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DESIGN AND FUNCTION OF A MODIFIED ATMOSPHERE
PACKAGE FOR TOMATO FRUIT

presented by

Walter Boylan-Pett

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DESIGN AND FUNCTION OF A MODIFIED ATMOSPHERE PACKAGE FOR TOMATO FRUIT

BY

Walter Boylan-Pett

A THESIS

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ABSTRACT

DESIGN AND FUNCTION OF A MODIFIED ATMOSPHERE PACKAGE FOR TOMATO FRUIT

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Walter Boylan-Pett

A method to determine the rate of $\mathbf{0}_2$ consumption versus $\mathbf{0}_{2}$ concentration was developed. The method employed a closed system containing a single fruit where 0, depletion was monitored continuously. The resulting curves were characterized by a mathematical equation. The derivative of the equation equals the rate of 0_2 consumption versus time. Simultaneous solution of the equation and its derivative results in curves of 0_2 consumption versus 0_2 concentration. Models utilizing the best fit equation of the curves and Fick's first law were developed to predict the equilibrium 0, concentrations for various fruit/film combinations. model was used to optimize a low density polyethylene package for red-ripe tomatoes to an equilibrium 0_2 concentration of 2%. The optimized package system prolonged tomato storage 2 times that of the control. Inclusion of MgO reduced CO₂ accumulation to less than 1% and tripled storage life compared to controls.

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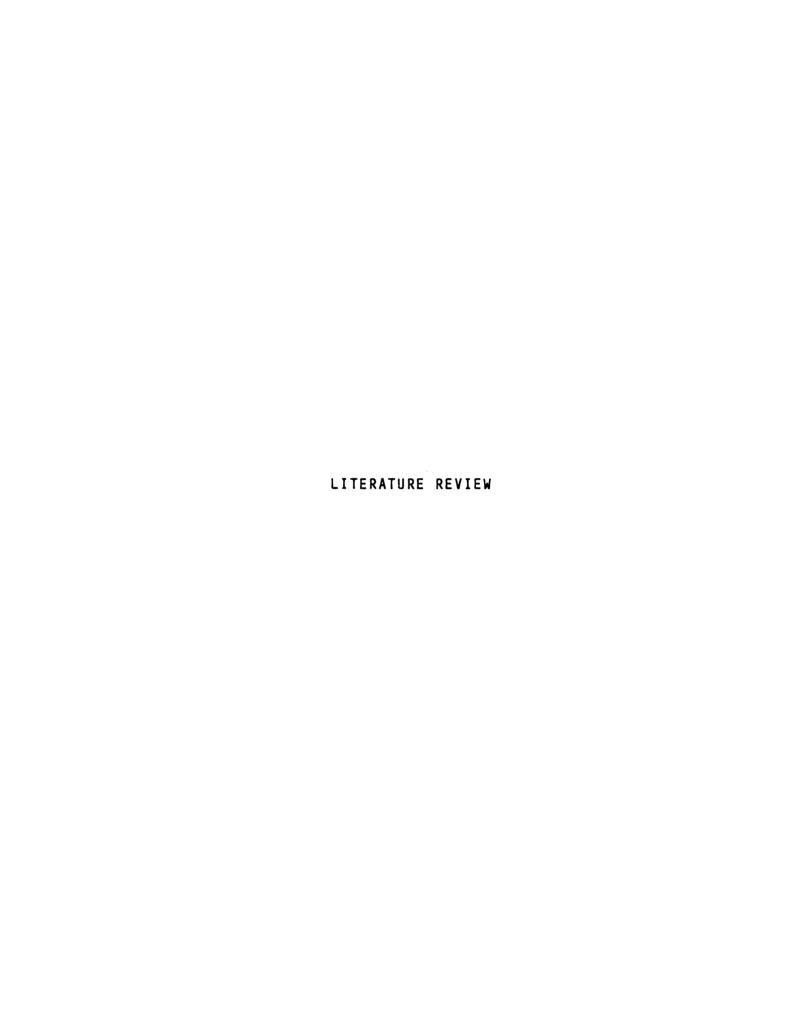
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LITERATURE REVIEW

Controlled atmosphere (CA) and modified atmosphere (MA) storage has been useful in extending the storage life of many horticultural commodities such as apples, pears and tomatoes (17,34). Lowering the 0_2 concentration reduces the rate of respiration and the rate of ethylene evolution (1). Elevated $C0_2$ levels have been reported to reduce the tissues sensitivity to ethylene action (5).

Kidd and West (23) first reported on the beneficial effects of CA storage with tomatoes and apples in the 1930's. Despite the abundance of subsequent positive reports, CA storage is applied chiefly to apples and pears at the commercial level (20). Reasons for its limited use relate to the costs involved in construction and maintanance of these storage rooms and the availability of imported produce during off-seasons. One other factor that may be important is the lack of agreement as to which concentrations produce the best results. With tomatoes 0_2 levels ranging from 1 to 7% and from 0 to 5% for $C0_2$ have been suggested for optimum storage (Table 1).

Table 1. Recommended $\mathbf{0}_2$ and $\mathbf{C0}_2$ concentrations for postharvest storage of tomatoes.

Cultivar (Maturity	()	0 (%)	CO ₂	Temp (°C)	Storage Life (days)	Ref
Homestead	(MG)	3-5	5	13	-	(8)
Scotian	(MG)	2.5-5	5	12.7	8 4	(9)
	(MG)	5	5	12.7	28	(10)
Sleaford	(MG)	5	5	>10	8 4	(11)
	(MG)	3	3	15	-	(15)
(Turi	(MG) ning)	3-5 3-5	0	12-20 8-12	-	(19)
	(MG)	5	5	12	5 7	(23)
Walter	(MG)	2.5	0	20	49	(24)
	(MG)	7	3	20	-	(26)
Homestead	(MG)	3	0	12.7	-	(28)
C X - 5 4	(MG)	1	0	12.	87	(32)
Sleaford VF 145-B78	(MG) 379	2.5	5	12.5	-	(35)
Dutch Vict Tuckswood (tur	tory ning)	2-3	5	15	-	(37)

Modified Atmosphere Packaging

An inexpensive method for generating modified atmospheres is with the use of polymeric films in a process commonly referred to as modified atmosphere packaging (MAP).

The resulting concentrations of $\mathbf{0}_2$ and $\mathbf{C0}_2$ are a function of the permeability characteristics of the film and the respiration rate of the fruit.

The movement of a gas through a film is dependent on several factors including chemical and physical properties of the film, of the permeating gas and the interaction between film and gas (6). With a particular film the flux of gas (J_i) may be described by rearrangment of Fick's 1st law of gas diffusion as follows:

$$J_{i} = P_{i} \cdot A \cdot \Delta x^{-1} \cdot (c_{i1} - c_{i2})$$
 (1)

Where: $J_i = Flux$ of gas (i) through the film $(cm^3 \cdot sec^{-1})$

P_i = Permeability

A = Film surface area (cm²)

 $\triangle x = Film thickness (mm)$

 $(c_{i1}-c_{i2})$ = Gas gradient partial pressure.

For a wide range of specific film types commonly used, values of P_{CO_2} range from 2 to 10 times those for P_{O_2} (12).

The respiration rate of the fruit is also affected by several factors such as fruit maturity, temperature, 0_2 concentration and the presence of other gases; i.e., $C0_2$, C0 and ethylene (30).

The package system is a dynamic one where permeation and respiration are occurring simultaneously (16). To

achieve the desired atmosphere within the package factors which effect film permeability and fruit respiration must be considered.

To optimize the package system several factors must be known. First the optimum $\mathbf{0}_2$ concentration for prolonging product storage must be determined. This information may be obtained from the literature (Table 1 for tomatoes) or experimentally.

The second factor which must be known for package optimization is the relationship between $\mathbf{0}_2$ concentration and the rate of $\mathbf{0}_2$ uptake by the fruit. The respiration rate is important in package optimization as it represents the flux (J) of the entire system at equilibrium. Limited information on this relationship exists in the literature for tomato.

Henig and Gilbert (16) compiled respiration data for tomatoes, plotted 0_2 consumption as a function of time and divided the resultant curve into linear and curvilinear segments. The curvilinear section was plotted on semilogarithmic paper yielding a straight line. Regression analysis was carried out on both lines and the resulting coefficients were used to calculate the 0_2 consumption and 0_2 evolution at various 0_2 and 0_2 concentrations. This approach was appropriate for their purpose but it does not adequately describe respiration in physiological terms.

The optimization concept may be explained mathematically for both 0_2 and CO_2 equilibrium

concentrations by substitution and rearrangement of equation 1 as follows:

$$[0_2]_{pkg} = [0_2]_{atm} - (RR_{02} \cdot x \cdot P_{02}^{-1} \cdot A^{-1} \cdot wt^{-1})$$
 (2)

Where: $[0_2]_{pkg}$ = Equilibrium 0_2 concentration in package

 $\begin{bmatrix} 0_2 \end{bmatrix}_{atm} = 0_2$ concentration in atmosphere

 $RR_{0_2} = 0_2$ consumption $(ml \cdot kg^{-1} \cdot h^{-1})$

wt = fruit weight (kg)

and

$$[CO_2]_{pkg} = [CO_2]_{atm} + (RR_{CO_2} \cdot x \cdot P_{CO_2}^{-1} \cdot A^{-1} \cdot wt^{-1})$$
 (3)

Where: $[CO_2]_{pkg}$ = Equilibrium CO_2 concentration in package

 $[CO_2]_{atm} = CO_2$ concentration in atmosphere $RR_{CO_2} = CO_2$ production $(ml \cdot kg^{-1} \cdot h^{-1})$.

These equations differ only in the direction of the gas gradient i.e., 0_2 is consumed as it enters the package and $C0_2$ escapes from the package to the environment.

Package System Modeling

Several researchers have developed models to predict the equilibrium gas concentrations within the package. It is assumed these models would eliminate the need for extensive experimentation required to match film with product for extending the storage life of a specific commodity.

Henig et al. (16) developed a computer-aided model that

predicted not only the equilibrium gas concentration of a package containing tomatoes but also the time to reach this condition. This method utilized the rate of $\mathbf{0}_2$ consumption and $\mathbf{C0}_2$ production at different $\mathbf{0}_2$ and $\mathbf{C0}_2$ concentrations within a film package of a known permeability. Two first-order differential equations were developed describing this condition and were solved for 1 hour intervals with the computer until equilibrium conditions were obtained. The computer-calculated results were in good agreement with results obtained experimentally. As expected, they also also reported (16) that increasing the net air volume in the package lenghtened the time to reach equilibrium but did not affect the equilibrium levels obtained.

They used 0.018 mm RMF-61 PVC film ($P_{02}1.35 \times 10^{-6}$; $P_{C02}7.0 \times 10^{-4} \text{ cm}^3 \cdot \text{mm} \cdot \text{cm}^{-2} \cdot \text{s}^{-1} \cdot \text{atm}^{-1}$) with a surface area of 342 cm². The packages contained 4 tomatoes, weighing approximately 0.45 kg, and were stored at 15 or 23°C. Equilibrium levels of about 6.9% 0_2 and 2% $C0_2$ were obtained at both storage temperatures. No data was presented as to the condition of the fruit after the 7 days of storage. Nor were any recommendations made for the best modified atmosphere for tomato storage.

Karel and co-workers (18,22) developed a graphical solution for predicting the steady state gas conditions of packages containing apples or bananas. Respiration and permeation rates, at different $\mathbf{0}_2$ concentrations, were plotted on the same set of coordinates. The point of curve

intersection represented the steady state gas concentration. The predicted equilibrium gas concentrations were in good agreement with the measured values.

Jurin and Karel (18) used 0.038 mm thick low density polyethylene (LDPE), with an area of 600 cm² and a 0_2 and $C0_2$ permeability of 2.65×10^{-7} and 1.03×10^{-6} cm³·mm²·cm⁻²·s⁻¹·atm⁻¹, respectively, which contained 2 apples (0.25 kg), stored at 20° C for 11 days. The equilibrium gas concentration was approximately 9% for 0_2 and 3% for $C0_2$. No data was reported for fruit condition after the 11 days of storage.

Packing green bananas, Karel and Go (22) used a LDPE film with the same characteristics listed above, however, the area was increased to 950 cm 2 and contained 0.363 kg of fruit. The bananas were stored for 10 days at 19 $^{\rm O}$ C and the 0 $_2$ and CO $_2$ concentrations within the package were approximately 7.0 and 3.5% respectively. These conditions delayed the onset of the respiratory climacteric but did not suppress it. No data on the condition of the fruit was reported.

Recently, Prince (29) utilized mathematical equations describing the respiration rate and film permeability to predict the film parameters required for tulip storage.

Even though models are available which would allow for optimization of the packaging system, a review of the literature indicates that only one packaging study utillized this approach and optimized the package system (29).

Experiments With Packaged Tomatoes

Non-Optimized Packaging

Early research with tomatoes packaged in polymeric films questioned the effectiveness of MAP. In 1947. Scott and Tewfik (33) reported deleteriously low 0_2 and high 0_2 levels within sealed packages containing 0.5 kg of firm ripe tomato fruit. They tested 7 cellophane films and a cellulose acetate (film area was not reported). The 0_2 and ${\tt CO}_2$ concentrations ranged from 0.4 to 1.2% and 11.0 to 18.9%, respectively, for 5 of the cellophanes after 4 days. The other cellophane film used had an 0_2 level of 12.8% and a CO_2 concentration of 5.5%. The cellulose acetate package had 0_2 levels of 15.7% while $C0_2$ accumulated to 2.8%. fruit sealed in the 6 cellophane films that had low 0_2 and elevated CO2 levels developed off-flavors with a fermented taste and showed no signs of further ripening. Tomatoes in the other 2 films did not develop off-flavors and ripened in The researchers concluded that none of the the package. films tested were suitable for tomato storage due to the alteration of the package atmosphere. They advocated film perforation to prevent the possibility of deleterious gas concentrations inside the package.

In another non-optimized study, Allen and Allen (2), in 1950, used mature-green tomatoes stored in 9 films that were either perforated or sealed air tight. After 10 days the gas concentration within the package and the color development of the fruit were examined. Oxygen levels in

the sealed bags were only 5% lower than for the perforated films and CO_2 increased to 2.4% in the sealed bags. The data for fruit color indicates that fruit in the sealed bags had less color development compared to those in the perforated packages. The authors concluded that the gas concentrations inside the sealed bags were detremental to tomatoes and recommended film perforation. Allen and Allen's interpetation of the data is very misleading since the fruit color data indicates that fruit stored in the sealed film actually had less color development and thus a potentially greater storage life. The O_2 and CO_2 levels reported were not at concentrations that would be expected to be deleterious to the fruit.

These researchers also examined taste and color development of pink tomato fruit stored in sealed or perforated cellophane for 4 days at 20°C (2). Color development data indicated that ripening of pink fruit was inhibited in the sealed containers, while fruit in the perforated bags developed full color. The taste test pannel judged the fruit from the sealed packages as inferior compared to fruit stored in the perforated bags. This should be expected as the comparison was between pink and ripe fruit.

The first positive results for MA packaging of tomatoes were reported in 1960 (4). In this study the effects of 8 films at 6 temperatures were examined with respect to the storage life of 5 varieties of mature green tomatoes. It

was reported that tomatoes sealed in 0.0254 mm thick cellulose acetate, 300 LSAD or 300 PHD cellophane, could be stored for 42 days at $15^{\,0}$ C. The 0_2 and $C0_2$ levels within the package were not reported. Nor were the permeabilities or area of the films given.

Other positive results were reported in 1975 where 'Marmande' tomatoes (breaker stage) stored for 21 days when sealed in polyvinyl chloride (PVC) film (31). The fruit were dipped in a 25 ppm solution of chlorine to reduce decay before sealing and were stored at 25° C. No data for film parameters was presented.

Duan et al. (7) compared tomatoes at 4 stages of ripening (green, turning, pink, pink-red) wrapped in 3 different PVC films. They reported that the PVC (Grade # RMF-61, $P_{02}1.35 \times 10^{-6}$; $P_{C0}7.0 \times 10^{-4} \text{ cm}^3 \cdot \text{mm} \cdot \text{cm}^{-2} \cdot \text{s}^{-1} \cdot \text{atm}^{-1}$) delayed ripening of the fruit at all maturity stages compared to the controls in air. The film was 0.018 mm thick, with an area of 484 to 613 cm² and contained 4 'Jetstar' tomatoes (approximatley 0.50 kg). The final 02 and C02 concentrations were 8.1 to 6.5% and 3.4 to 2.8%, respectively. After 14 days the flavor of the fruit stored in this film was unaffected.

It is clear from the above studies that films are available which can generate atmospheres suitable for tomato storage. It is also clear that determination of the best film combination can be tedious and involve elaborate experiments. As previously mentioned, models have been

developed which predict the equilibrium $\mathbf{0}_2$ and $\mathbf{C0}_2$ concentrations within the package and allow for package optimization although studies employing these models are limited.

Optimized Packaged Studies

Although models have been developed to predict the equilibrium gas concentration within plastic storage packages for tomatoes, apples and bananas (16,18,22) only 1 study (29) has been published which utilized the optimization concept.

Prince (29) optimized a package system for the storage of precooled tulips. His model indicated a LDPE film with a permeability of 9.5 x 10^{-5} and 3.7 x 10^{-4} cm³·mm·cm⁻²·s⁻¹·atm⁻¹ for 0_2 and $C0_2$, respectively, would produce the desired equilibrium gas concentration within a package containing 5 bulbs. The package was 0.051 mm thick with an area of approximately 800 cm² and tulips so packaged were stored at 20° C. The equilibrium levels obtained were approximately 5% 0_2 and 4% $C0_2$. These concentrations were previously determined to be the optimal range. The tulips maintained excellent flowering ability through 4 weeks of storage.

This example illustrates that much time can be saved when a method of predicting the permeability of a film is utilized before extensive experimentation is started. The methods should indicate a range of acceptable film

permeabilities for a commodity that will yield the proper MA within the package.

Other Factors Effecting The Package System

Factors which effect either fruit condition or film permeability should be considered when optimizing the package. Variables such as temperature, elevated ${\rm CO}_2$ and the formation of condensation inside the package may lead to undesirerable package conditions. The effects of low temperature on increasing the storage life of most horticultural commodities is well documented (20,30). However, low temperatures can damage tomatoes and other crops which are subject to chilling injury (25). Mature green tomatoes stored at $5^{\rm O}{\rm C}$ for more than 1 day may be injured. As tomatoes mature their susceptablity to chilling injury is reduced (21). However, it should be noted that even red-ripe tomatoes held at $5^{\rm O}{\rm C}$ will develop off-flavors and upon transfer to higher temperatures will soften and decay rapidly (14).

Temperature also effects the permeation rate of the film. Tomkins (36) reported that elevated storage temperatures increased the CO_2 concentrations within sealed packages. Hardenburg (13) concluded that temperature had a profound effect on the package O_2 and CO_2 equilibrium levels and offered little hope for a practical MAP system.

Other studies report that temperature changes affect both respiration rate and film permeability to the

same degree (16,29). Tomatoes stored at 15 or 23°C showed little difference in the final equilibrium 0_2 and $C0_2$ concentrations (16). Tulips packaged in LDPE and subjected to temperature fluctuations showed little change in 0_2 and $C0_2$ equilibrium levels (29).

Carbon dioxide does not have an effect on the permeation rate of other gases. Each gas is independent and diffuses through the film as if it were alone (12). However, CO_2 may have an effect on the condition of the fruit. Mature green tomatoes are susceptible to injury when exposed to levels of CO_2 greater than 2% (27). As the the fruit matures it can tolerate higher CO_2 levels. Symptoms of CO_2 injury include surface blemishes, increased softening and uneven ripening. Carbon dioxide also aggravates chilling injury at low temperatures (1).

To alleviate the problem of excessive ${\rm CO}_2$ accumulation, one may choose a film with a higher ${\rm CO}_2$ permeability. Unfortunately, of the films currently available those which have good ${\rm CO}_2$ permeability also have high ${\rm O}_2$ permeability. Thus solving the ${\rm CO}_2$ problem results in higher ${\rm O}_2$ levels in the package.

One practical solution would be to enclose a ${\rm CO}_2$ absorbant inside the package. Eaves and Lockhart (9) demonstrated the effectiveness of this method in 1960. They constructed chambers, each which contained 420 tomatoes, and were able to control the levels of ${\rm CO}_2$ accumulation by passing the chamber air over specific amounts of ${\rm Ca(OH)}_2$.

Condensation inside the package may also lead to package problems. In a sealed package one would assume that the relative humidity might approach 100, an ideal environment for mold development. To eliminate condensation on the film surface an anti-fogging agent may be used. Henig and Gilbert (16) utilized this type of film in their work, however no data were presented as to its effectiveness.

Saguy and Mannheim (31) utilized a different approach to control mold development. They suggested that fruit be dipped in a 25 ppm solution of chlorine to reduce decay.

Finally, one might also control humidity levels by including a desiccant in the package system. Natural Pak System has utilized this approach to control not only water vapor but also ${\rm CO}_2$ accumulation by adding a packet containing ${\rm Ca(OH)}_2$ and ${\rm CaCl}_2$ next to the produce (3).

It is clear from the above reports that many factors affect the package system. In the following study an attempt was made to develop a simple and sensitive method to mathematically describe tomato respiration rate as a function of $\mathbf{0}_2$ concentration. The resulting equation was utilized for modeling package systems which would generate a suitable MAP for the storage of red ripe tomatoes. The addition of a $\mathbf{C0}_2$ absorbant (MgO) to the package system was also examined with respect to its absorbing ability.

LITERATURE CITED

LITERATURE CITED

- Abeles, F. B. 1973. Ethylene in Plant Biology. Academic Press, New York. 302 p.
- Allen, A. S. and N. Allen. 1950. Tomato-film findings. Mod. Pack. 23(6):123-126, 180.
- 3. Anon. 1985. Controls ripening rate of packaged fruits/vegetables. Food Proc. 46(7):84.
- 4. Ayres, J. C. and L. C. Peirce. 1960. Effect of packing films and storage temperature on the ripening of mature green tomatoes. Food Tech. 14:648-653.
- 5. Burg, S.P. and E. A. Burg. 1969. Interaction of ethylene, oxygen and carbon dioxide in the control of fruit ripening. Qual. Plant. Mater. Veg. XIX, 1-3:185-200.
- 6. Cairns, J. A. 1974. The theory of permeation, 4-22. In: F. A. Paine (ed). Packaging for Climatic Protection. Newnes-Butterworths, Lodon.
- Daun, H. and S. G. Gilbert. 1974. Film permeation: The key to extending fresh produce shelf life. Pack. Eng. 19(8):50-54.
- Dennis, C., K. M. Browne, and F. Adamicki. 1979. Controlled atmosphere storage of tomatoes. Acta Hort 93:75-83.
- 9. Eaves, C. A., and C. L. Lockhart. 1961. Storage of tomatoes in artificial atmospheres using the calcium hydroxide absorption method. J. Hort. Sci. 36:85-92.
- 10. Furlong, C. R. 1947. The storage of green tomatoes with special reference to open-air fruit and end-of-season fruit from glasshouses. J. Hort. Sci. 22:197-208.
- 11. Goodenough, P. W. 1982. Tomatoes in CA storage. Grower. 98(9):17,19.

- 12. Hanlon, J. F. 1971. Handbook of Package Engineering. McGraw-Hill, New York.
- 13. Hardenburg, R. E. 1971. Effects of in-package environment on keeping quality of fruits and vegetables. HortSci. 6(3):198-201.
- 14. Hall, C. B. 1961. The effect of low storage temperature on the color, caratenoid pigments, shelf-life and firmness of ripened tomatoes. Proc. Amer. Soc. Hort. Sci. 78:480-487
- 15. Herregods, I. M. 1971. Storage of tomatoes. Acta Hort. 20:137-145.
- 16. Henig, Y. S. and S. G. Gilbert. 1975. Computer analysis of the variables affecting respiration and quality of produce packaged in polymeric films. J. Food Sci. 40:1033-1035.
- 17. Isenberg, F. M. R. 1979. Controlled atmosphere storage of vegetables. Hort. Rev. 1:337-394.
- 18. Jurin, V. and M. Karel. 1963. Studies on control of respiration of McIntoch apples by packaging methods. Food Tech. 17(6):104-108.
- 19. Kader, A. A. 1980. Prevention of ripening in fruits by use of controlled atmosphere. Food Tech. 34(3):51-54.
- 20. Kader, A. A. 1985. Modified atmosphere and low-pressure systems during transport and storage. In: A. A. Kader (ed). Postharvest Technology of Horticultural Crops. Univ. Calf. Div. Agric. and Nat. Res. Publ. 3311. 58-64.
- 21. Kader, A. A., J. M. Lyons and L. L. Morris. 1974. Postharvest responses of vegetables to preharvest field temperature. HortSci. 9(6):523-527.
- 22. Karel, M. and J. Go. 1964. Control of respiratory gases. Mod. Pack. 37(6):123-127,190,192.
- 23. Kidd, F. and C. West. 1932. Gas storage of tomatoes. Gt. Brit. Dept. Sci. Indus. Res. Food Invest. Bd. Rept. 209-211.
- 24. Kim, B. D. and C. B. Hall. 1976. Firmness of tomato fruit subjected to low concentrations of oxygen. HortSci. 11(5):466.

- 25. Lyons, J. M. 1973. Chilling injury in plants. Ann. Rev. Plant Physiol. 24:445-466.
- 26. Mizuno, S. 1971. The effect of carbon-dioxide and oxygen on ripening of tomatoes at 20°C. J. Jap. Soc. Hort. SCi. 40292-299. (Japanese with English summary).
- 27. Morris, L. L. and A. A. Kader. 1977. Physiological disorders of certain vegetables in relation to modified atmospheres. Proc. 2nd. Nat. CA Res. Conf., Mich. St. Univ. Hort. Rept. 28:142-148.
- 28. Parsons, C. S., R. E. Anderson, and R. W. Penny. 1970. Storage of mature green tomatoes in controlled atmosphere. J. Amer. Soc. Hort. Sci. 95:791-794.
- 29. Prince, T. A. 1980. Design and function of a modified atmosphere package for precooled tulip bulbs. PhD Dissertation, Mich. State Univ., East Lansing, Mi.
- 30. Ryall, A. L. and W. J. Lipton. 1972. Handling, Transportation and Storage of Fruits and Vegetables. Vol. 1. Avi, Westport, Conn.
- 31. Saguy, I. and C. H. Mannheim. 1975. The effects of selected plastic films and chemical dips on the shelf life of Marmande tomatoes. J. Food Tech. 10:547-552.
- 32. Salunkhe, D. K. and M. T. Wu. 1973. Effects of low oxygen atmosphere storge on ripening and associated biochemical changes of tomato fruits. J. Amer. Soc. Hort. Sci. 98(1):12-14.
- 33. Scott, L. E. and S. Tewfik. 1947. Atomospheric changes occurring in film-wrapped packages of vegetables and fruits. Proc. Amer. Soc. Hort. Sci. 49:130-136.
- 34. Smock, R. M. 1979. Controlled atmosphere storage of fruits. Hort. Rev. 1:301-336.
- 35. Thomas, T. H., D. Gray, and R. L. K. Drew. 1977. Potential for outdoor tomato production and storage in the U.K. Acta Hort. 62:101-108.
- 36. Tomkins, R. G. 1962. The conditions produced in film packages by fresh fruits and vegetables and the effect of these conditions on storage life. J. Appl. Bact. 25(2):290-307.

37. Tomkins, R. G. 1963. The effects of temperature, extent of evaporation, and restriction of ventilation on the storage life of tomatoes. J. Hort. Sci. 38:335-347.

SECTION I

DEVELOPMENT OF PREDICTION MODELS FOR OXYGEN

CONCENTRATIONS IN PACKAGED TOMATO FRUITS

The extension of fruit and vegetable storage life by reducing the 0_2 concentration and increasing the concentration of CO_2 of the atmosphere surrounding the produce was first reported by Kidd and West (10). An inexpensive method of creating these conditions is by enclosing fruit within polymeric films. Modified atmosphere packaging (MAP) has been used to extend the storage life of comodities such as banana (5), tomatoes (2) and lettuce (1).

Equilibrium 0_2 and $C0_2$ concentrations are determined by the respiration rate of the product, the permeability, area and thickness of the film, and the storage temperature (12). At equilibrium, the rate of gas movement across a barrier can be expressed mathematically by Fick's law of gas diffusion:

$$J_{i} = P_{i} \cdot A \cdot \Delta x^{-1} \cdot (c_{i1} - c_{i2}) \tag{1}$$

where: $J_i = Flux of gas 'i'$

P_i = Permeability of the film to gas 'i'

A = Surface area of the film

 $\Delta x = Film thickness$

 $c_{i1} - c_{i2} = Concentration gradient of gas 'i'.$

The $\mathbf{0}_2$ concentration within the package can be predicted by substitution and rearangement of equation 1 where:

$$[0_2]_{pkg} = [0_2]_{atm} - J_{0_2} \cdot \Delta x \cdot P_{0_2}^{-1} \cdot A^{-1}$$
 (2)

where: J_0 = Flux of 0_2 through film which at equilibrium is the rate of 0_2 uptake of the packaged fruit.

 P_0 = Permeability of a film to 0_2 .

Equation 2 allows mathematical estimation for package optimization if the film and fruit parameters are known.

Obtaining the parameters for the film is a straightforward matter. Permeation rates for a large variety of films is available (3,6). The area and thickness of the film is limited by a pratical size for the product and current manufacturing technology. The rate of 0_2 uptake of the product (RR 0_2) is more difficult to obtain as it is dependent on the 0_2 concentration within the package and the amount of fruit.

Determination of 0_2 consumption by tissues as a function of 0_2 concentration is a straight forward procedure but requires highly accurate analytical equipment. In a continuous flow system it is analytically difficult to detect a small 0_2 change (ml·h⁻¹) when the background 0_2 is in the range for optimum product storage. To overcome this deterent, the rate of $C0_2$ production is sometimes measured and a RQ of 1 is often assumed. Measuring $C0_2$ production is quite feasible; background levels are close to 0 and analytical instrumentation based on infra red absorption by $C0_2$ is sufficiently accurate.

To eliminate the extensive experimentation required to

develop the optimum package system several models have been developed. Karel and co-workers (8,9) developed a graphical solution for predicting the steady state gas concentration inside the package. A complex computer aided method utilizing differential equations to estimate package equilibrium 0_2 and $C0_2$ concentrations has also been developed (7). Recently Prince (11) utilized mathematical descriptions of respiration and film permeation to optimize film parameters for the packaging of tulip bulbs.

The respiration rate of the packaged product is an important factor for each of these models. Yet the method of determining these values may be questioned. In the graphical method (8,9) the calculations are based on the assumption that accumulated CO_2 has no effect on the tissue O_2 consumption. Oxygen was measured directly from respiration chambers at 12 hour intervals and O_2 consumption curves were developed. The amount of time elapsed between sampling may be too long to obtain accurate description of the O_2 consumption.

In the computer aided method, respiration rates were determined by plotting the 0_2 consumption rate as a function of time, and dividing the curve into linear and curvilinear portions (7). The curvilinear segments were plotted on semilogarithmic paper yielding a straight line. Regression analysis was carried out on both portions of the curve and the resulting coefficients were used to calculate the 0_2 consumption and 0_2 evolution rates at various 0_2 and 0_2

concentrations. Dividing the curve into 2 portions facilitates data manipulation but does not accurately describe respiration in a physiological sense. Sample collection was at constant time intervals but no mention as to the number or rate of sampling is noted. If much time elasped between samples accuracy of the curve may be questioned.

Prince (11) placed tulips in containers covered with films with different permeability characteristics and monitored 0_2 and CO_2 changes within the containers over time. Regression analysis was used to mathematically describe the resulting 0_2 and CO_2 curves. These equations were then utilized together with equations describing the permeability characteristics of the film to design a package for tulip storage. The limitations of this method include the long time periods required for data collection, the limited number of data points used in the regression analysis, and the use of film-covered containers which decrease the sensitivity of the system due to the variability of the film's permeation rate. This system also lacks respiration data at low 0_2 levels and does not examine the effects of 0_2 independently from CO_2 .

The objectives of the following research were to develop a simple and sensitive method of determining fruit respiration rates, expressed in term of $\mathbf{0}_2$ uptake as a function of $\mathbf{0}_2$ concentration. The respiration rate is described as a continuous mathematical function over a range

of 0_2 from 0 to 20%. Utilizing the mathematical function, models were developed for predicting the 0_2 concentration within polymeric packages containing tomatoes for variety of situations.

MATERIALS AND METHODS

Tomatoes (<u>Lycopersicon esculentum</u> cv. Tropic) were harvested at the breaker, pink and red stage of ripeness and placed in wide mouth canning jars (pint size). The jars contained 4.30g MgO ($\rm CO_2$ absorbant) and were sealed air tight with lids and screw rings. The jar lids had 1 inch holes through which an oxygen probe (Beckman Oxygen Analyzer, Model No. 0260) and rubber stopper were fitted. The jars were submerged in a water bath and held at $25^{\rm OC}$.

The oxygen probe was calibrated to known oxygen concentrations before and after each run. The probe output was monitored continuously with a strip chart recorder (Linear, Model No. 1200) and at 5 minute intervals with a data-logger (Omniscribe Polycorder, Model No. 516). Experiments lasted 28.5 to 60.0 hours depending on the weight of the fruit and the net air volume of the jar. Over this interval $\mathbf{0}_2$ content declined from 21% to ca. 0%. Oxygen depletion curves were measured for 3 fruit at each ripening stage.

At the end of each experiment, data was transferred from the data-logger to computer for analysis. For

convenience of data manipulation the $\mathbf{0}_2$ data was averaged over $\mathbf{0.5}$ hour intervals.

RESULTS

Respiration Model

Percent $\mathbf{0}_2$ values were plotted against time for each experiment (Fig.1). The best fit equation of the averaged $\mathbf{0}_2$ data was found to have the form:

$$[0_2] = a [1-e^{-(b+ct)}^d]$$
 (3)
where: $[0_2] = percent oxygen$
a,b,c and d = Arbitrary constants of the equation

t = time (hrs).

Figure 2 reports the averaged 0_2 data and the best fit line developed by equation 3. Fruit weight, net air volume and constant values are presented in Table 1. All r^2 values were 0.999 or better.

The first derivative of equation 3 gives the rate of change in $\mathbf{0}_2$ percent as a function of time:

$$d[0_2]/dt = acd [(b+ct)^{d-1}]^d [e^{-(b+ct)}]$$
 (4).

From equation 4 the rate of respiration (ml $0_2 \cdot kg^{-1} \cdot h^{-1}$) can be calculated as a function of time:

$$RR_{02} = (d[0_2]/dt) (v/w)$$
 (5)
where: $v = Void volume of jar (ml)$

w = Weight of fruit (kg).

Combining equations 4 and 5 defines the rate of respiration as a function of time:

$$RR = acdvw^{-1} [(b+ct)^{(d-1)}]^{d} [(e^{-(b+ct)})]$$
 (6)

Solving equations 3 and 6 simultaneously for the same value of 't' yields 0_2 concentration and respiration rate data respectively (Fig. 3).

A best fit equation for the curves in Fig. 3 was determined and found to have the form:

$$RR = q(1-e^{-r[0_2]})^s (7)$$

Equation 7 represents the average respiration rate expressed in 0_2 (ml·kg⁻¹·h⁻¹) as a function of 0_2 concentration at 25° C.

The best fit line and data values for each ripening stage are plotted with individual data in Fig. 4 and summarized in Fig. 5. The constant values for equation 7 for breaker, pink and red fruit are presented in Table 2.

Application Of Curves

To determine the $~0_2$ equilibrium concentration within a plastic package containing red ripe tomatoes, it is necessary to solve equations 1 and 7 at simultaneously given $~0_2$ concentrations. Equation 1 describes the flux of $~0_2$ through a polymer with ~k nown P_0 , A and $~\Delta x$. The 2 respiration rate of the packaged fruit is expressed by

equation 7, and is a function of 0_2 concentration and fruit weight. Solving equations 1 and 7 may be accomplished graphically as shown in Fig. 6. In this model situation the respiration rates of red tomatoes (0.2, 0.4, 0.6, 0.8 and 1.0 kg) are plotted along with the permeabilities of 5 films (P·A· Δx^{-1} values of 10, 20, 30, 40 and 50 ml·h⁻¹) on the same x,y ordinates. The point of intersection between any respiration curve for a given fruit weight and a particular film represents the 0_2 equilibrium concentration expected in the package for that film/fruit combination.

These equations may also be solved numerically with the aid of a computer. This method was utilized to generate data plotted in Fig. 7 which shows the effect of fruit weight and various $P \cdot A \cdot \Delta x^{-1}$ values on 0_2 equilibrium concentrations. It is seen that for any given film, increasing fruit weight has a decreasing impact on the drop in equilibrium 0_2 concentration.

The time required to reach equilibrium 0_2 levels after packaging is a function of tomato respiration rate $(RR_{0_2},$ eq. 7), the rate of 0_2 flux through the film $(J_{0_2},$ eq. 1) and the net air void volume of the package (V_0) :

$$[0_2]_{t} + \Delta_t = [0_2]_{t} + (J_{\Delta t} - RR_{\Delta t}) \cdot V_0^{-1} \tag{8}$$
 where:
$$[0_2]_{t} + \Delta_t = \text{New } 0_2 \text{ concentration after } \Delta t \text{ time}$$

$$[0_2]_{t} = 0_2 \text{ concentration at any time } t$$

$$J_{\Delta t} = \text{flux through film over } \Delta t \text{ time}$$

$$RR_{\Delta t} = \text{respiration rate of fruit over } \Delta t \text{ time.}$$

Solving this equation at time intervals of 0.1 hours where $P \cdot A \cdot \Delta x^{-1} = 7.48$, $V_0 = 310~cm^{-3}$ and fruit weight = 0.473 kg results in an estimated takedown time of about 25 hours. The 0_2 depletion of a package with the above conditions was monitored. These results, as well as the predicted 0_2 concentrations are presented in Fig. 8.

Using eq. 8 and changing the void volume (V_0) results in increased takedown times to reach equilibrium conditions within the package (Fig. 9). The final equilibrium 0_2 concentration is not altered.

DISCUSSION

Accurate data describing the rate of 0_2 uptake versus 0_2 concentration has limited the development of models for predicting equilibrium 0_2 conditions in MAP systems. The 0_2 depletion method presented offers one approach to the generation of this data in a mathematical form which can readily be used for modeling. Curves generated using this method were similar for 3 stages of ripening (Fig. 5). This observation should be further substantiated since it has a strong and positive bearing on packaging. According to this data, films optimized for the breaker stage of ripening should continue to be valid as the fruit ripens.

There were certain potential problems with the method. Carbon dioxide accumulation was minimized by the addition of MgO and never exceeded 1% (data not shown). With the

absorption of ${\rm CO}_2$, there was an accompanying drop in pressure within the container but according to Henry's Law, the pressure of ${\rm O}_2$ should be independent of total pressure. In addition, the ${\rm O}_2$ electrode utilized was found to be accurate under the range of pressures expected.

Another potential problem is that gases within the fruit may not be at equilibrium during the course of the experiment due to resistance to gas movement by the flesh. This would cause an underestimation of the rate of $\mathbf{0}_2$ uptake at any given $\mathbf{0}_2$ concentration. Cameron and Yang (4), have shown that tomato fruits behave essentially as hollow spheres based on efflux analysis of preloaded ethane. Thus, tissue resistance may not have a significant effect, particularly at lower $\mathbf{0}_2$ concentrations where the rate of change in the system is small and hence closer to equilibrium.

Although further refinement of the relationship between 0_2 uptake and concentration may be required, the general trends developed in the model should remain valid. The relationship between fruit weight and equilibrium 0_2 is particularly interesting (Fig. 7). The model predicts that it should be possible to select films with permeability characteristics such that the package conditions would be nearly optimized over a range of fruit weights. This is a result of the fact that at lower 0_2 concentrations, a small drop in 0_2 concentration has a greater effect on the rate of 0_2 uptake than at higher 0_2 concentrations (Fig. 5). This

effect would greatly enhance the versatility of the MAP system.

In addition, the model predicts that establishment of equilibrium 0_2 concentrations should occur within reasonable periods of time if the ratio of void volume to fruit weight is sufficiently small. Figure 9 shows this relationship in a film package containing 0.80 kg of tomato, $P \cdot A \cdot x^{-1} = 25$ ml·h⁻¹, with void volumes of 100, 200, 300 and 400 ml. Rapid establishment of equilibrium is needed for practical applications of MAP.

LITERATURE CITED

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- Aharoni, N. and S. Ben-Yehoshua. 1973. Delaying deterioration of romaine lettuce by vacuum cooling and modified atmosphere produced in polyethylene packages. J. Amer. Soc. Hort. Sci. 98(5):464-468.
- 2. Ayres, J. C. and L. C. Peirce. 1960. Effect of packing films and storage temperature on the ripening of mature green tomatoes. Food Tech. 14:648-653.
- 3. Cairns, J. A. 1974. The theory of permeation, 4-22. In: F. A. Paine (ed). Packaging for Climatic Protection. Newnes-Butterworths, Lodon.
- 4. Cameron, A. C. and S. F. Yang. 1982. A simple method for the determination of resistance to gas diffusion in plant organs. Plant Physiol. 70:21-23.
- 5. Daun, H., S. G. Gilbert, Y. Ashkenazi and Y. Henig. 1973. Storage quality of bananas packaged in selected permeability films. J. Food Sci. 38:1247-1249.
- 6. Hanlon, J. F. 1971. Handbook of Package Engineering. McGraw-Hill, New York.
- 7. Henig, Y. S. and S. G. Gilbert. 1975. Computer analysis of the variables affecting respiration and quality of produce packaged in polymeric films. J. Food Sci. 40:1033-1035.
- Jurin, V. and M. Karel. 1963. Studies on control of respiration of McIntoch apples by packaging methods. Food Tech. 17(6):104-108.
- 9. Karel, M. and J. Go. 1964. Control of respiratory gases. Mod. Pack. 37(6):123-127,190,192.
- Kidd, F. and C. West. 1932. Gas storage of tomatoes. Gt. Brit. Dept. Sci. Indus. Res. Food Invest. Bd. Rept. 209-211.
- 11. Prince, T. A. 1980. Design and function of a modified atmosphere package for precooled tulip bulbs. PhD Dissertation, Mich. State Univ., East Lansing, Mi.

12. Tomkins, R. G. 1962. The conditions produced in film packages by fresh fruits and vegetables and the effect of these conditions on storage life. J. Appl. Bact. 25(2):290-307.

equation [0 ₂] = a [breaker, pink and re	a [1 -	e (0 * matoes.	(1) 3	a [1 - e -(0 * ct)] and inflection point values red tomatoes.	tion poin	t values	for equation 3 and 7 for	ion 3 ar	id 7 for
STAGE		BREAKER			PINK			RED	
FRUIT NUMBER	-	2	က		2	m	1	5	m
FRUIT WEIGHT(g)	132.42	164.18	177.08	194.62	189.01	177.55	177.79	219.50	196.62
NET AIR VOLUME(ml)	232.0	243.0	273.0	242.0	219.0	106.5	228.5	175.0	198.0
CONSTANT VALUES									
Q	23.886	37.945	49.200	28.458	25.002	33.608	39.372	34.600	35.695
q	1.019	0.945	0.784	1.022	1.050	066.0	0.951	0.962	0.952
U	-0.003	-0.019	-0.020	-0.010	-0.012	-0.046	-0.024	-0.037	-0.035
р	33.421	3.645	2.465	11.088	10.695	3.872	2.925	3,324	2.603
INFLECTION POINT VALUES(%)	14.95	17.85	17.85 20.23	17.06	14.82	17.42	19.00	17.30	16.39

TABLE 2. Constant values for the equation RR = $q(1-e^{-r[0}2])^s$ describing respiration rate as a function of oxygen concentration for breaker, pink and red tomatoes.

BREAKER	PINK	RED
	عاد العادية في العادية العادية في	
15.695	17.477	14.371
0.156	0.109	0.138
0.959	0.963	0.748
	15.695 0.156	15.695 17.477 0.156 0.109

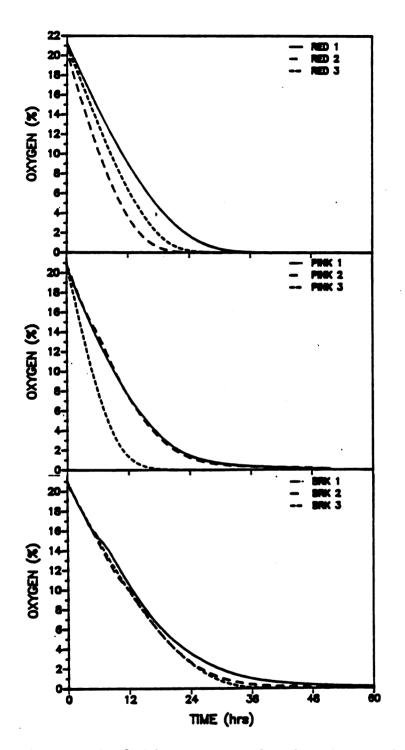


Figure 1. Oxygen depletion curves for breaker, pink and red tomatoes as a function of time following transfer to closed jar at time 0. (25 $^{\rm O}{\rm C})$

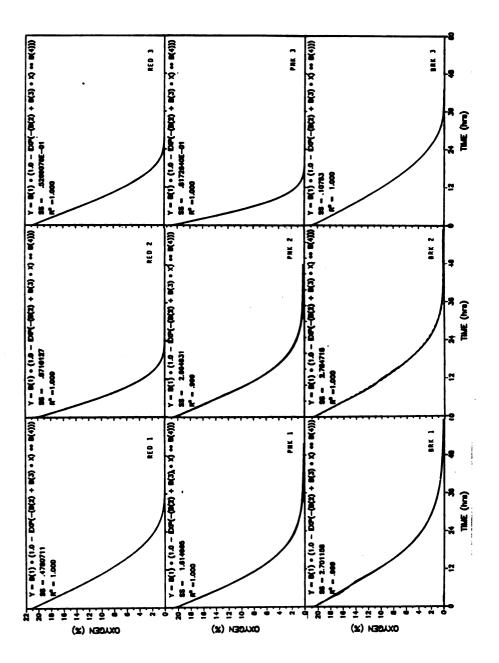


Figure 2. Oxygen depletion curves (solid line) and the best fit equation (dashed line) of the data for breaker, pink and red fruit.

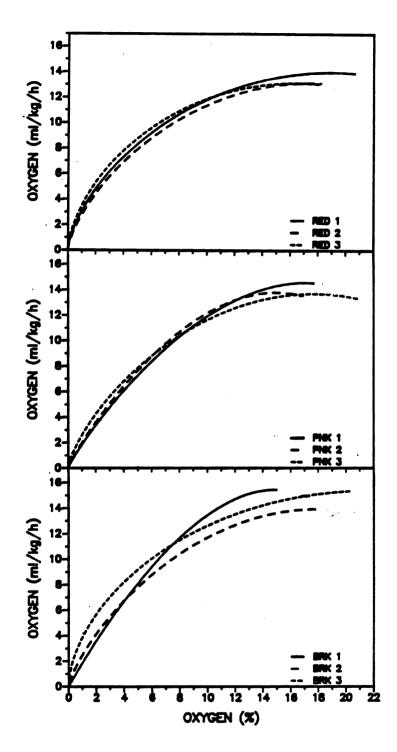


Figure 3. Respiration rate as a function of oxygen concentration for breaker, pink and red fruit. These curves were calculated from the derivative of the equations shown in Table 1 plotted versus oxygen concentration.

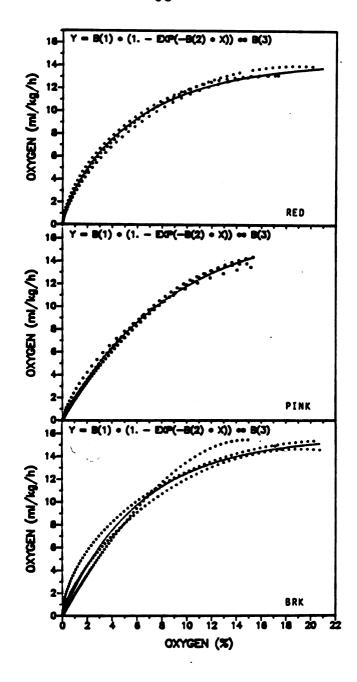


Figure 4. Best fit equation (solid line) for the average respiration rate of breaker, pink and red tomato fruit. Dashed lines show data for 3 individual fruit at each stage of ripeness from Fig. 3. Values for constants given in Table 2.

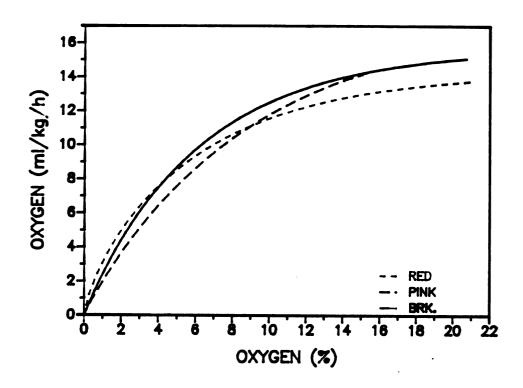


Figure 5. Average respiration rate for breaker, pink and red tomato fruit as a function of oxygen concentration as estimated from oxygen depletion curve analysis. All 3 equations of the form RR = $q(1 - e^{r[0_2]})^s$. Constant values given in Table 2.

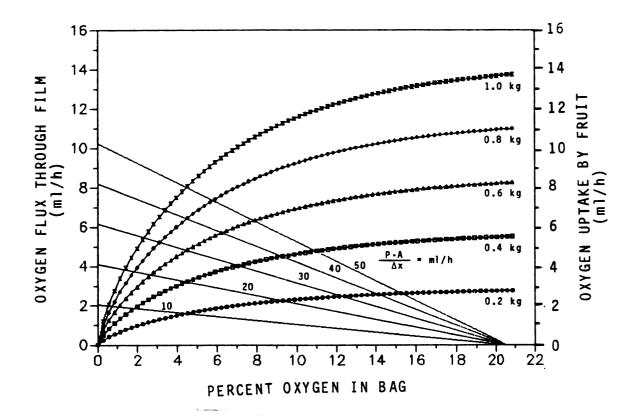


Figure 6. Simultaneous plots of the rate of oxygen flux through film (solid line) and rate of 0_2 uptake by fruit (symbol) as a function of film permeability characteristics and tomato fruit weight (kg) (P·A· Δ x⁻¹; ml·h⁻¹, respectively). Each intersection indicates the 0_2 concentration and flux of oxygen at equilibrium for that film/fruit combination.

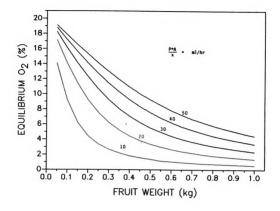


Figure 7. Estimated equilibrium concentrations of oxygen as a function of fruit weight (kg) and film permeability characteristics (P·A· Δ x⁻¹; ml·h⁻¹). The data was generated from solutions to eq. 1 and eq. 7 solved simultaneously.

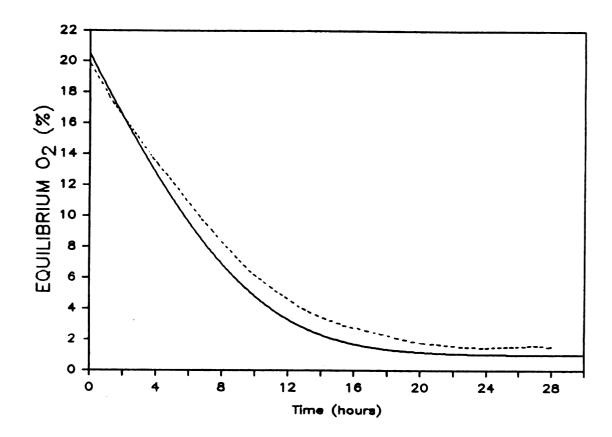


Figure 8. Estimated (solid) and actual (dashed) plots of oxygen concentration in a package system with fruit weight of 0.47 kg, void volume of 310 ml and P·A· \triangle x⁻¹ of 7.48 ml·h⁻¹ at 25°C.

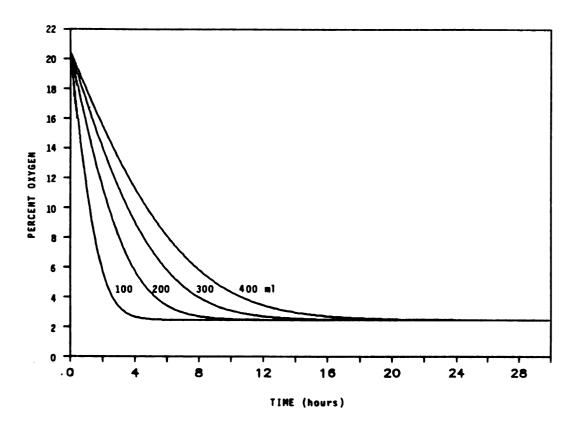


Figure 9. Estimated change in oxygen concentration in packaged tomato fruit (o.8 kg, $P\cdot A\cdot \Delta x^{-1}=25$ ml·h⁻¹) as a function of the void volume in the package.

SECTION II

MODIFIED ATMOSPHERE PACKAGING OF RED-RIPE TOMATOES

Fresh market tomato consumption is second only to lettuce in the United States (2). Postharvest storage losses are estimated to be approxamately 5 to 20% of the harvested crop (12). Spoilage occurs at all handling points following harvest including the consummer's home. A product which consummers could use in their homes to prolong fruit shelf life of red ripe tomatoes would be highly desirable. It has been proposed that selectively permeable packages could be used to create modified atmospheres to meet these demands.

Modified atmospheres (MA) can be generated by enclosing horticultural commodities within specific permeability plastic films. This approach is commonly referred to as Modified Atmosphere Packaging (MAP). Such an approach has been demonstrated effective for certain horticultural commodities (1,5,6). However, the few applications remain at the commercial level since it has been assumed that modified atmospheres exert their greatest influence on preclimacteric fruit.

Several early studies using films to generate modified atmospheres failed due to using low permeability films which caused unacceptably low 0_2 and high CO_2 levels in the packages (19,20). To overcome this problem, the optimum 0_2 and CO_2 concentrations to be established in the package must be known and the permeability of the film must be matched to fruit respiration.

Optimum atmosphere concentrations for fruit storage is

usually determined under controlled conditions. Using this approach, concentration ranges of 1 to 7% 0_2 and 0 to 5% $C0_2$ have been found to effectively prolong tomato storage life (3,6,7,8,10,11,13,14,15,17,18,21,22). The most effective range is assumed to be 2 to 3% 0_2 and 0 to 2% $C0_2$ for preclimacteric and turning fruit (11,12).

As far as can be determined, no research results have been published on the effects of MAP or controlled atmosphere (CA) storage for use with red ripe tomatoes. However, one report indicates that MAP retarded ripening of pink-red fruit (4).

The intent of this research was to determine whether 2% 0_2 concentration could effectively prolong red ripe tomato fruit shelf life. Once this was established, we attempted to select LDPE films to generate the low 0_2 atmosphere in sealed bags containing fruit based on the prediction model developed in Section 1. In addition, we tested the effect of a $C0_2$ absorber (MgO) to depress $C0_2$ levels within the bag.

Materials and Methods

Controlled Atmosphere Experiments

Mature green tomatoes (<u>Lycopersicon esculentum</u>. Mill) purchased locally on April 29, 1985 were washed, dried and weighed. The fruits were placed in wide mouth canning jars which were sealed with lids and screw rings. The lids were

fitted with inlet and outlet ports through which $20.5\%~0_2$ (ambient air) or $2\%~0_2$ in N_2 was passed through the jar at approximately $10\text{ml}\cdot\text{min}^{-1}$. On day 1 of the experiment 3 jars were transferred to the $2\%~0_2$ gas flow and the remaining jars were fitted to the ambient flow. On the second day 3 jars were transferred to the $2\%~0_2$ from the ambient flow. Thereafter on every other day 3 jars were transferred to the $10\%~0_2$. After 42 days, all fruit from the $2\%~0_2$ treatment were returned to ambient air flow.

Production of ethylene and ${\rm CO}_2$ were monitored during the experiment. Color development was determined subjectively using the "Michigan Tomato Color Chart" (Cooperative Extension Service, Michigan State University).

The experiment was divided into 2 parts for statistical analysis: days of storage (39 days for all stages) at 2% 0_2 and days after 2% 0_2 storage. The experiment was analyzed as a 2 way factorial. Each treatment was replicated 3 times.

In a second experiment, red ripe tomatoes purchased locally on December 16, 1985 were washed, dried and weighed. The tomatoes were held at 2 or 20.5% 0_2 at either 0 or 10% 0_2 in a continuous flow system. The storage containers were the same as those described in experiment 1.

Ethylene concentrations were determined 6 days after initiation of the experiment. The effective shelf life of the fruit was estimated on external appearance of mold development or skin cracking.

The experiment was analyzed as a completely randomized 2-way factorial design. Each treatment was replicated 6 times.

Modified Atmosphere Packaging Experiments

Low density polyethylene (LDPE) 0.044 mm thick and 0.069 mm thick films were used for the packaging experiments. The film's permeability to 0_2 is $2.28\cdot10^{-7}$ cc·mm·cm $^{-2}\cdot$ s $^{-1}\cdot$ atm $^{-1}$, (500cc·mil·100in $^{-2}\cdot$ day $^{-1}$.atm $^{-1}$) (Carl Beyer, personal communication). The bags were sealed with a hot bar sealer (SealnServe, Sears). Magnesium oxide was weighed and packed in pouches made of bonded cloth fibers (Miracloth). The pouches were approximately 5 x 8cm in size and contained 4.3 q of MgO unless otherwise noted.

<u>Packaging Experiment 1</u> Red ripe tomatoes purchased locally on June 25, 1985 were washed, dried and weighed. The fruits were sealed in LDPE (0.044 mm thick) bags having a surface area of 1370 cm². The bags contained 1, 2, 3 or 4 fruit with or without $4.30g \, \text{MgO}$.

Two 1 ml air samples were collected daily for 8 days through a silicone septum taped to the bag. The samples were analyzed for 0_2 , $C0_2$ and ethylene content.

The experiment was analyzed as a completly randomized design, 3-way factorial. The treatments were replicated 4 times.

<u>Packaging Experiment 2</u> Red ripe tomatoes purchased locally on August 27, 1985 were washed, dried, weighed and sealed in either 0.044 or 0.069 mm thick LDPE bags with or without 2.0 g MgO. The bag had a surface area of 1370 cm² and contained 1, 2, 3 or 4 fruits. Two 1 ml air samples were collected daily for the first 4 days, and again on day 8, and analyzed for 0_2 , 0_2 and ethylene.

The experiment was analyzed as a completely randomized design, 4-way factorial. Each treatment was replicated 4 times.

Packaging Experiment 3 Red ripe tomatoes ('Tropic') were harvested on January 3, 1986, from the Plant Science Greenhouse, Michigan State University, East Lansing, Michigan. The fruit were washed, dried, weighed and sealed in LDPE bags (0.069 mm thick). Each bag had a surface area of 640 cm² and contained 2 fruit (average total weight; 271.06 g) with or without MgO. Controls were stored in plastic fish net onion bags. Two days after sealing two 1 ml gas samples were collected with a syringe via a silicone septum bonded to the film. The samples were analyzed for 0₂, CO₂ and ethylene content. Fruit condition was checked daily and the fruit was considered inedible at the first signs of mold. Controls were terminated at the first sign of shrivelling or cracking.

The experiment was analyzed as a completly randomized design. The treatments were replicated 3 times.

Chilling Experiment Mature-green tomatoes ('82-VFM-685') were harvested at the Harrow Research Station, Harrow, Ontario, Canada, and transported to Michigan State University, where they were washed, dried, weighed and then exposed to 5° C for 0, 1, 2, 3, 4 and 5 days. The tomatoes were held at 20° C until red-ripe and then sealed in 0.069 mm thick LDPE bags (surface area 640 cm², 2 fruit per bag). The bags were fitted with a silicone septum. Two 1 ml samples were collected on the second day after sealing for analysis of 0_2 and $C0_2$. The fruits were examined daily and the number of days to the appearance of mold was recorded as days of potential shelf-life.

The experiment was analyzed as a completly randomized 2-way factorial. Each treatment was replicated 4 times.

RESULTS

No further color development was noted for mature green, breaker and turning fruit when held 39 days in continuous flow atmospheres of 2% 0_2 (Fig. 1). Pink and red fruit did have some color development in the 2% 0_2 atmosphere (Fig. 1). Upon transfer to ambient air at day 39, all fruit developed full red color within 6 days. After ripening, fruit were edible with one exception and no observable defects were apparent (results not shown).

Carbon dioxide production dropped to constant values for fruits at all stages of ripening within 6 to 8 days (Fig. 1). Steady state production of ${\rm CO}_2$ at 2% ${\rm O}_2$ for all

stages of ripening was an average of 3.62 ml·kg $^{-1}$ ·h $^{-1}$. No apparent differences were noted between respiration rate of fruit at the different stages of ripening.

Ethylene production dropped sharply within 24 hours of exposure to 2% 0_2 to approximately 0.2 ul·kg⁻¹·h⁻¹ regardless of the maturity of the fruit (Fig. 1). Transfer to ambient air flow after 39 days resulted in an apparent climacteric peak for all fruit with the less mature fruit generally producing the greatest amounts of ethylene.

Mature green fruit stored in an ambient air flow system ripened to red within 8 to 10 days (Fig. 2) and had a shelf life of approximately 15 days (results not shown).

A respiratory climacteric was observed while the fruit was at the turning stage and then declined slightly (Fig. 2). No obvious ethylene peak was noted but production declined markedly once fruit reached the red stage.

Carbon Dioxide Toxicity Red ripe tomato fruit stored at 2% 0_2 in the absence of $C0_2$ had a significantly longer storage life than the other treatments (Fig. 3). The addition of 10% $C0_2$ to the atmosphere reduced storage life under 2% 0_2 storage conditions. Typical $C0_2$ injury were observed on many of the fruit stored at the 10% $C0_2$ atmospheres such as cell wall degradation followed by mold development.

The addition of 10% $\rm CO_2$ significantly reduced ethylene production at ambient $\rm O_2$ concentrations (Tab. 1).

<u>Packaging Experiment 1</u> Levels of CO_2 increased linearly with increasing fruit number (Fig. 4). The addition of MgO suppressed the accumation of CO_2 within the package (Fig.

4). As expected, an inverse relationship existed between 0_2 and fruit number (Fig. 4). Bags containing 1 fruit had 0_2 levels of 16.18% while bags with 4 fruit had an average 0_2 concentration of 5.20%.

No trends were noted with respect to effect of MgO or fruit number on ethylene levels (Fig. 4). In all packages ethylene concentrations exceeded 5 ppm.

Oxygen equilibrium levels were reached 1 day after sealing and remained essentially constant over duration of experiment (data not shown). Package concentrations of ${\rm CO}_2$ and ethylene exhibited a slightly different pattern (Fig. 5). Both gases obtained the greatest concentration within the bag 1 day after sealing these levels gradually declined for the next 4 days.

<u>Packaging Experiment 2</u> As the number of fruit per bag was increased the 0_2 levels decreased as in Modified Atmosphere Experiment 1 (Fig. 6). The effects of film thickness on 0_2 concentrations was significant only with bags containing 1 fruit. As the number of fruit increased, the effect of film thickness was difficult to distinguish statistically.

Equilibrium 0_2 conditions for Modified Atmosphere Experiment 2 were obtained within 1 day after sealing and remained nearly constant throughout the experiment (data not

shown). The 0_2 levels of the bags with 1, 2, 3 and 4 fruit averaged 11.9, 8.0, 5.5 and 4.7% respectively (LSD_{.05} = 0.665).

The trend for equilibrium CO_2 conditions within the package were established 2 to 3 days after packaging (Fig 7). Magnesium oxide reduced the level of CO_2 accumulation for 4 days regardless of the number of fruit or film thickness (Fig. 7). However, between 4 and 8 days, CO_2 increased to levels nearly equal to those of bags without MgO with 3 and 4 fruit per bag.

A linear relationship existed between increasing fruit number averaged over days and CO_2 levels within the package (Fig. 8). Carbon dioxide levels averaged 2.88% for bags with 1 fruit and 6.52% for bags containing 4 fruit with and without MgO. Film thickness had a small effect on the package CO_2 levels.

Statistically, ethylene equlibrium was reached by the second day of the experiment and remained so throughout the remainder of the experiment in all treatments (data not shown).

Packaging Experiment 3 The fruit sealed in 0.069 mm film with MgO attained about 2% 0_2 and had twice the shelf life of the fruit sealed without MgO and 3 times that of the controls (Table 2). Magnesium oxide did not effect the 0_2 or ethylene levels (ca. 2% and 4ul/l, respectively), but did reduce the CO_2 accumulation to below 1% (Table 2).

Chilling Experiment In this test, mature green fruits were held at 5° C for 0 to 5 days, subsequently ripened to red ripe and then packaged in film with or without MgO for storage evaluation at 20° C. Tomatoes in packages which contained MgO had twice the storage life of fruits packaged without MgO. After 24 hours of storage, condensation was noted in packages without MgO but not when the chemical was present. Equilibrium 0_2 levels were approximately 2% and were not affected by the presence of MgO. The addition of MgO to the package system reduced $C0_2$ accumulation to below levels of 2% compared to 11% in packages without MgO regardless of the length of the chilling period (Fig. 9).

DISCUSSION

Figure 1 illustrates the effectiveness of 2% 0_2 storage atmosphere in reducing the production of CO_2 and ethylene by tomatoes regardless of maturity stage. This 0_2 concentration is at the lower end of the recommended storage atmospheres (11,12), but was very effective in the current experiment as the fruit stored at this condition had a shelf life of at least 45 days without observable effects on quality.

Levels of 10% CO_2 had a deleterious effect on the storage life of red ripe tomatoes (Fig. 3). Carbon dioxide toxicity on mature green and turning fruit has been reported in the past (16). This high level of CO_2 can be expected in LDPE packages where the equilibrium O_2 level of 2% is

obtained (Table 2 and Fig. 9). To control the accumulation of CO_2 , MgO was added to the package system. Magnesium oxide was effective in reducing the levels of CO_2 to below 2% in most cases (Fig. 4 and 9) and to below 0.5% in 1 experiment (Table 2). The exception was when only 2.0 g of MgO was used with bags containing 3 and 4 fruit. In this situation the MgO was apparently saturated between 4 and 8 days (Fig. 7) and could no longer absorb CO_2 .

Ethylene levels in all packages were quite high in a physiological sense but this may be inconsequential because the fruits were red ripe when packaged. Ethylene plays an important role in initiating ripening of tomatoes and may limit storage life in CA storage (12). The role of ethylene on post climacteric fruit is not well documented. The effects of ethylene were not measured in these experiments. Future studies may indicate that inclusion of an ethylene absorbant may be desireable.

The predicted equilibrium 0_2 concentrations within packages of red-ripe tomatoes obtained from the model developed in section 1 are presented in Fig. 10. The actual 0_2 levels are higher than the predicted values, thus our attempt at optimization was not reached in the first 2 packaging experiments. This discrepancy, in part, is due to the inability to seperate argon from 0_2 with the gas chromatograph used for determining 0_2 concentrations. Argon composes 0.93% of the atmosphere and should be factored out. This discrepancy could also be caused by leaks in the film

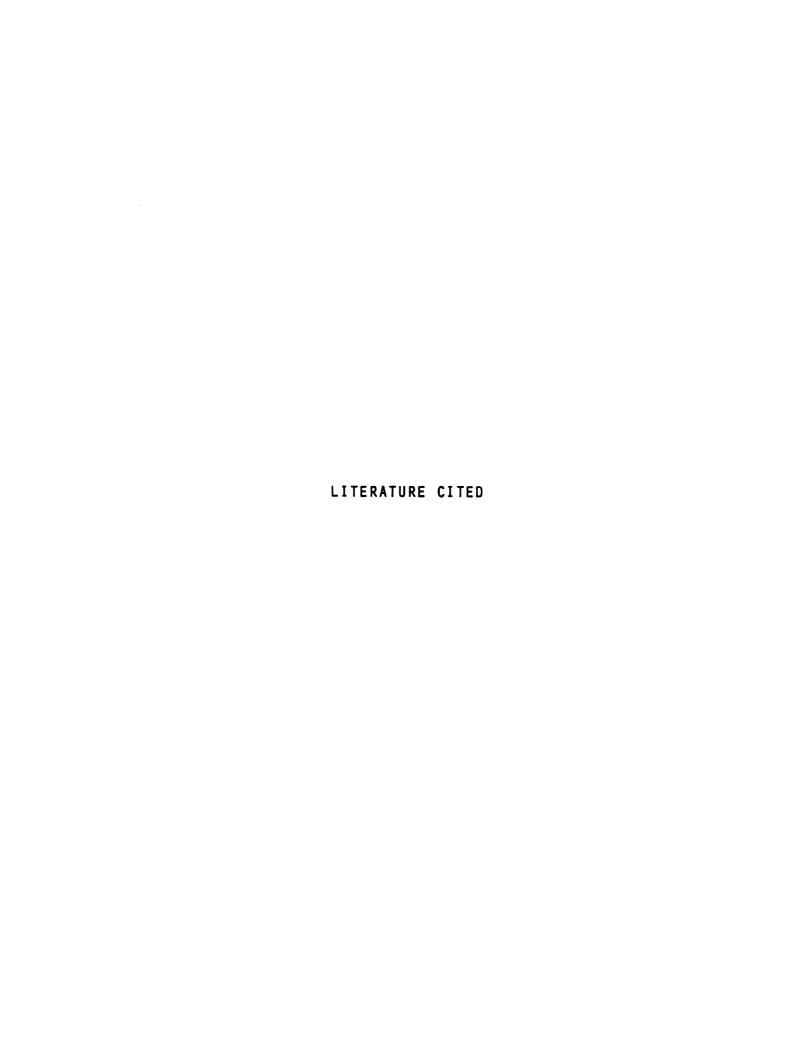
but this is unlikely since all treatments showed the same trend. A more likely explanation is a discrepancy between reported and actual film permeabilities. Rearranging eq. 2 from section 1 and solving for P_{02} with the fruit weight, surface area and film—thickness—data from packaging experiment 2 results in an apparent 0_2 permeability of 3.42 x 10^{-7} cm³·mm·cm⁻²·s⁻¹·atm⁻¹ compared to the 2.28 x 10^{-7} cm³·mm·cm⁻²·s⁻¹·atm⁻¹ value used in the prediction equation. Part of this difference could be a result of the variability in film thickness. Present production technology allows for a given thickness plus or minus 10% (9).

Small holes can have a dramatic effect as demonstrated by the effect of a single pin hole (26 guage needle) on the change in equilibrium 0_2 concentrations in packaged tomato fruit (Fig 11). The bag contained 0.47 kg of fruit, had a surface area of 630 cm² and an initial equilibrium 0_2 concentration of 1.71%. Twenty-five hours after puncturing the film the package 0_2 equilibrium level rose to 11.68%.

Package optimization was achieved when the surface area of the film was reduced as in packaging experiment 3 (Table 2). Yet red-ripe tomatoes stored only 16 days, not the 40 plus days that were noted in the continuous flow experiment (Fig. 1). Storage life of tomatoes in film packages was most often terminated by mold development most probably caused by condensation which was noted in the packages.

Future packaging studies are needed to determine the effects and limitations of packaging on different

cultivars. More information is also nessecary on the hummidity levels in the package, and the effect of MgO on these levels. Although future experiments are needed, our results indicate that the MgO incorporated into an optimized package system may be an effective means to extend storage life of red-ripe tomatoes.



LITERATURE CITED

- 1. Aharoni, N. and S. Ben-Yehoshua. 1973. Delaying deterioration of romane lettuce by vacuum cooling and modified atmosphere produced in polyethylene packages. J. Amer. Soc. Hort. Sci. 98(5):464-468.
- 2. Anon. 1984. Vegetable outlook and situation report. USDA Publ. TVS-233:28.
- 3. Daun, H., S. G. Gilbert, Y. Ashkenazi and Y. Henig. 1973. Storage quality of bananas packaged in selected permeability films. J. Food Sci. 38:1247-1249.
- 4. Daun, H. and S. G. Gilbert. 1974. Film permeation: The key to extending fresh produce shelf life. Pack. Eng. 19(8):50-54.
- 5. Dennis, C., K. M. Browne and F. Adamicki. 1979. Controlled atmosphere storage of tomatoes. Acta Hort. 93:75-83.
- 6. Eaves, C. A., and C. L. Lockhart. 1961. Storage of tomatoes in artificial atmospheres using the calcium hydroxide absorption method. J. Hort. Sci. 36:85-92.
- Furlong, C. R. 1947. The storage of green tomatoes with special reference to open-air fruit and end-ofseason fruit from glasshouses. J. Hort. Sci. 22:197-208.
- B. Goodenough, P. W. 1982. Tomatoes in CA storage. Grower. 98(9):17,19.
- 9. Hanlon, J. F. 1971. Handbook of Package Engineering. McGraw-Hill, New York.
- 10. Herregods, I. M. 1971. Storage of tomatoes. Acta Hort. 20:137-145.
- 11. Kader, A. A. 1980. Prevention of ripening in fruits by use of controlled atmosphere. Food Tech. 34(3):51-54.

- 12. Kader, A. A. 1985. Modified atmosphere and low-pressure systems during transport and storage. In: A. A. Kader (ed). Postharvest Technology of Horticultural Crops. Univ. Calf. Div. Agric. and Nat. Res. Publ. 3311. 58-64.
- 13. Kidd, F. and C. West. 1932. Gas storage of tomatoes. Gt. Brit. Dept. Sci. Indus. Res. Food Invest. Bd. Rept. 209-211.
- 14. Kim, B. D. and C. B. Hall. 1976. Firmness of tomato fruit subjected to low concentrations of oxygen. HortSci. 11(5):466.
- 15. Mizuno, S. 1971. The effect of carbon-dioxide and oxygen on ripening of tomatoes at 20°C. J. Jap. Soc. Hort. Sci. 40292-299. (Japanese with English summary).
- 16. Morris, L. L. and A. A. Kader. 1977. Physiological disorders of certain vegetables in relation to modified atmospheres. Proc. 2nd. Nat. CA Res. Conf., Mich. St. Univ. Hort. Rept. 28:142-148.
- 17. Parsons, C. S., R. E. Anderson, and R. W. Penny. 1970. Storage of mature green tomatoes in controlled atmosphere. J. Amer. Soc. Hort. Sci. 95:791-794.
- 18. Salunkhe, D. K. and M. T. Wu. 1973. Effects of low oxygen atmosphere storge on ripening and associated biochemical changes of tomato fruits. J. Amer. Soc. Hort. Sci. 98(1):12-14.
- 19. Schomer, H. A. 1953. Films for produce. Mod. Pack. 26(8):191-196.
- 20. Scott, L. E. and S. Tewfik. 1947. Atmospheric changes occurring in film-wrapped packages of vegetables and fruits. Proc. Amer. Soc. Hort. Sci. 49:130-136.
- 21. Thomas, T. H., D. Gray, and R. L. K. Drew. 1977. Potential for outdoor tomato production and storage in the U.K. Acta Hort. 62:101-108.
- 22. Tomkins, R. G. 1963. The effects of temperature, extent of evaporation, and restriction of ventilation on the storage life of tomatoes. J. Hort. Sci. 38:335-347.

Table 1. Ethylene production of red ripe tomatoes as a function of oxygen concentration (2% and ambient) and carbon dioxide concentration (0 and 10%).

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STORAGE	ATMOSPHERE	ETHYLENE PRODUCTION*
02 (%)	co ₂ (%)	$ul\cdot kg^{-1}\cdot h^{-1}$
2	0	0.500
2	10	0.325
21	0	1.819
21	10	0.825

^{*}LSD (P=0.05) = 0.575

Table 2. The storage life of red ripe tomatoes held in ambient air (control), packaged in film optimized to 2% oxygen with and without the presence of MgO. Experiment conducted at 20°C .

Package	Control	Film	Film + MgO
Storage life (days)	5	8	16*
0xygen (%)	20.5*	2.02	2.13
Carbon Dioxide	0.03	9.18*	0.44
(%) Ethylene (ul/l)	0.0*	4.21	5.09

Film and fruit specifications:

Film permeability; $2.28 \times 10^{-7} \text{ ml·mm·cm}^{-2} \cdot \text{sec}^{-1} \cdot \text{atm}^{-1}$ (500 cm²·mil·100in²·24hr⁻¹·atm⁻¹)

Film thickness; 0.069 mm (2.7 mil)

Film area; $598 \text{ cm}^2 (92.7 \text{ in}^2)$

Average fruit weight per bag; 271.06g

Numbers with superscripts indicates significant difference between treatments within the row at P = 0.05.

Table 3. The storage life (days) of red-ripe packaged tomatoes as a function of presence or absence of MgO and exposure to 5°C for different time intervals when at the mature green stage.

DAYS AT 50C	STORAGE LIFE (days) Mg0				
	M	-	X		
0	11	6	8 a		
1	11	5	8		
2	9	5	7		
3	8	4	6		
4	10	5	7		
5	9	4	6		
X	10*	5	الله الله الله الله الله الله الله الله		

Film and fruit parameters:

Film Permeability; 2.28 x 10^{-7} cm³·mm·cm⁻²·sec⁻¹·atm⁻¹ (500 cm³·mil·100in⁻²·24hr⁻¹·atm⁻¹)

Film thickness; 0.069 mm (2.7 mil)

Film area; $598 \text{ cm}^2 (92.7 \text{ in}^2)$

Average fruit weight per bag; 285.51 g

^{*} Significantly different at P=0.05 a LSD_05 = 1

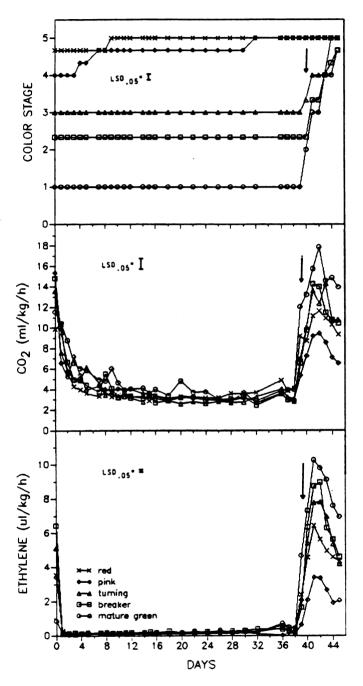


Figure 1. Color development, carbon dioxide and ethylene production of tomatoes at different ripening stages held at 2% 0_2 (20° C). Arrow indicates transfer from 2% 0_2 back to ambient air. LSD $_{05}$ for ambient air data = 0.44, 1.39 and 1.14 for color development, carbon dioxide and ethylene production, respectively.

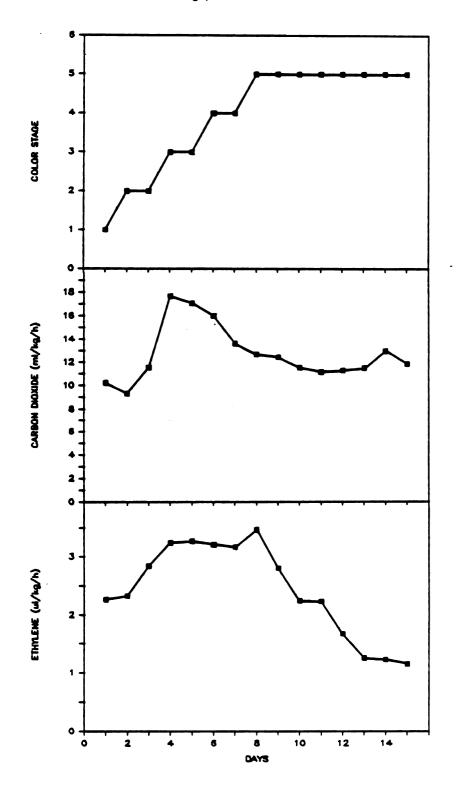


Figure 2. Change in color development, respiration and ethylene evolution during ripening of mature green tomatoes held in ambient air at 20°C .

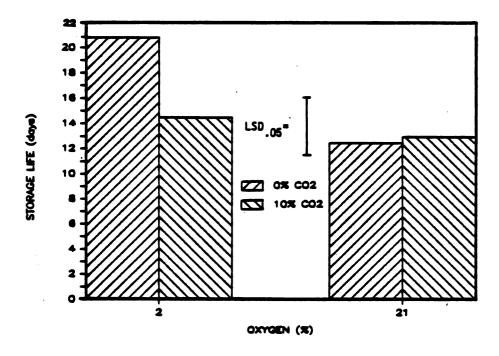


Figure 3. The storage life (days) of red-ripe tomatoes as a function of oxygen concentration (2% and ambient) and carbon dioxide concentration (0 and 10%) held at 20° C. LSD calculated on basis of significant 2-way interaction.

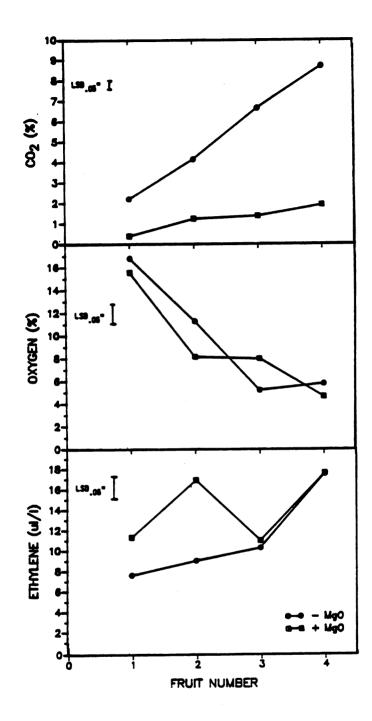


Figure 4. Carbon dioxide, oxygen and ethylene concentration in packaged tomato fruits as a function of fruit number and presence or absence of 4.0 g MgO averaged over 8 days at 20°C for package experiment 1. LSD calculated on basis of significant 2-way interaction.

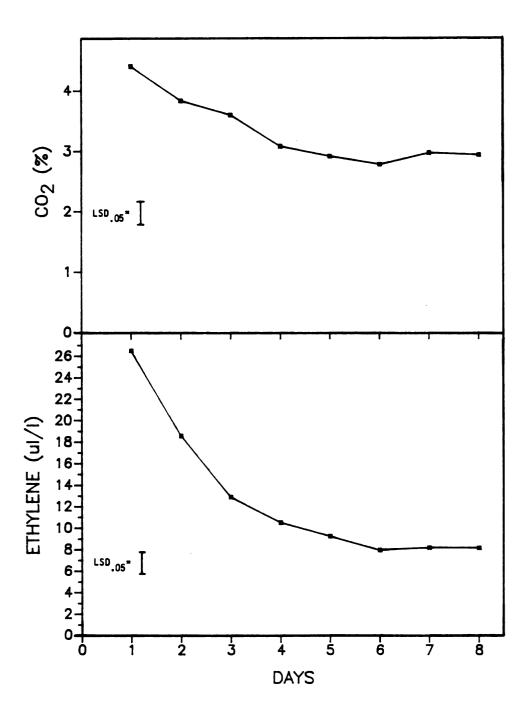


Figure 5. Carbon dioxide and ethylene concentrations in packaged tomato fruits as a function of time averaged over fruit number and MgO treatment st $20\,^{\circ}\text{C}$ from package experiment 1. LSD calculated on basis of main effect.

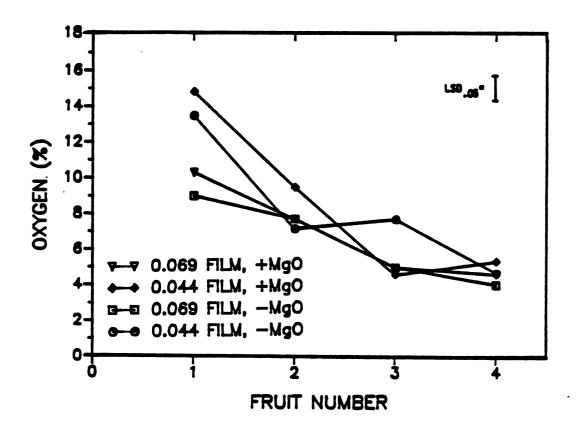
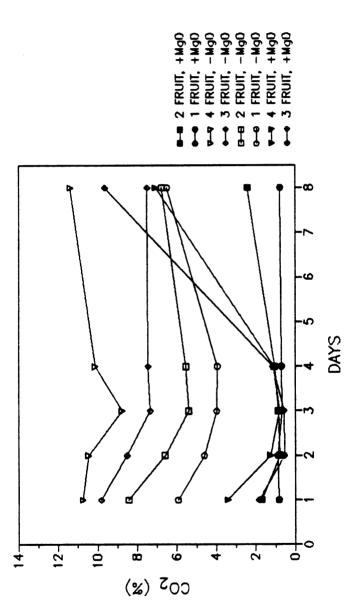


Figure 6. Oxygen concentration as a function of fruit number, MgO treatment and film thickness averaged over days at 20°C . LSD calculated on basis of of significant 3-way interaction.



concentrations calculated on basis of dioxide a function of Carbon experiment 2. interaction. tomatoes treatment Figure

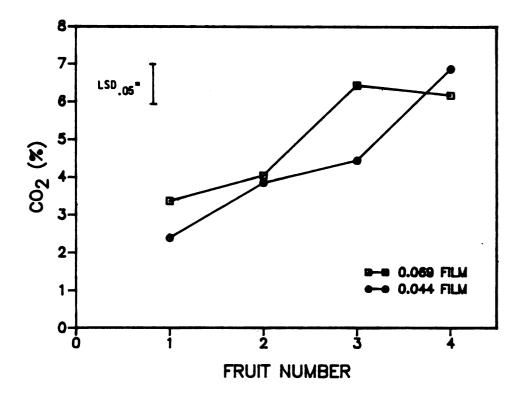


Figure 8. Carbon dioxide concentrations in tomato packages as a function of fruit number and film thickness averaged over days and MgO treatment held at $20\,^{\circ}\text{C}$ for package experiment 2. LSD calculated on basis of significant 2-way interaction

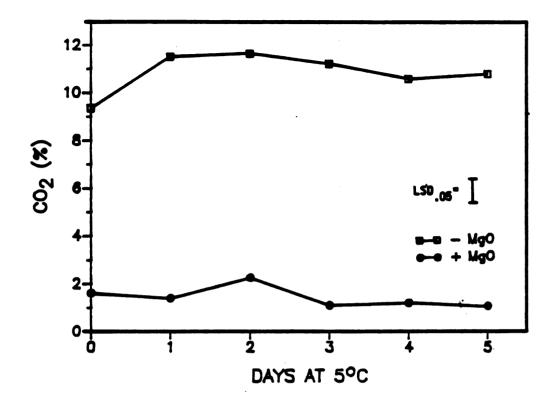


Figure 9. Equilibrium carbon dioxide concentrations in packaged red ripe tomatoes following chilling at 5°C for different time intervals when at the mature green stage. All fruit were held at 20°C except during chilling period.

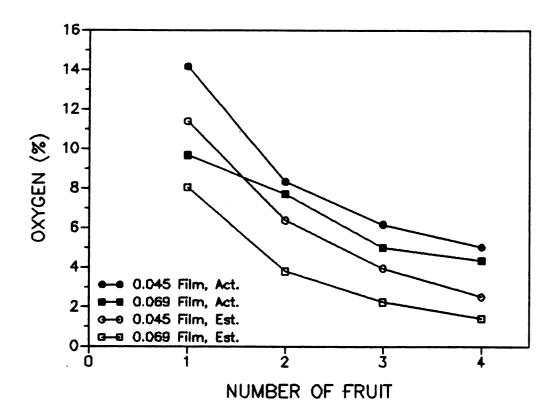


Figure 10. Estimated and measured equilibrium oxygen concentrations as a function of fruit weight and film thickness. Measured data taken from packaging experiment 2. Estimated data generated from model developed in Section 1.

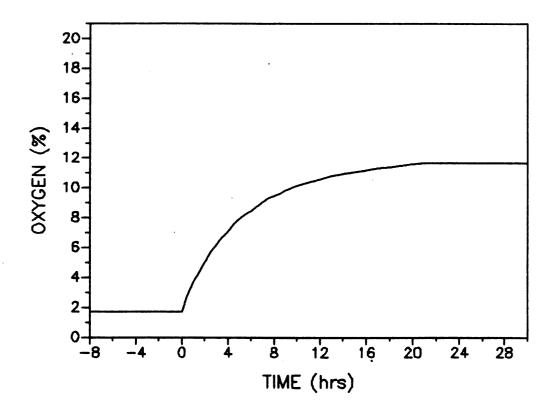


Figure 11. The change in oxygen concentration within packaged tomato fruit following single puncture with 26 gauge needle at time 0.

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