CONTROL OF NON-ENZYMATIC BROWNING IN THE DEHYDRATION OF FRUITS AND VEGETABLES

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Abstract — The development of potato flakes depended on sulfiting, low sugar content, and antioxidants for the retention of flavor. Flavor deterioration via non-enzymatic browning (Maillard reaction) is commonly experienced in dehydrated foods either during processing or while in storage. Therefore, it is essential to obtain as low a level as possible of Maillard reaction products. In the development of the batch explosion-puffing process for potatoes, non-enzymatic browning became a major flavor and odor problem. A proven and easily adaptable GC method devised by Buttery was used to trace Maillard reaction products throughout the process. By analyzing headspace for selected volatile compounds, it was found that the explosion-puffing step caused most of the browning. The injection of an inert gas in combination with the superheated steam reduced the level of these volatile browning compounds. A trained taste panel could not detect any browning flavor in the potato dice when an inert gas-steam combination was used. When the process was replaced by a continuous-puffing system, better control over the product's thermal history was achieved. By monitoring samples processed through the continuous system, moisture, pressure, and temperature conditions were found in which the inert gas was no longer necessary for potato processing. Apple segments were investigated as a possible dehydrated product. Because apple volatile compounds differ from potato volatiles, gas chromatography was not used. Hydroxymethylfurfural (HMF) formation was followed in order to determine the extent of browning during the processing of apples. When dried apple pieces were passed into the continuous explosion-puffing system at various conditions, the resulting values of HMF correlated well with other factors such as bulk density, disintegration, rehydration and color, and could be utilized in predicting the operating optimum. When carrots were processed, however, a fast, simple method for measuring non-enzymatic browning suggested by Baloch *et al.* (1973) was used. The non-enzymatic browning of the dehydrated carrots was determined by measuring the absorbance at 420 mm of a carrot extract.

INTRODUCTION

Non-enzymatic browning is a major route for the deterioration of fruits and vegetables during dehydration and in storage (Braverman, 1963). In recent years, the Strecker degradation has been recognized as one of the principal paths of this non-enzymatic browning. During the development of a new process for dehydrating potatoes, two of the Strecker aldehydes, 2-methylpropanal and 2- and 3-methylbutanal, were identified as a cause of off-flavors.

Research in the Engineering Laboratory of the Eastern Regional Research Center near Philadelphia, Pennsylvania, is principally on the development of new processes for agricultural material. To have the processes accepted commercially, the products must be competitive. If the product is a food, it must have good color, texture, flavor and nutritional value.

The development of two dehydration processes, with drum drying and explosion-puffing, will be described. In these processes, three of the four quality attributes, color, flavor and nutrient content, are directly affected by non-enzymatic browning. Thus, at sometime during process development, the cost of reduction of non-enzymatic browning must be determined.

Potatoes, apples and carrots required different methods of analysis for measuring non-enzymatic browning. The selected methods were used successfully to determine,

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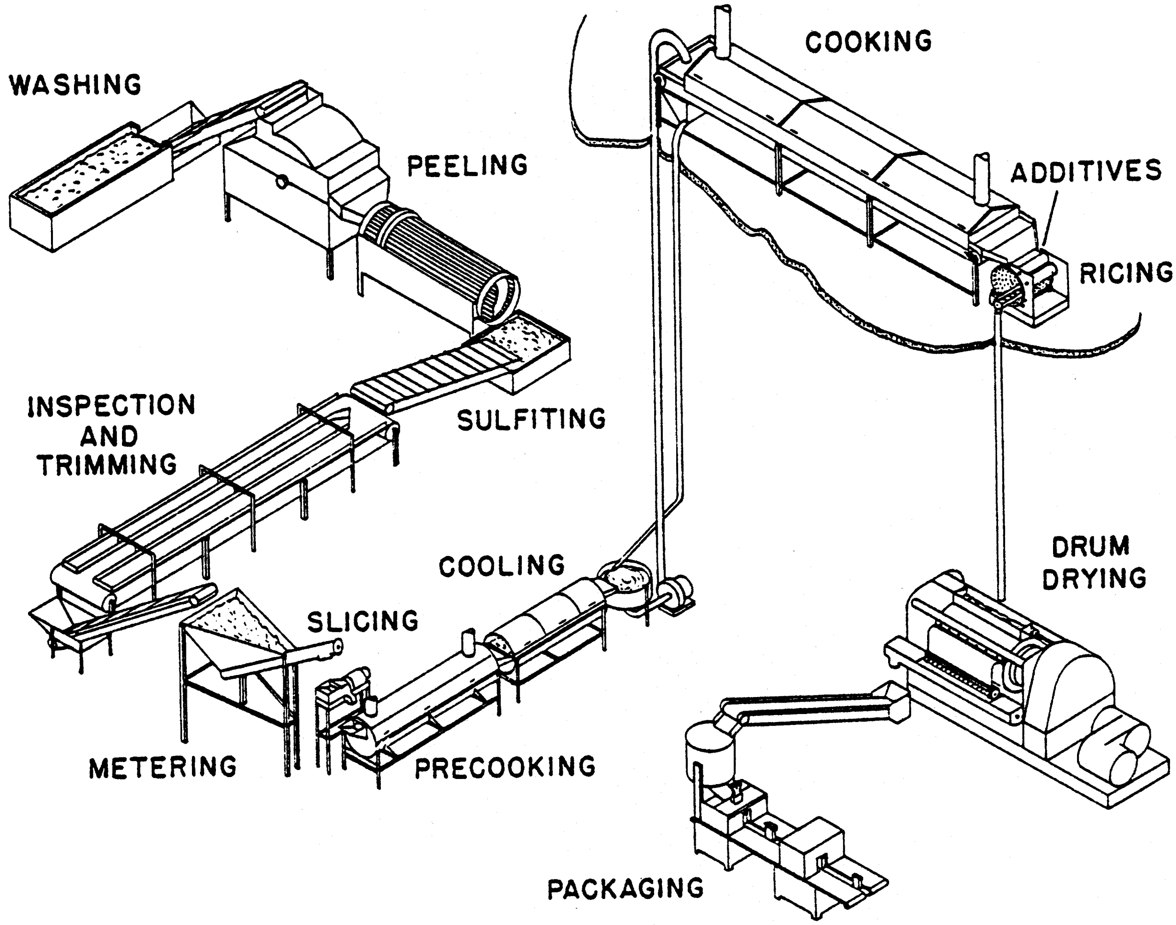

FIG. 1. Potato flake process developed at ERRC. Won First Industrial Achievement Award given by the Institute of Food Technologists in 1959. Process is in production throughout the world.

Table 1. *Volatile Products of Sugar-Amino Acid Reactions in Headspace Vapor of Commercial Potato Flakes*

Component	Mean peak area ratio[1]
2-methylpropanal	0.17
2- and 3-methylbutanal	0.10
Furfural	0.58
Benzaldehyde	0.51
Pheynlacetaldehyde	1.76

[1]Internal standard = ethylbutyrate.

Explosion-puffing

Development. Explosion-puffing (Eisenhardt *et al.*, 1962; Cording and Eskew, 1962) was developed to provide shelf stable, quick-cooking fruit and vegetable piece products. The explosion-puffing process has been successfully applied to many commodities such as white potatoes, sweet potatoes, carrots, beets, rutabagas, peppers, celery, onions, apples and blueberries. One of the principal advantages to this process compared to an all-hot air process is the reduction of about two-thirds in the drying time. The products have excellent texture, flavor and color (Cording *et al.*, 1963, 1974; Eisenhardt *et al.*, 1964).

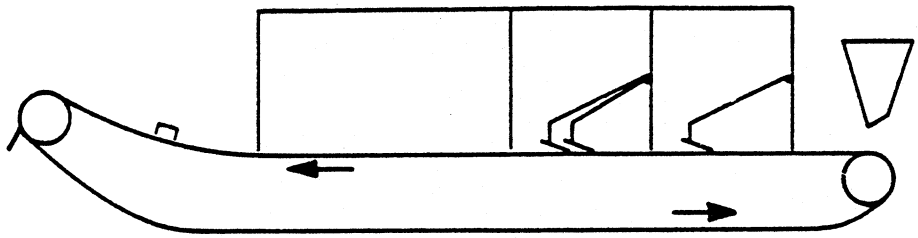

FIG. 3. Schematic of first stage of a continuous belt dryer depicting doctoring of belt in first and second zones.

distribution. After case hardening or surface drying is accomplished, food pieces become 'free-flowing'. This characteristic remains throughout the rest of the explosion-puffing process.

Final drying or drying after explosion-puffing is performed at temperatures lower than the critical temperature (Jacobs, 1951) for a particular fruit or vegetable. Drying time usually increases in proportion to the square of the thickness of the piece. Therefore, as the piece size is increased, the opportunity for non-enzymatic browning to occur is also increased. Explosion-puffing greatly reduces this probability. The porosity of the food pieces, regardless of size, facilitates a fast, final drying. The explosion-puffing process becomes more desirable as the desired piece size increases.

Batch gun. Initial experiments in explosion-puffing were in a small cereal type batch gun. The pressure developed within this gun was created by the vaporized moisture from within the food pieces. The gun was externally heated. The complete operational cycle required about 10–15 min to build sufficient pressure to subsequently explode the pieces. If the gun pressure was released within the operational time an acceptably colored product was obtained. If the operational limits were exceeded non-enzymatic browning occurred.

Because of the ease with which the products browned, another type of batch gun was designed to reduce the operational time. In this specially designed gun (Heiland and Eskew, 1965) the pressure is developed internally by the use of superheated steam and the operation time is about 1 min, greatly reducing the chance for non-enzymatic browning.

When processing white potatoes, it was evident that a browning-type odor was released into the atmosphere. Organoleptic evaluation confirmed the off-flavor development. Vapors, collected from the gun's nozzle with specialized equipment (Filipic, 1967), were analyzed by Buttery's (Buttery and Teranishi, 1963) gas chromatographic method and identified by a mass spectrometer coupled to the chromatograph. The principal offending components were identified as the Strecker aldehydes, 2-methylpropanal and 2- and 3-methylbutanal, and the antoxidative aldehyde, hexanal.

Samples were taken after each processing step (Fig. 2) up to and including explosion-puffing. These samples were dried separately in an air tray dryer to about 4% moisture. When their headspace vapors were analyzed, peak areas for 2- and 3-methylbutanal (Table 2) indicated that the off-flavors were developed or greatly increased during the explosion-puffing.

Experimentation was begun to reduce these offending aldehydes to a point where a competent taste panel could not detect them. In the study of the Strecker degradation, CO_2 was identified as one of the reactants (Schonberg and Moubacker, 1952):

$$\text{–CO·CO–} + \text{R·CH(NH}_2\text{)·CO}_2\text{H} \rightarrow \text{–C(NH}_2\text{)} = \text{C(OH)–} + \text{R·CHO} + \text{CO}_2.$$

For this reason, CO_2 was injected into the gun with the superheated steam to reduce or impede the Strecker degradation. Potato dice were explosion-puffed while varying amounts of CO_2 were injected into the gun, then dried in a tray dryer to about 4% moisture. Table 3 shows that as the amount of CO_2 was increased the level of 2-methylpropanal decreased. Potatoes, explosion-puffed with 159 g/min of CO_2 or higher, were judged acceptable for taste and odor. However, when 272 g/min of CO_2 was used, the content Kennebec potatoes. The dried samples were stored at three temperatures: –18°C, 23°C and 38°C. The samples stored at 23°C were canned in air and nitrogen, while those stored at –18°C and 38°C were canned in nitrogen only. Samples were evaluated monthly, both chromatographically and organoleptically (Tables 5 and 6). With the high reducing sugar Kennebecs (Table 5) the nitrogen packed samples did not materially increase in 2- and 3-methylbutanal levels at –18 and 23°C during a 5-month storage period. Organoleptic scores over a 12-month period reinforced this observation. However, storage at 38°C in nitrogen was discouraging because a non-enzymatic browning flavor was detected and the 2- and 3-methylbutanal value increased threefold. Oxidative off-flavor also became apparent, after 2 months in the air-packed sample.

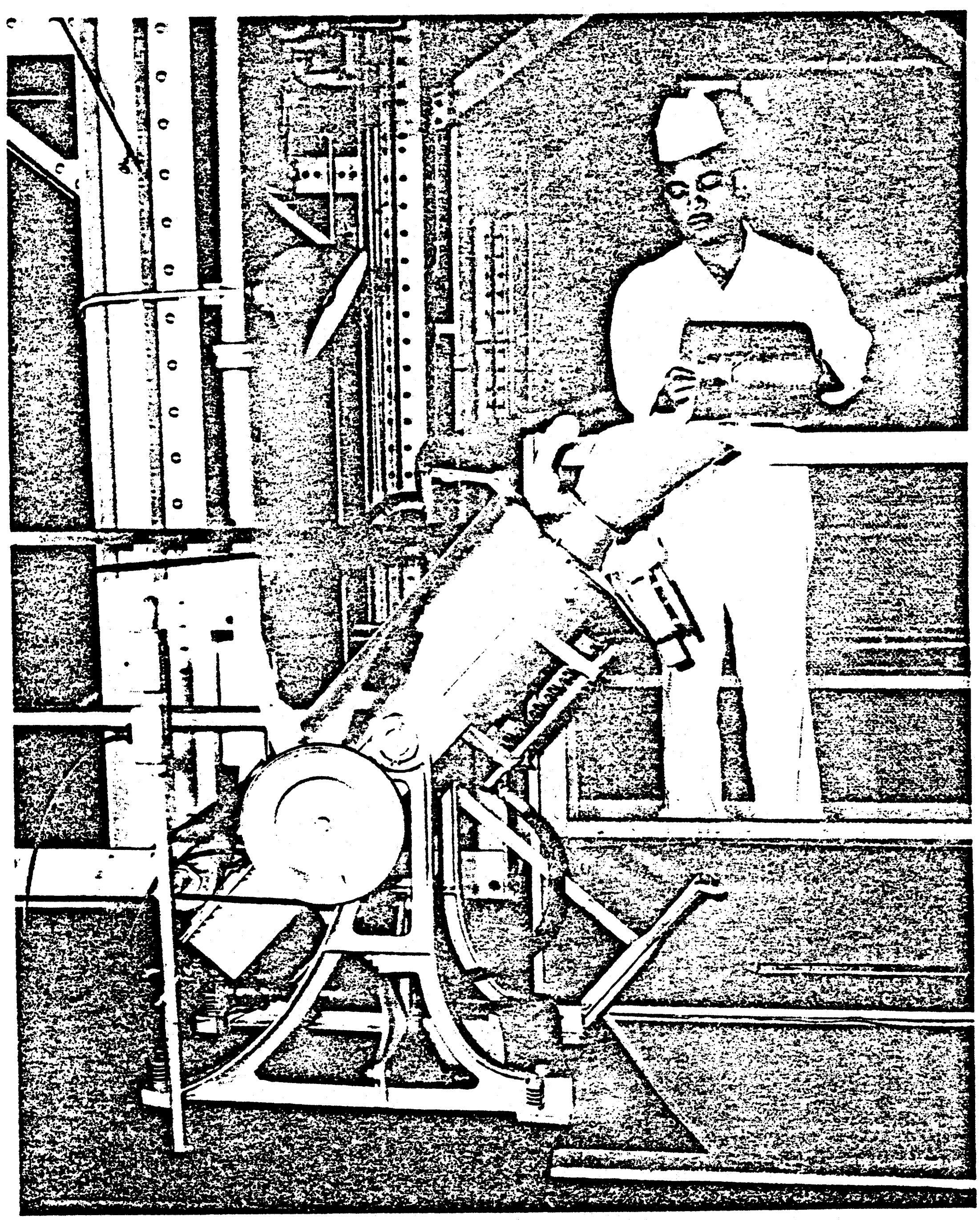

FIG. 4. One of the experimental batch guns used in developing the explosion-puffing process.

The low reducing sugar storage samples (Table 6) increased only slightly in 2- and 3-methylbutanal and had no detectable off-flavors. The hexanal values (Tables 5 and 6) of the air packed samples at 23°C increased 3-fold or more within 2 months. The oxidative off-flavors can be retarded by the use of antioxidants (Konstance *et al.*, 1978) or prevented by canning in nitrogen.

Table 5. *Storage Test 2: Change in Amount of Headspace Volatiles and Organoleptic Evaluation of Explosion-puffed Dice Made from High Reducing Sugar Potatoes*

Storage condition	Comp.	Time in storage (months) 0	2	3	5	12
		Mean peak area ratio[1]				
−18°C, N_2	2 + 3 MB	0.210	0.216	0.194	0.270	—
	Hexanal	0.027	0.028	0.026	0.082	—
	Taste[2]	4.00	3.93	4.00	4.21	3.87
23°C, N_2	2 + 3 MB	0.210	0.244	0.292	0.296	—
	Hexanal	0.027	0.030	0.033	0.100	—
	Taste[2]	4.00	4.15	—	4.08	3.87
23°C, air	2 + 3 MB	0.210	0.270	0.261	0.291	—
	Hexanal	0.027	0.222	0.395	0.565	—
	Taste[2]	4.00	3.69	3.44[3]	2.92[3]	2.47[3]
38°C, N_2	2 + 3MB	0.210	0.646	0.670	0.794	—
	Hexanal	0.027	0.032	0.024	0.043	—
	Taste[2]	4.00	3.40[3]	3.36[3]	3.14[3]	—

[1]Mean peak area ratio = area aldehyde peak/area internal standard peak.
[2]Taste score as per Kramer and Twigg (1962).
[3]Indicates a confidence level of 95% or greater relative to control at same storage time.

Table 6. *Storage Test 2: Change in Amount of Headspace Volatiles and Organoleptic Evalution of Explosion-puffed Dice made from Low Reducing Sugar Potatoes*

Storage condition	Comp.	Time in storage (months) 1	4	6	12
		Main peak area ratios[1]			
−18°C, N_2	2 + 3 MB	0.107	0.122	0.114	—
	Hexanal	0.064	0.092	0.105	—
	Taste[2]	4.00	4.05	4.12	3.92
23°C, N_2	2 + 3 MB	0.130	0.132	0.158	—
	Hexanal	0.083	0.102	0.112	—
	Taste[2]	4.13	3.94	—	3.62
23°C, air	2 + 3 MB	0.129	0.134	0.131	—
	Hexanal	0.461	1.276	1.170	—
	Taste[2]	3.19[3]	2.72[3]	3.00[3]	2.62[3]
38°C, N_2	2 + 3 MB	0.178	0.273	0.316	—
	Hexanal	0.048	0.047	0.051	—
	Taste[2]	3.80	4.06	4.00	—

[1]Mean peak area ratio = area aldehyde peak/area internal standard peak.
[2]Taste scores as per Kramer and Twigg (1962).
[3]Indicates confidence level of 95% or greater relative to control at same storage time.

browning Strecker aldehydes increased in CEPS as they had in the batch operation, as gas chromatographic values of the headspace vapors and the odor from the system attested.

CEPS potato experimentation. After many preliminary product tests, a qualitative experiment was begun. Low sugar (2.0% total reducing sugars (fresh basis) Kennebec potatoes were obtained for the tests. They were peeled, cut into 1 cm dice, precooked, cooled, blanched, dipped into 0.25% $NaHSO_3$ solution (30 sec to give 200 ppm SO_2 in final product), and partially dried to *ca.* 25% moisture (wet basis). The partially dried potatoes (*ca.* 35 kg) were well-mixed and equilibrated; 3.5 kg were allotted per test for the ten experiments, two batch and eight CEPS. The batch tests were made with nitrogen injection (159 g of N_2/min) with superheated steam at two pressures, 345 kPa and 414 kPa. The tests in CEPS were without nitrogen injection, at the same two pressures and at four internal temperatures, 163, 168, 176 and 191°C.

After being explosion-puffed, all samples were dried in a tray dryer at 66°C, or below the critical temperature for potatoes (Jacobs, 1951). 2-Methylpropanal and 2- and 3-methylbutanal were determined in all samples (Table 7). Organoleptic evaluation were made on all samples. No off-flavors, non-enzymatic browning or oxidative could be detected in the two samples from the batch gun or in two of the eight samples from CEPS.

Table 7. *Change of Amount of Headspace Volatiles with Pressure and Temperature as Developed from Batch and CEPS Operations*

Operation	Temp (°C)	345 kPa Mean peak area ratio[1]		Temp (°C)	414 kPa Mean peak area ratio[1]	
		2-MP	2- and 3-MB		2-MP	2- and 3-MP
Batch	—	0.30	0.35	—	0.33	0.38
CEPS	163	0.32	0.36	163	0.43	0.46
	168	0.37	0.45	168	0.51	0.67
	176	0.70	0.88	176	0.85	1.07
	191	0.76	0.95	191	0.96	1.26

[1]Mean peak area ratio = area aldehyde peak/area internal standard peak.

The two CEPS samples with no detectable off flavors had been explosion-puffed at 345 kPa, one at an internal temperature of 163°C and the other at 168°C. The 2-methylpropanal and the 2- and 3-methylbutanal values of both these CEPS samples are close to the aldehyde values of the batch operation (Table 7).

Thus, at least two operational conditions were found for CEPS in which nitrogen injection is not needed. Therefore, a dehydrated potato product without a detectable non-enzymatic browning off-flavor can be made without the use of nitrogen addition in the continuous explosion-puffing system.

CEPS apple experimentation. Apple pieces (32 half segments per apple) were investigated as a possible product for CEPS. Because apple volatile compounds differ from potato volatiles, Buttery's gas chromatographic method for Strecker aldehydes was not used. Instead hydroxymethylfurfural (HMF) formation was followed (Winkler, 1955). HMF values were found for about 500 apple samples from many experimental designs in which pressure, temperature and moisture of the apple pieces were evaluated.

Dehydrated apples or apple pieces of 3.5% moisture, can be made economically by the use of the explosion-puffing process (Stabile *et al.*, 1971). CEPS provided the innovative step in the process. Apples were prepared for drying for CEPS experimentation by following the conventional processing steps of peeling, coring, segmenting, sulfiting and washing. The apple segments were dried to various moistures around 18% moisture. Non-enzymatic browning precursors are formed from the degradation of sugars (Resnik and Chirife, 1979) during the dehydration. HMF, one of the browning precursors formed, was curbed by the sulfite dip. However, its formation increased 50–70% during explosion-puffing in CEPS.

The smaller the increase of HMF during processing, the better the storage stability imparted. An experimental design study of CEPS was made. The experimental apple pieces were dried to five moisture levels (10–22%). They were processed through CEPS at four pressures over the range of 62.1–124.2 kPa and at five temperatures over the range of 154–185°C. After being explosion-puffed, all samples were dried to about 2% moisture and HMF levels determined. From these HMF values, response surface plots were made of HMF values at various pressures as moisture and temperature varied (Fig. 7). CEPS operating conditions can be selected from this plot to give a specific low HMF.

Figure 8 shows two apple products obtained from the explosion-puffing process. The light-colored sample was processed through CEPS at conditions selected to give a low HMF value. A high HMF value coincided with the darkening effect in the other sample; and conditions were selected to accomplish this.

CEPS carrot experimentation. Carrots are one of the top ten crops grown and processed in the USA. Explosion-puffing carrots in CEPS was an extension of the dehydration study. A non-enzymatic browning evaluation of the explosion-puffing dehydration process was again necessary to define the CEPS operating conditions. Color changes in carrots during dehydration were more difficult to observe than those that occurred in potatoes or apples.

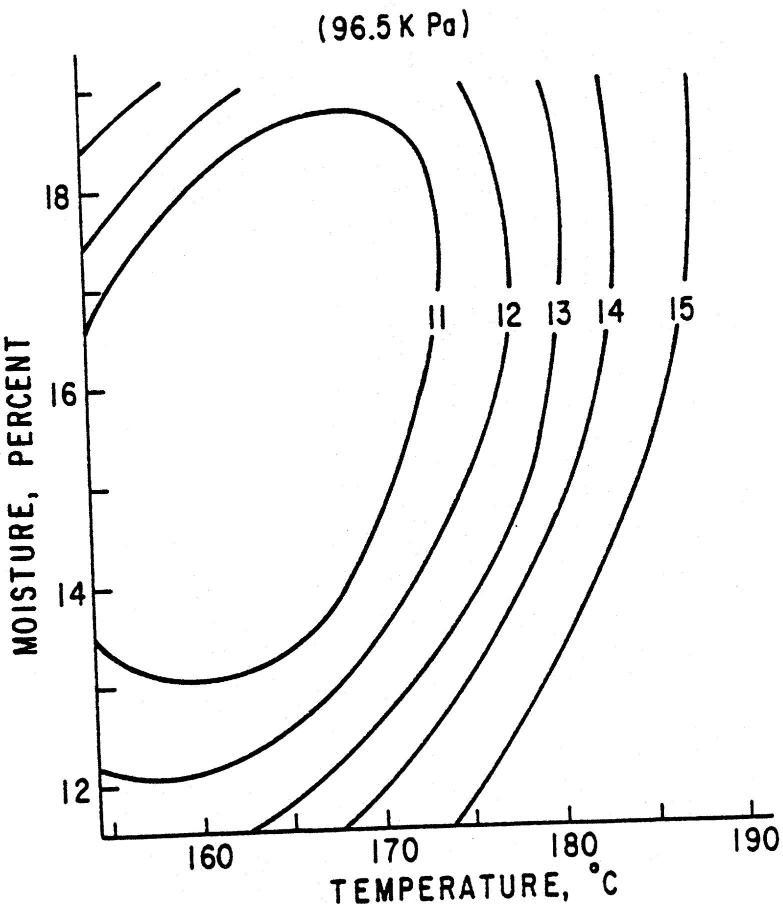

FIG. 7. Contour plot of HMF values at 95 kPa for apple pieces.

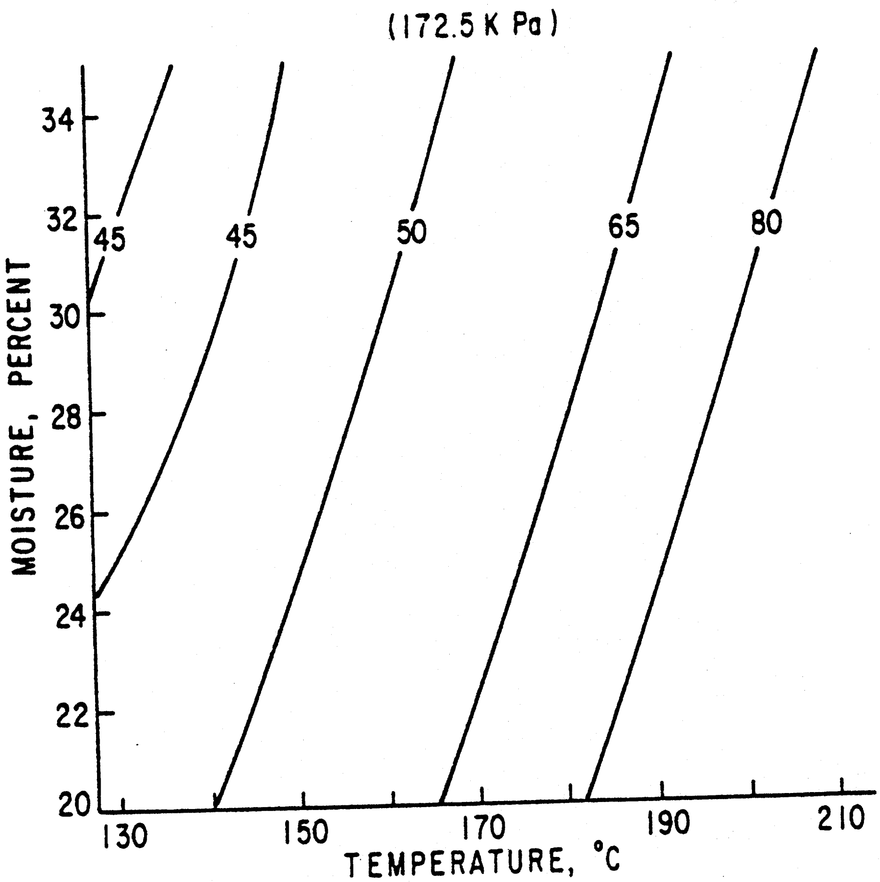

FIG. 9. Contour plot of NEB values at 172.5 kPa for carrot dice.

Carrot color eliminated HMF as a means of evaluating non-enzymatic browning. Volatiles were a possibility, but extensive background research was required. Baloch's (Baloch *et al.*, 1973) NEB method was tried and proved successful.

Non-enzymatic browning formed during the explosion-puffing dehydration process was found by this method. Carrot dice of varying moistures were tested in CEPS at different pressures and temperatures to obtain minimum NEB formation. Figure 9, a contour plot, shows NEB for dehydrated carrots. NEB values are plotted as a function of moisture and temperature at one operating pressure. This figure shows that, as operating temperature is increased and moisture is decreased, NEB increases. From this contour plot one could select CEPS operating conditions to give a minimum NEB value.

CONCLUSIONS

The work presented here shows that potato flakes of good color, flavor and texture were made and will store for at least 6 months. During processing, non-enzymatic browning Strecker aldehydes are formed at low levels. The use of low reducing sugar content potatoes and SO_2 are required for good quality control.

Explosion-puffing of white potatoes produces the Strecker aldehydes 2-emthylpropanal and 2- and 3-methylbutanal in quantities sufficient to produce off-flavors. Careful processing controls suppress these off-flavors, holding them below the taste threshold.

Explosion-puffed potato dice canned in nitrogen will store for 12 months at 23°C or below without developing non-enzymatic browning or autoxidative off-flavors. If canned in air, the potato dice must be protected with an antioxidant.

Three methods have been successfully used to determine non-enzymatic browning or

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