87055 431 X. U.S. $32.50.

Quality Control in Foodservice describes inspection and control procedures which enable maintenance of quality standards in catering operations. It is claimed by the authors to be a text book or training manual for all categories of personnel in the Foodservice (catering) Industry and includes sections on sampling of raw materials, their storage, control of cooking methods, food spoilage and sanitation, energy management, and maintenance of equipment.

Inevitably perhaps, such broad treatment is instructional rather than educational. Material is presented in the form of lists of recommendations, methods and standards with limited explanation and no references in the body of the text. More importantly, and as in previous editions, quality control is not discussed in the context of productivity and profitability in catering operations. The perceived relevance of the text to practising caterers is thus diminished and this is made worse by the fact that all standards and specifications quoted are American, as are the names of equipment and food materials used as examples.

At a time when the attention of the Catering Industry and of Catering Education is focussed on the whole 'catering product', not just food and beverages but also style of service, eating environment and atmosphere, and the control of quality in each of these areas, the food production-centred approach of this text seems strangely dated. A further curiosity is that when the role of quality assurance in catering operations is well accepted, and evidenced in the fast food chain, the brand images created by hotel groups, the theme restaurants developed by brewery companies, and in the market orientated response of institutional and industrial catering to the current economic climate, *Quality Control in Foodservice* remains the only text book in this area.

Clive Robertson

Nicotinic Acid: Nutrient—Cofactor—Drug. By Murray Weiner and Jan van Eys.
New York: Marcel Dekker, 1983. Pp. x+308. ISBN 0 8247 7015 3. U.S. $66.00.

The authors' preface states that this book 'organises and correlates the available information about nicotinic acid and metabolically related compounds in a manner designed to be useful to students, research scientists and medical practitioners' and that they have placed emphasis on 'correlating rather than cataloging data'. However, there is little critical evaluation of the literature cited. A great many very old papers are quoted, and the conclusions drawn by the original authors are recited without regard to the changes in knowledge during the last 50 years.

It is distressing to read, in relation to the hypothesis of a pellagragenic toxin '... two unretracted claims in the *recent* literature' (my italics), and then to discover that these are the papers of Woolley in 1946 and Borrow *et al.*, in 1948. The authors do not discuss the more recent suggestion that some of the carcinogenic mycotoxins may be pellagragenic as a result of their activation of poly-ADP-ribose polymerase and the consequent depletion of tissue nicotinamide nucleotides. A later chapter does discuss this enzyme in the context of DNA repair and the regulation of nucleic acid metabolism.

Much of the biochemistry in this book is confused and difficult to follow. Indeed, had I not spent the last 5 years working on the oxidative metabolism of tryptophan, I do not think that I would have understood the description of this pathway at all. On the front cover (and in the text) thiamin is shown involved in tryptophan oxygenase, and riboflavin in kynurenine hydroxylase activities! It is not only in biochemistry that the authors make curious statements; at one point five papers are cited to back up the statement that 'it has also been considered that corn is difficult to digest . . . these undigested fragments make the intestinal bacteria more virulent'—the references cited here span the period 1887–1903!

I am not sure that we need to be treated to a relatively long discussion of the early work on the determination of the essential amino acids; but even so, should not the list in 1983 include histidine, and at least a mention of the need for arginine in the growing child? When tryptophan requirements are discussed, the authors appear to be surprised that the requirement per unit body weight falls at lower intakes of total N. Surely this follows logically since the requirement of any essential amino acid is as a proportion of protein intake.

In a specialist monograph, I would hope to find an extensive critical review of areas of controversy, yet the evidence of the pellagragenic action of a dietary excess of leucine is dismissed in a couple of lines as being 'not uniformly accepted'.

The more directly clinical area of 'nicotine acid as a drug' (the last quarter of the book) is very much better covered that the nutrition and biochemistry of the vitamin. There is a good discussion of the hypolipidaemic, fibrinolytic and vascular actins of nicotinic acid, as well as a comprehensive survey of its pharmacokinetics and pharmacodynamics.

The book has been produced by use of a relatively crude typesetting system that has left ragged unjustified right hand margins and some unnatural breaks in words at the ends of lines. This would be acceptable if the price were significantly lower than $66, or if publication had been rapid, yet the book seems to be at least 3 years out of date, with no references later than 1980, and indeed relatively few for the late 1970s. There are a number of typographical errors, including some very distorted names of well known workers in the field (apparently the result of transcription of handwritten notes), and there is one reference to '*J. Biochim. Biophys. Acta* **000:** 000 (0000)'—a challenge to any librarian!

David Bender

Food Microbiology: Advances and Prospects. By T. A. Roberts and F. A. Skinner. London: Academic Press, 1983. Pp. xiv+394. ISBN 0 12 589670 0. £29.95.

This book comprises the Proceedings of the Annual Summer Symposium of the Society for Applied Bacteriology held at the University of Bristol in 1981. Since it was the occasion of the 50th Anniversary of the Society, which originated in dairy microbiology and was formerly named the Society of Agricultural Bacteriologists, it was very appropriate that the subject of the Symposium should be 'Food Microbiology; Advances and Prospects'. Contributors had been asked both to review progress in their field since the Symposium on Food Microbiology held 10 years previously at the University of Bristol ('Microbial Changes in Foods', reported in the *Journal of Applied Bacteriology* (1971) **34,** 1–213) and to look into a crystal ball and predict possible future trends. An

interesting continuity was provided by four of the contributors in 1981, (A. C. Baird-Parker, R. H. Dainty, B. Jarvis and D. A. A. Mossel) also having been contributors in 1971. The twenty invited contributions which appear as chapters in this book give an extremely comprehensive coverage of the subject. The chapters are: Essentials and perspectives of the microbial ecology of foods (D. A. A. Mossel); Food borne infections and intoxications—recent trends and prospects for the future (R. J. Gilbert); Mechanisms of action of food preservation procedures (G. W. Gould, M. H. Brown & B. C. Fletcher); Predictive modelling of food safety with particular reference to *Clostridium botulinum* in model cured meat systems (T. A. Roberts and B. Jarvis); Developments in heat treatment processes for shelf-stable products (P. G. Bean); New interest in the use of irradiation in the food industry (F. J. Ley); New methods for controlling the spoilage of milk and milk products (B. A. Law and L. A. Mabbitt); Microbial and chemical changes in chill-stored red meats (R. H. Dainty, B. G. Shaw & T. A. Roberts); Microbial spoilage of cured meats (G. A. Gardner); Effect of packaging and gaseous environment on the microbiology and shelf life of processed poultry products (G. C. Mead); Microbial spoilage of fish (G. Hobbs); Microbial ecology of prepared raw vegetables (P. C. Koek, Y. de Witte & J. de Maaker); New prospects and problems in the beverage industry (F. W. Beech & R. R. Davenport); Properties of and prospects for cultured dairy foods (K. M. Shahani & B. A. Friend); Fermented fish and meat products: the present position and future possibilities (Inger Erichsen); Genetic engineering for food and additives (J. R. Pellon & A. J. Sinskey); Potential for fermentation processes in the food supply (D. C. Bull & G. L. Solomons); Sampling programmes for the microbiological analysis of foods (D. C. Kilsby & A. C. Baird-Parker); Guidelines, specifications and standards for foods (B. Simonsen); and Food microbiology into the twenty-first century—a Delphi forecast (B. Jarvis). In addition there are abstracts of twenty-two papers and posters presented at the Symposium.

It can be seen from the titles, and it is also evident in the content of the contributions, that the authors had taken seriously the request of the Symposium organizers, and most were not afraid to give their opinions on the directions likely to be taken by food microbiologists in their subject area and of the possible problems and tasks awaiting us in the years to come. Only one or two contributors failed to meet this 'end-product specification'.

The final chapter giving the findings of a Delphi forecast based on questionnaires completed by thirty randomly chosen practising food microbiologists provided interesting reading even though there were few surprises in the forecasts. However, the prediction that by the end of the century a licence to practise based on academic qualifications and appropriate practical experience would be required for food microbiologists and persons involved in food inspection services may provide some comfort to students, as this would lead to an increase in the observed status of food microbiologists!

In addition to being packed with facts and data concerning the investigations and technological developments of the 1970s, this book time and time again proves to be thought provoking. This volume is worth a place in every food microbiologist's personal library.

W. F. Harrigan

Handbook of Tropical Foods. Edited by Harvey T. Chan.
New York: Marcel Dekker, 1983. Pp. viii+639. ISBN 0 8247 1880 1. SFr. 203.

This is a compilation of monographs on fifteen tropical foods, comprising two grain crops (rice and amaranth), four root crops (aroids, cassava, ginger and yam), five fruits (banana, citrus fruit, guava, mango and papaya), a nut (macadamia) and three kinds of products derived by processing (palm oil, fruit wine and fermented fish). Though it cannot, therefore, claim to be comprehensive, it does include some very important tropical staples as well as economically important cash crops and less developed but potentially valuable food sources.

Each monograph aims at a full treatment, including agronomic, economic, processing and preservation, composition and utilization aspects. The editor's declared intention was 'to unearth and collect the most recent and available knowledge on selected tropical foods'. Such information is not readily accessible. Not being of primary practical interest in developed or temperate parts of the world it tends to be relegated to secondary publications. Nevertheless, it is most important that it should be available in the form in which it is provided in this handbook, not least to make its contribution to the alleviation of Third World hunger and poverty. It should be studied by agronomists, technologists and administrators in the tropics as well as by expatriates concerned with scientific, educational and relief programmes.

Though the standard of presentation is generally good the fifteen chapters vary somewhat in style and content. The palm oil monograph (Berger) goes into great detail as to chemical composition but processing, especially fractionation, is treated lightly. Conversely, the cassava monograph (Odigboh) handles processing technology very thoroughly but is uninformative on biochemical aspects. The outlets and potential for byproducts, an important consideration in ensuring the viability of a food product, deserve more thorough treatment. In the mango chapter (Stafford) the kernels, a source of valuable fat, receive no mention. Perhaps the varying nature of the commodities involved is partly the cause of this lack of uniformity.

The book is well produced and illustrated, though a number of printers' erros have been noted. Referencing is good, if by no means complete, but titles of papers are not always given. The index, which is, in effect, by chapters, is sketchy. At the risk of splitting hairs, the chapter heading 'Palm oil' should be 'Palm oils' because it deals with palm kernel oil as well as palm oil proper. All in all, however, this is a valuable book. Perhaps we may hope for another covering other subjects—e.g. melon, coconut, sugar, tea, sorghum and goat meat?

B. J. F. Hudson

Tomato Production, Processing and Quality Evaluation, 2nd ed. By W. A. Gould.
Westport, Conn.: AVI, 1983. Pp. xii+445. ISBN 0 87055 426 3. U.S. $54.00.

This book covers the breeding, growing, harvesting and processing of tomatoes with particular reference to quality assurance and control procedures. The use of tomato products in recipe foods is only briefly outlined. The author is aiming to provide a summary of principles, technology and methods in the tomato industry for use by students, technologists and management. Because of the wide scope of the book its

treatment of individual topics is too superficial to meet the needs of technologists working in the industry. However, this wide scope and the logical development from topic to topic provides an overview which should be useful to students.

The book is based almost exclusively on U.S.A. conditions and developments. In certain parts this can be confusion to European readers especially those unfamiliar with American practices and standards. An example is the section on mechanical harvesting where hand harvesting is considered to be obsolete. In fact land climatic conditions in many growing areas in Europe are unsuited for the available mechanical harvesters.

In the chapter dealing with genetics and breeding the potential of biotechnology and the impact of cell culture techniques are not discussed. The sections on handling and processing give a good general outline of the steps involved but on several occasions omit reference to the most recently developed equipment. It is surprising that the growing use of aseptic packaging for tomato products is not discussed. Quality assurance control and evaluation are much more comprehensively dealt with than other topics. These sections give a valuable insight into the scope and limitations of quality programmes.

The text is supported by numerous references; however, relatively few are from recent publications and the developments in Europe are largely omitted. The book is well laid out, has few typographical errors and the typeface is highly legible. The illustrations are relevant to the text and the diagrams are clear and easy to follow.

N. G. Hodgson and B. A. Harrison

Errata

Please note the following corrections of errors which occurred in the last issue of the journal.

On page 318, Equation (1) *should* read:

$$m^* = (m - m_\infty)/(m_0 - m_\infty) = 6/\pi^2 \sum_{\kappa=1}^{\infty} \frac{1}{\kappa^2} \exp(-\kappa^2 \pi^2 D\theta/r^2).$$

On page 359, the third paragraph *should* read:

Changes in the composition of the sporulation media have been shown to alter the resistance of *B. subtilis* (NCDO 2130) spores to hydrogen peroxide, peracetic acid, chlorine, heat and UV irradiation (Bayliss, Waites & King, 1981) which may be due to changes in the spore coat properties. The present data indicate that spores of *B. subtilis* SA22 produced on different media show a difference in resistance to peracetic acid and 9.9% (v/v) alcohol/peracetic acid combinations. However the difference was not apparent at all ethanol concentrations.

Finally, the sentence which starts on the last line of page 382 and finishes on the first line of page 383 *should* read:

The chapter on 'Dietary Fibre as a Tool for the Clinician' takes the bold step taken by so few others of recommending a target intake of fibre of 40 g a day.

Corrected.
A.V
23/02/85

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JOURNAL OF FOOD TECHNOLOGY: NOTICE TO CONTRIBUTORS

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Typescripts (three complete copies) should be sent to the Editor, *Journal of Food Technology*, c/o Institute of Food Science and Technology (U.K.), 20 Queensberry Place, London SW7 2DR. Papers should be typewritten on one side of the paper only, with a 1½ inch margin, and the lines should be doubled-spaced. In addition to the title of the paper there should be a 'running title' (for page headings) of not more than 45 letters (including spaces). The paper should bear the name of the author(s) and of the laboratory or research institute where the work has been carried out. The full postal address of the principal author should be given as a footnote. (The proofs will be sent to this author and address unless otherwise indicated.) The Editor reserves the right to make literary corrections.

Arrangement. Papers should normally be divided into: (a) Summary, brief, self-contained and embodying the main conclusions; (b) Introduction; (c) Materials and methods; (d) Results, as concise as possible (both tables and figures illustrating the same data will rarely be permitted); (e) Discussion and conclusions; (f) Acknowledgments; (g) References. Authors should consult the current issue in order to ensure that their manuscript conforms to the Journal conventions on such things as subheadings, layout of tables, etc.

References. Only papers closely related to the author's work should be included; exhaustive lists should be avoided. References in the text should be made by giving the author's surname, with the year of publication in parentheses. When reference is made to a work by three authors all names should be given when cited for the first time, and thereafter only the first name, adding *et al.*, e.g. Smith *et al.* (1958). The '*et al.*' form should always be used for works by four or more authors. If several papers by the same author and from the same year are cited, a, b, c, etc. should be put after the year of publication, e.g. Smith *et al.* (1958a). All references should be brought together at the end of the paper in alphabetical order. References to articles and papers should mention (a) name(s) of the author(s) (b) year of publication in parentheses; (c) title of paper; (d) the title of the journal given in full and not abbreviated, set in italics (underlined once in typescript); (e) the volume number; (f) the first and last page numbers of the paper—e.g.

Steiner, E. H. (1966). Sequential procedures for triangular and paired comparison tasting tests. *Journal of Food Technology*, **1**, 41–53.

References to books and monographs should include (a) name(s) and initials of author(s) or editor(s); year of publication in parentheses; (b) title, underlined; (c) edition; (d) page referred to; (e) place of publication and publisher—e.g.

Lawrie, R. A. (1979). *Meat Science*, 3rd edition. Oxford: Pergamon Press.

In the case of edited multi-author monographs, the editor(s) should be indicated in parentheses after the book title—e.g.

Hawthorn, J. (1980). Scientific basis of food control. In *Food Control in Action* (edited by P. O. Dennis, J. R. Blanchfield & A. G. Ward). Pp. 17–33. Barking, Essex: Applied Science.

Standard usage. The *Concise Oxford English Dictionary* is used as a reference for all spelling and hyphenation. Statistics and measurements should always be given in figures, i.e. 10 min, 20 hr, 5 ml, except where the number begins the sentence. When the number does *not* refer to a unit of measurement, it is spelt out except where the number is one hundred or greater.

Abbreviations. Abbreviations for some commoner units are given below. The abbreviation for the plural of a unit is the same as that for the singular. Wherever possible the metric SI units should be used unless they conflict with generally accepted current practice. Conversion factors to SI units are shown where appropriate.

SI UNITS

gram	g	Joule	J
kilogram	kg = 10^3 g	Newton	N
milligram	mg = 10^{-3} g	Watt	W
metre	m	Centigrade	°C
millimetre	mm = 10^{-3} m	hour	hr
micrometre	μ = 10^{-6} m	minute	min
nanometre	nm = 10^{-9} m	second	sec
litre	l = 10^{-3} m^3		

Chemical formulae and solutions. The correct molecular formula should be used indicating whether the substance is anhydrous or hydrated. Solutions should be given in terms of molarity. The arithmetic basis of other expressions of concentration must be clearly defined.

Species names. In addition to common or trivial names of plants, animals or microorganisms, the species should normally also be indicated by use of the latin binomial at least once. This should be given in full and italicized (underlined once in typescript). In subsequent use, the generic name may be abbreviated to a single letter provided that this does not result in ambiguity.

Figures. In the text these should be given Arabic numbers, e.g. Fig 3. They should be marked on the backs with the name(s) of the author(s) and the title of the paper. Where there is any possible doubt as to the orientation of a figure the top should be marked with an arrow. Each figure must bear a reference number corresponding to a similar number in the text. Photographs and photomicrographs should be unmounted glossy prints and should not be retouched. Line diagrams should be on separate sheets; they should be drawn with black Indian ink on white paper and should be about four times the area of the final reproduction. Lines and lettering should be of sufficient thickness and size to stand reduction to one-half or one-third. Whenever possible, the originals of line diagrams, prepared as described above, should be submitted and not photographs, The legends of all the figures should be typed together on a single sheet of paper headed 'Legends to figures'.

Tables. There should be as few tables as possible and these should include only essential data; the data should not be crowded together. The main heading should be in bold with an Arabic number, e.g. **Table 2.** Each table must have a caption in small letters. Vertical lines should not be used.

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