Fractional Surface Coating Modifies Gas Diffusion and Ripening in Bananas

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ABSTRACT. We hypothesized that the blocking of O₂ influx and CO₂ efflux in banana (*Musa acuminata*) by sealing nearly 100% of the pores over a fraction of the surface would generate a modified internal atmosphere in a manner similar to fruit coatings that cover 100% of the banana surface but only block a fraction of the pores. This hypothesis was based on the observation made by previous workers that the flesh of mature green bananas has insignificant resistance to O₂ diffusion relative to the resistance imposed by the skin of the fruit. We modified the O₂ diffusion pathway in bananas by covering, beginning at one end, 1/4, 1/2, 3/4, and 7/8 of the fruit surface with paraffin, which sealed essentially 100% of the surface where it was applied. Large end-to-end O₂ and CO₂ gradients developed within coated fruit, relative to the uncoated control, suggesting that the diffusive resistance in the pulp was not insignificant. Since the large gradients of O₂ generated caused uneven ripening, using fractional coatings may help analyze gas exchange properties, but it is not suitable for commercially controlling ripening of bananas.

Investigation of the composition of the internal atmosphere in bulky plant organs has been very useful in evaluating the nature of gas diffusion pathways in fruit and vegetables (Burg and Burg, 1965). Internal partial pressures of O₂ and CO₂ are particularly important considerations for maintaining quality when controlled-atmosphere (CA) and modified atmosphere storage are used (Banks, 1983; Beaudry et al., 1992; Burg, 1990; Cameron, 1989; Cameron et al., 1995); internal C₂H₄ partial pressures should also be considered when fruit are treated with ethylene (Knee et al., 1987; Peacock, 1972) or when C₂H₄ removal is attempted during storage (Dover, 1985). Many conceptual and mathematical models have been developed to predict and investigate gaseous diffusion through the flesh and across the skin of fruit and vegetables (Burg and Burg, 1965; Cameron, 1989; Cameron and Yang, 1982; Knee et al., 1991; Rajapakse et al., 1989; Rakitin and Rakitin, 1986; Rodriguez et al., 1989). These models assume that the pores are the primary avenues of gas exchange and that internal tissue resistance to O₂ is negligible in the investigated fruit and have collectively been termed hollow-sphere models.

Impeding gas exchange by applying coatings to the surface of some commodities is one method of altering the internal gases sufficiently to retard ripening (Banks, 1983; Perez, 1994). Banks (1984) observed that the effect of surface coatings in reducing O₂ and CO₂ permeability of the skin of fruit and vegetables is largely the result of residues of the coating material lodging in skin openings (stomata, lenticels). However, this coating technique results in a high variability in the internal atmospheres obtained and poor control over ripening. Banks (1983) suggested that the fruit-to-fruit variability that occurs in the internal atmosphere stems from variability in the degree to which the coating material blocks gas exchange. This variability might be reduced if a means could be developed to block fractions of the primary diffusion pathways more precisely. We hypothesized that blocking essen-

tially 100% of the pores over a precisely controlled fraction of the surface of the fruit might reduce gas exchange more uniformly than using coatings that cover 100% of the surface, but block only a fraction of the pores. This approach will lead to diffusive pathways of greater length and, for this approach to work well, internal (flesh or pulp) resistance to gas diffusion must be sufficiently low such that internal gradients are negligible. The banana makes a good model system to examine the effects of fractional coating because fractional coating of the elongated fruit has a more marked effect on the diffusion path length than on more spherical fruit. In addition, the more linear diffusion pathway of the banana permits the construction of a simple conceptual model.

We have constructed a conceptual model to depict the effect of sealing 100% of the pores of a fraction of the fruit surface on the internal O₂ content for banana (Fig. 1). In this model, as the fraction of surface coated increases, the internal O₂ partial pressure declines. Importantly, if gases move freely through the flesh or pulp of a fruit as suggested in the hollow-sphere model, fractional surface coating should result in a depletion of the internal O₂

Fig. 1. Conceptual model depicting effects of fractional coating on the internal O₂ profile through the length of bananas. Dotted lines and open symbols indicate the O₂ partial pressure assuming no oxygen gradient results from fractional coating as predicted by the hollow sphere hypothesis. Solid lines and closed symbols indicate the O₂ profile assuming significant resistance to O₂ diffusion in the pulp. The thicker solid lines show the fraction (1/4, 1/2, 3/4, and 7/8) of the length of the fruit coated with paraffin.

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Fig. 2. Diagram of vial location and paraffin coating treatment on bananas used in study. Bars indicate fraction of fruit coated with paraffin. Vial 5 is farthest from the coated end.

uniformly throughout the fruit (Fig. 1, dashed lines). However, if significant diffusive resistance is encountered in the flesh, an end-to-end gradient in O_2 should be detected (Fig. 1, solid lines).

Several researchers have suggested that the diffusive resistance to O_2 in the flesh of mature green bananas is relatively negligible compared to the skin diffusive resistance, which is considered the primary barrier to gas exchange (Banks et al., 1989; Burg and Burg, 1965; Park, 1990). However, Elyatem et al. (1994) and Rajapakse et al. (1990) suggested that the flesh of banana does offer a significant resistance to O_2 diffusion. Provided a precise means for applying a surface coating can be devised, fractional blocking has the potential to be a practical method of altering gas exchange to extend the green life of banana or other fruit. Our goals were to use fractional coating to modify the internal atmosphere of bananas and determine if the diffusive resistance of the pulp is negligible or sufficient to produce gradients in O_2 and CO_2 such that ripening is nonuniform.

Materials and Methods

PLANT MATERIAL. Mature, preclimacteric green bananas from Costa Rica were obtained from a commercial banana ripening facility at the Detroit Eastern Produce Terminal before gassing with C_2H_4 . Fruit of uniform size and shape were selected for experiments. To determine whether the fruit were preclimacteric, representative samples (three to four fruit) were examined for ethylene biosynthesis. Fruit were sealed for 1 h in 1.2-L air-tight glass jars and the headspace was analyzed for C_2H_4 by gas chromatography. A production rate of $<20 \text{ nmol} \cdot \text{h}^{-1} \cdot \text{kg}^{-1}$ was taken to indicate preclimacteric status.

FRACTIONAL COATING. Paraffin was used as the coating material and was applied by dipping the fruit into melted wax. Paraffin will seal essentially 100% of the surface where it is applied (Jones et al., 1981). Paraffin was melted using a double boiler apparatus and maintained at 98 to 100 °C. The fruit were dipped into the melted paraffin twice, for $\approx 2 \text{ s}$ each time. Preliminary experiments revealed that contact with melted paraffin did not result in visible damage.

Four fractional surface coating treatments were given: 1/4, 1/2, 3/4, and 7/8 coated. The fraction of the surface coated was controlled by adjusting the depth to which the fruit were dipped in the

paraffin. Additional fruit were left uncoated as controls. Fruit were held at 16 °C at 85% to 90% relative humidity (RH). Fruit were divided into two sets. One set ($n = 3$) was used to monitor continuously internal gases. A second set was used to measure flesh firmness and soluble solids, which required destruction of the sample. Internal ethylene was monitored in all fruit destined for destructive measurements to determine the onset of the ethylene climacteric. Three fruit per day were analyzed in each coating treatment and in controls.

GAS ANALYSES. Internal O_2 , CO_2 , and C_2H_4 partial pressures were measured using gas-trapping vials attached to the surface of the fruit, as described by Beaudry et al. (1989), adapted from Banks (1983). Vials were made by cutting 1.4-cm-diameter glass tube into pieces 2.5 cm long (4.3 mL volume) and glued to the skin surface at five locations along the length of the fruit using Dow Corning 3140 RTV silicone adhesive (Fig. 2). The open end of the vial was sealed with a rubber serum cap. The adhesive was allowed to dry for 24 h before gas sampling began. Gas composition in the vials reached steady state after 5.5 h (data not shown), which is consistent with data obtained by Banks (1983). At steady state, equilibrium was assumed to exist between the headspace inside the vial and the internal atmosphere of the fruit (Banks, 1983). Gas composition was determined daily by withdrawing a 0.5-mL gas sample for O_2 and CO_2 and a 1-mL gas sample for C_2H_4 from the vials using an insulin-type plastic syringe. For O_2 and CO_2 measurements, a sequential combination of O_2 (series 1100 paramagnetic O_2 transducer; Servomex Inc., Norwood, Mass.) and CO_2 (model 225-MK3 infrared gas analyzer; Analytical Development Co., Hoddesdon, England) analyzers were used. Gas concentrations were calculated relative to a certified standard gas mixture (1.95% O_2 , 4.85% CO_2) and converted to partial pressures assuming an atmospheric pressure of $1 \times 10^5 \text{ Pa}$. Sampling for C_2H_4 took place 6 to 7 h after sampling for O_2 and CO_2 to allow equilibrium or steady state between vial atmosphere and the internal atmosphere of the fruit. Ethylene concentration was determined using a gas chromatograph (Carle Series 100 AGC; Hach Co., Loveland, Colo.) equipped with a flame ionization detector. Ethylene concentration was calculated relative to a certified standard gas of $0.979 \mu\text{L} \cdot \text{L}^{-1}$ (Matheson Gas Products, Inc., Dayton, Ohio) and converted to partial pressure (Pa).

DESTRUCTIVE MEASUREMENTS. Firmness was assessed using a Twist Tester, which measured the torque required to shear and compress of a small, cylindrical plug of tissue as the tissue is twisted on a probe having two small steel blades (Studman, 1992). The blades of the Twist Tester probe were 3 mm wide $\times$ 8 mm long.

Fig. 3. Internal O_2 (circles), CO_2 (triangles), and C_2H_4 (diamonds) partial pressures throughout the length of uncoated control bananas. This figure represents three fruit synchronized temporally such that ethylene climacteric peak occurs on the same date.

Fig. 4. Internal O_2 (open and solid circles) and CO_2 (open and solid triangles) partial pressures at the uncoated end (solid symbols) and coated end (open symbols) of bananas synchronized temporally such that ethylene climacteric onset occurs on the same date (indicated by arrows).

This textural assay was more sensitive than either a mounted or hand-held penetrometer at low firmness values, since the sensitivity range could be adjusted by altering the load on the lever arm. Data are reported in units of torque (N-m).

Pulp soluble solids were measured with a refractometer (model H-1733X; ZEISS Opton-Zr 122365, Germany). The extract was obtained by crushing 5 to 10 g of tissue and filtering the macerate through 2 to 4 layers of cheesecloth.

Results and Discussion

The O_2 partial pressure in control fruit decreased from 19.2 kPa to 14 kPa during ripening (Fig. 3). The observed decline was coincident with the ethylene climacteric and was uniform at each of the five positions along the length of the banana. Carbon dioxide increased as O_2 decreased, changing uniformly throughout the fruit. No gradient was detected for either O_2 or CO_2 from one end of the fruit to the other.

For coated fruit, the O_2 level declined and CO_2 increased as ripening progressed (Fig. 4). At the uncoated end, the preclimacteric O_2 level was lower for fractionally coated fruit than controls, with the degree of O_2 suppression increasing as the fraction coated increased (Fig. 4). Conversely, the preclimacteric CO_2 level increased as the fraction coated increased. These data suggest there was a significant impairment in gas diffusion due to paraffin coating. For coated fruit undergoing ripening, the O_2 levels after the climacteric peak of ethylene tended to decline, and CO_2 levels to increase, as the fraction coated increased.

End-to-end gradients in O_2 and CO_2 were present in pre- and postclimacteric fractionally coated fruit (Fig. 5). Thus, the data are consistent with the conceptual model for bananas with significant diffusion resistance in the flesh as depicted by the solid lines in Fig. 1 and as suggested by Elyatem et al. (1994) and Rajapakse et al. (1990). The end-to-end O_2 and CO_2 gradients suggest thereby that the hollow sphere model for diffusion of gas as described by Banks et al. (1989), Burg and Burg (1965), and Park (1990) is not suitable for banana.

Only minor end-to-end gradients were detected in the soluble solids of uncoated fruit during ripening (Fig. 6). However, marked end-to-end soluble solids gradients were detected in partially coated fruit. Gradients in coated fruit were transient in nature as the starch in the uncoated end was converted to sugar more rapidly than in the

coated end. The gradient transients, peaked ≈ 2 d after the C_2H_4 climacteric. Starch conversion to sugar in the uncoated end and in control fruit was nearly complete (80%) by this time. The timing between C_2H_4 production and sugar interconversion is consistent with previous studies (Beaudry et al., 1989). The highest gradient was observed in the 1/2 coated treatment, decreasing with either a higher or a lower coated fraction.

Firmness did not differ between ends of control fruit or between coated and uncoated ends of treated fruit (Fig. 6). There was a sudden decline in firmness 1 to 2 d after the ethylene climacteric. These data imply that the internal O_2 and CO_2 levels obtained by fractionally coating bananas was sufficient to interfere with the conversion of starch to sugar that is involved in the ripening process of banana, but insufficient to retard the process of softening. Some ripening characteristics may have different sensitivities to different levels of C_2H_4 , O_2 , and/or CO_2 . The data suggest that starch conversion to sugars is more sensitive to O_2 and CO_2 levels than softening.

Since surface area can be accurately determined, fractional coating has the potential to be a more precise means of altering gas exchange than whole-fruit coatings that partially block surface pores. Fractional coating of the banana surface was expected to avoid unpredictable and variable results observed in previous works using some commercial coating materials to modulate gas exchange and internal atmosphere of bulky plant organs (Banks, 1983), provided the fruit behaved like hollow spheres relative to gas exchange and there was uniform pore permeability and distribution. The hollow-sphere hypothesis predicts that blocking of O_2 influx and CO_2 efflux of banana by sealing nearly 100% of the pores over a fraction of the surface generates an internal atmosphere similar to that achieved by using fruit coatings that cover 100% of the surface but block only a fraction of the pores. Optimally, O_2 would be lowered, CO_2 raised, and negligible end-to-end gradients would be produced.

Using the technique of fractional coating, we found large O_2 and CO_2 gradients, indicating significant flesh resistance as Elyatem et al. (1994) had suggested. Thus, we can reject the hollow-sphere model used by other workers (Banks et al., 1989; Burg and Burg, 1965; Park, 1990) as a general model for describing gas exchange in mature green and ripening bananas. While fractional coating is not recommended as a commercial approach to control ripening in banana, it may be useful for other fruit and vegetables that may have significantly lower tissue resistance to O_2 diffusion. The technique of fractional coating of the surface of fruit may have a

Fig. 5. End-to-end O_2 (circles) and CO_2 (triangles) gradients for control (uncoated) and fractionally coated bananas. Data were synchronized temporally such that ethylene climacteric occurs on the same day (indicated by arrows).

Fig. 6. End-to-end soluble solids gradient (hexagons) and firmness of uncoated (solid squares) and coated (open squares) ends of bananas from control and fractionally coated treatments. Each point on the curve represents the average of three fruit, synchronized temporally such that ethylene climacteric onset occurs on the same day (indicated by arrows).

role as a tool to study gaseous diffusion in fruit and other bulky plant organs.

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