Butylated Hydroxyanisole (BHA) Retention during the Extrusion of Corn

Omololu O. Fapojuwo and Joseph A. Maga*

The Brabender plasticoder was used to extrude corn grits, containing 2000 ppm of BHA, under different extruder conditions. Parameters varied during the extrusion process included temperature, screw size, screw speed, and the die size, and all these were statistically found not to influence the retention of BHA. Losses were due partially to volatility. However, other factors were assumed to include thermal degradation and thermal rearrangement.

Relatively few reports exist in the literature concerning the thermal stability of BHA. Monte and Maga (1973) reported that during a sterilization process, there was extensive rearrangement and condensation of BHA. Kurechi (1967) found similar compounds in his experiment on photodegradation of BHA. Ishikawa and Yiki (1974) also found that BHA dimers were formed when they subjected BHA to heat treatment.

Maga and Monte (1977a) studied the influence of various storage and processing variables on BHA dimer production. Sunlight, water, pH, temperature, time, and air were shown to decrease monomeric BHA while increasing the levels of dimeric forms. Dimeric products were found at levels as high as 7.2%. The highest temperature reached in their study was 124 °C. Maga and Monte (1977b) also studied the effect of BHA on amino acid and carbohydrate concentrations during heating. They found that the addition of 200 ppm BHA resulted in a statistically significant reduction in the losses observed for various amino acids and carbohydrates when these systems were autoclaved at 124 °C for 15 min compared to controls containing no added BHA.

Information about the stability of other antioxidants under thermal stress is also limited. Tatum et al. (1969) reported that 15 products were formed when a 30% solution of ascorbic acid in water was heated for 5 h at 100 °C. Telegdy et al. (1971) showed that in vitro decomposition of tocopherols resulted in the formation of dimers and quinone. No published work has appeared on what happens to BHA during extrusion processing. Therefore, the primary objective of this study was to examine the extrusion factors that could influence BHA loss.

MATERIALS AND METHODS

Extrusion Process. A Brabender plasticorder (Model PL-V500) equipped with a variable speed DC motor, tachometer, and a torque indicator was used to extrude corn grits. The barrel had a diameter of 19.05 mm with a 20:1 length to diameter ratio. Two different screw compression ratios (1:1 and 3:1) were used. The 1:1 screw had a constant flight depth of 3.81 mm throughout its length while the 3:1 screw had a flight depth of 3.81 mm at the feed section end which reduced to 1.27 mm at the metering end. Two different die sizes were also used. The larger one had a diameter of 2.78 mm and the smaller one 1.59 mm in diameter.

The extrusion was carried out at three different temperatures. When the extruder temperature control was set at 100 °C, recorded temperatures at the feed section, transition section, and metering section were 93, 103, and 112 °C, respectively. At the 125 °C setting, 121, 128, and 132 °C were recorded, while at the 150 °C setting, 149, 157,

Colorado State University, Department of Food Science and Nutrition, Fort Collins, Colorado 80523.

and 164 °C were recorded for the three sections, respectively. The temperature of the barrel was monitored with a thermocouple in each of the three sections of the barrel. At the start of the process, the extruder was allowed to warm up while the screw speed was set at 25 rpm and the temperature controls set at the lowest desired temperature (100 °C). When the desired temperature was reached, the screw speed was increased to the desired speed (50, 100, or 150 rpm).

Yellow corn grits were commerically obtained. Before extrusion the corn meal was mixed with a measured amount of distilled water to attain an added moisture level of 25%. Also blended with the moistured corn grits was a measured amount of BHA to give a level of 0.2% (2000 ppm) since a preliminary run involving the addition of 200 ppm of BHA to corn grits followed by extrusion resulted in a retention too small to be quantitatively measured. A Patterson-Kelly Model LB-P-8 twin shell blender was used for the mixing. Enough time (10 min) was allowed for the materials to become thoroughly blended. A small amount of this mixture was saved to served as the control.

The corn grit mixture was fed into the feed section of the extruder and a separate run for all combinations of temperature, screw speed, die size, and screw size was made. Each time there was a change in the operating conditions, and at the very beginning of the day's run, some time was allowed (about 5 min) for the extruded product to attain a constant physical characteristic before samples were collected. The physical characteristics were determined by the color and size of the extruded product. Three 30-s samples were taken for each extruder operating condition, and the torque reading was recorded. The 30-s samples were dried and weighed, and the average dry weight output was calculated in g/30 s. Readings were obtained for all different combinations of temperature, screw size, screw speed, and die size.

A slight variation was made in the above procedure in an experiment designed to measure the effect of BHA retention without volatility being present. Instead of allowing the extruded product to flow into an open container, the 30-s samples were collected directly into bottles which were closed immediately to minimize loss of vapor. The bottles used had flat edges at the open end and to minimize loss of vaporized BHA during the time of collection, the flat edges were held tightly in contact with the flat end of the extruder barrel. Under these circumstances, the die was inside the bottle. After each sample collection, the bottle was closed as quickly as possible and the contents allowed to cool down to room temperature before the extraction of BHA for analysis.

Extraction of BHA. The extruded products were first ground to pass through a No. 20 sieve. A small plug of glass wool was placed at the bottom of a liquid chromatographic tube (25 × 200 mm) and 20 g of the extruded product added. A tamping rod was used to pack the

Table I. Extrusion Data Obtained for the Various Extruder Variables Evaluated

die diam., mm	dough temp, °C	rpm	extrusion rate, g/30 s	torque, N·m	% BHA retent.	die diam., mm	dough temp, °C	rpm	extrusion rate, g/30 s	torque, N·m	% BHA retent.
						3:1 Screw					
2.78	112	50	13.7	5.88	6.2	1.59	112	50	11.1	6.37	8.7
		100	26.7	8.33	7.5			100	24.7	6.86	6.9
		150	41.4	10.29	10.8			150	38.0	9.31	6.4
	132	50	12.8	4.41	5.7		132	50	12.7	4.41	6.8
		100	26.0	6.37	6.9			100	25.7	6.37	5.7
		150	41.5	7.35	6.5			150	41.3	7.84	6.7
	164	50	13.8	3.43	8.0		164	50	12.3	3.43	8.1
		100	26.3	5.39	7.4			100	23.8	4.90	7.9
		150	39.0	6.37	6.3			150	40.3	6.37	5.5
						1:1 Screw					
2.78	112	50	17.0	4.90	6.2	1.59	112	50	14.9	5.39	7.9
		100	35.2	5.88	11.6			100	33.6	7.84	5.6
		150	54.6	7.35	9.0			150	52.7	8.82	7.0
	132	50	16.7	3.43	6.6		132	50	15.1	4.41	5.9
		100	30.1	4.90	6.9			100	30.0	5.39	6.6
		150	53.6	6.62	6.6			150	48.2	6.37	14.0
	164	50	16.0	3.43	14.9		164	50	17.0	3.92	9.1
		100	34.0	4.41	6.7			100	32.3	4.90	6.5
		150	52.4	5.39	6.3			150	51.0	5.88	5.0

material firmly without solvent. A small glass wool plug was then placed on top of the column and tamped down.

A 100-mL beaker marked at the 50-mL level was placed under the column to collect the eluate. Three 5-mL portions of carbon disulfide were added to the column, and each portion was allowed to flow into the column before adding another aliquot. The carbon disulfide was eluted at the rate of 5 mL/min. Several 10-mL portions of carbon disulfide were later added until 50 mL of eluate was collected. The tips of the column were rinsed with small amounts of carbon disulfide. The eluate was then evaporated under gentle stream of nitrogen in the hood at room temperature to 2 mL. The concentrated eluate was then transferred into a 25-mL volumetric flask and diluted to the mark.

Analysis of BHA. The AOAC (1975) gas chromatographic method for the analysis of monomeric BHA in ready-to-eat breakfast cereals was followed. Three separate analyses were made for each sample and the peak areas recorded with the aid of a Hewlett-Packard Model 3370B integrator. A standard with BHA was used to identify the peak resulting from BHA. The standard sample was injected at intervals throughout the analysis to assure that all conditions remained constant throughout the analysis. From the average area obtained for the control and the average area for each sample, it was possible to calculate the percentage BHA retention during the extrusion process as follows:

$$\% \text{ BHA retention} = \frac{\text{average area of sample}}{\text{average area of control}} \times 100$$

RESULTS AND DISCUSSION

Data obtained for BHA retention, extrusion rate, and extrusion torque under varying conditions of die size, rpm, screw size, and temperature are summarized in Table I.

The extrusion rate or through-put of the extruded product was found to be significantly influenced by changes in screw speed, screw size, and die size. Extrusion rate increased with increasing screw speed and decreasing screw compression ratio. These results agree with the observations and theoretical explanations made by Harmann and Harper (1973).

Extrusion rate increased through the large die (diameter 2.78 mm) as compared to the small die (diameter 1.59 mm).

The change can be attributed to the difference in pressure required by the two dies for approximately equal flows. A greater pressure drop is required to achieve the high flow rates through the small die. The extrusion rate was found to be independent of the barrel temperature.

Significant interactions were found on extruder torque with temperature, screw size, and screw speed. These interactions are expected according to Harmann and Harper (1973) since they proposed that torque is proportional to the screw speed as well as the viscosity which in turn is inversely proportional to the temperature. These theoretical predictions agreed with the observations made in this study since torque was found to increase with increasing screw speed and decreasing temperature. In addition, torque increased with increasing compression ratio.

BHA Retention. The amount of monomeric BHA retained under different extrusion operating conditions was found to vary between 5 and 15% (Table I). The range of BHA retention corresponds to a range of 100–300 ppm BHA in the finished product.

A general trend was not observed for BHA retention relative to any particular variable. Retention likely depends on the interactions of many factors. Efforts were then made to look into the factors responsible for the monomeric BHA loss with the hope of finding out more about the effects of some of these parameters.

Factors Responsible for BHA Loss. The temperature vapor curve for BHA indicates that at 635 mm of mercury (Fort Collins atmospheric pressure), BHA will not boil until 250 °C. However, volatility was found to be one of the factors responsible for the loss of BHA in this study despite the fact that the highest temperature of operation was only 164 °C. The volatility observed can be explained considering the condition existing at the discharge of the extruder when vapor flashes off.

Based on the knowledge of the behavior of BHA in other thermal processing systems (Monte and Maga, 1973; Kurechi, 1967; Isikawa and Yiki, 1974; Maga and Monte, 1977a), it was envisaged that thermal rearrangement may account for some of the monomeric BHA loss. An experiment was therefore designed to prevent loss of BHA volatility so that polymeric transformation of BHA could be estimated. Table II shows the results of this experiment. It was found that only part of the BHA loss during

Table II.   Data Relating the Contributions of Volatility and Thermal Rearrangement to BHA Loss

dough temp, °C	screw speed, rpm	shear energy, cal g⁻¹ s⁻¹	shear rate, s	through-put, g/30 s	torque, N·m	% BHA loss due to volatility (measured)	% BHA retent. (meas-ured)	% BHA loss due to thermal rearrange. (calcd)[a]
112	50	10.40	3.12	17.3	500	35	6.2	58.8
	100	12.53	6.23	35.3	600	47.8	11.6	40.6
	150	14.78	9.35	54.8	750	64.2	9.0	26.8
132	50	9.69	3.12	16.7	450	25.4	6.6	68.0
	100	12.00	6.23	30.0	500	25.4	6.9	67.7
	150	13.35	9.35	54.6	675	28.7	6.6	64.7
164	50	7.82	3.12	16.1	350	54.3	14.9	30.8
	100	9.53	6.23	34.0	450	47.6	6.7	45.7
	150	11.40	9.35	52.1	550	34.8	6.3	58.9

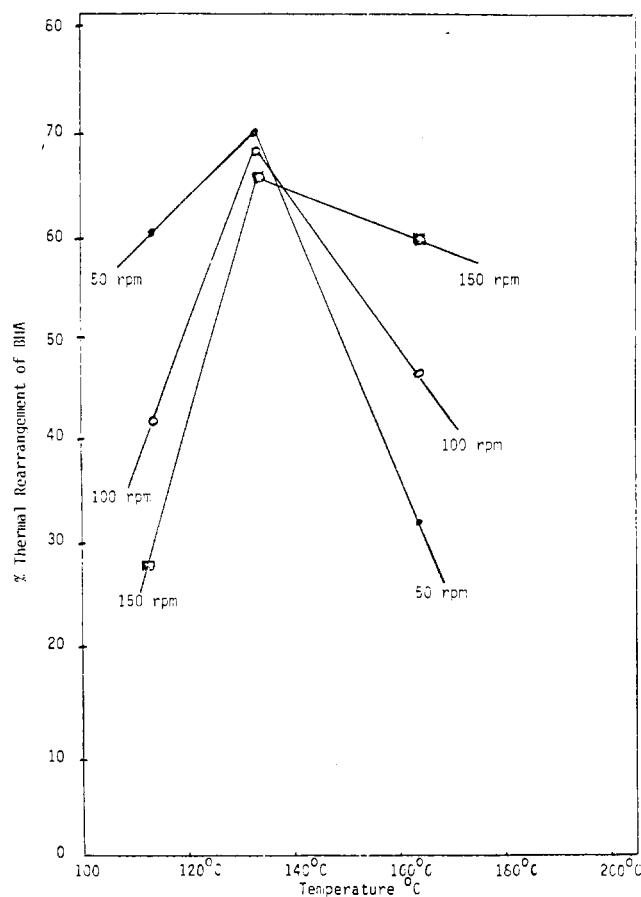[a] 100 − (% BHA retained + % BHA lost to volatility).

Figure 1. Relationship between the screw speed (rpm) and temperature relative to BHA loss through thermal rearrangement and/or thermal degradation.

extrusion resulted from volatility. Since an appreciable amount of BHA was lost, even when volatility was prevented, it follows that there must be other mechanisms by which BHA is lost or unavailable to the analytical methods.

In this study, only the monomeric form of BHA was measured because the polymeric forms are difficult to measure quantitatively. Thus, the polymeric forms represent loss of monomeric BHA and they can account for the loss due to thermal rearrangement shown in Table

II. There is also the possibility that some of the BHA may be lost through thermal degradation.

Statistical evaluation of the volatility and thermal degradation data, shown in Table II, revealed no significant effect of temperature and rpm, even though the data showed some trends. The observed trend in the data did not show a linear relationship as revealed in Figure 1 and probably this, coupled with few data points, was responsible for the lack of significance in the results obtained from the statistical analysis. However, it is interesting to note in Figure 1 that for some unexplained reason, the percentage of thermally rearranged BHA was higher at 132 than at either 112 or 164 °C.

A closer look at Table II clearly shows that the loss of monomeric to volatility shows trends different from the loss through calculated thermal rearrangement. The more thermal rearrangement occurring, the less volatility effect observed. Such an observation suggests that the volatility effect depends upon the quantity of the monomeric forms of BHA. It was observed by Ishikawa and Yiki (1974) that the polymeric forms of BHA are not as volatile as the monomers. This is probably because of the size of the polymeric molecules. Obviously, the availability of the monomeric forms depends upon the level of thermal rearrangement. Thus, the higher the thermal rearrangement the smaller the quantity of monomers available for volatilization.

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