Prediction of Changes in O₂ and CO₂ Partial Pressures in Modified Atmosphere Packages of Tomatoes

Suparlan and Kazuhiko ITOH

*Graduate School of Agricultural Science, Hokkaido University,
Kita 9, Nishi 9, Kita-ku, Sapporo 060-8589, Japan*

A model for predicting changes in O₂ and CO₂ partial pressures in modified atmosphere packages of tomatoes stored at 10°C was developed by using a respiration model based on enzyme kinetics and a simple mathematical model. The respiration models of tomatoes were determined using a Michaelis-Menten-type equation without inhibition by CO₂ by means of a closed system experiment. Mathematical model equations were solved simultaneously by the fourth-order Runge-Kutta method using Microsoft Excel software to predict changes in O₂ and CO₂ partial pressures inside the package. The validity of the model was verified by results of simulation and an experiment using two types of model package, one containing about 0.24 kg of tomatoes with a film surface area of 0.01 m² and the other containing about 0.55 kg of tomatoes with a film surface area of 0.02 m². The predicted values of gas composition inside the package agreed well with the experimental data. This model enables prediction of changes in O₂ and CO₂ partial pressures inside a package of tomatoes by using input variables that are used in the design of modified atmosphere packaging to prevent fruit damage caused by anaerobic respiration.

Key words: modeling, modified atmosphere packaging, enzyme kinetics, tomatoes

1. Introduction

The use of an appropriate method of modified atmosphere packaging (MAP) of tomatoes delays changes in color, soluble solids content (SSC), firmness and acidity, and it reduces weight loss due to maintenance of a high relative humidity [1-4]. The delay in changes in those variables may be correlated with reduction in the level of O₂ or elevation in the level of CO₂ inside the package, which can reduce respiration and ethylene production rate and thus delay the ripening process. However, exposure of tomatoes to a level of CO₂ above their CO₂ tolerance limit may cause physiological damage, and exposure to a level of O₂ below their O₂ tolerance limit may increase anaerobic respiration and the development of off-flavors due to accumulation of ethanol and acetaldehyde [2,5]. Therefore, steady-state O₂ and CO₂ partial pressures inside a modified atmosphere package during storage are important factors that must be determined to reduce fruit damage. The O₂ and CO₂ tolerance limits for tomatoes have been reported to be about 3-5 kPa and 3-10 kPa, respectively [2,6]. Steady-state O₂ and CO₂ partial pressures inside a package

are affected by various factors such as respiration rate of produce, mass of fruit, permeability of the package, internal free volume, surface area of film, and temperature of storage. Therefore, in order to achieve and maintain O₂ and CO₂ partial pressures in desired ranges, selection of appropriate design parameters of an MAP system is necessary.

MAP is a dynamic system involving two simultaneous processes: respiration and permeation [7]. Produce inside a package continuously consumes O₂ and produces CO₂. Numerous mathematical models for predicting gas exchange of O₂ and CO₂ in MAP systems have been proposed [7-11]. These models enabled the prediction of gas compositions inside packages. Some researchers have solved these mathematical models numerically by taking into account the respiration rate of produce as a function of O₂ and/or CO₂ partial pressures [7,10-11]. A simple respiration model based on enzyme kinetics using a Michaelis-Menten-type equation developed by Lee et al. [10] has been applied to a wide variety of commodities [12].

The purpose of this study was to apply a respiration model based on enzyme kinetics and a simple mathematical model for an MAP system to simulate changes in gas compositions in modified atmosphere packages of tomatoes. The results obtained by using two different types of model package were compared.

1.1 Mathematical model for an MAP system

Modeling of changes in gas concentrations in modified atmosphere packages of tomatoes was based on the principles of O₂ and CO₂ mass balances to describe the interaction between respiration of tomatoes and permeability of the package. Based on Fick's law of gas diffusion, the amount of O₂ diffused into the package from the surrounding atmosphere (J_{O_2} , mol · h⁻¹) was calculated as follows:

$$J_{O_2} = \frac{P_{O_2}A}{L} ([O_2]_{op} - [O_2]_{ip}) \quad (1)$$

Similarly, the amount of CO₂ fluxed out through the package to the surrounding atmosphere (J_{CO_2} , mol · h⁻¹) was calculated as follows:

$$J_{CO_2} = \frac{P_{CO_2}A}{L} ([CO_2]_{op} - [CO_2]_{ip}) \quad (2)$$

where P_{O_2} and P_{CO_2} are the permeability of film to O₂ and CO₂, respectively (mol · m · m⁻² · h⁻¹ · kPa⁻¹), A is the film surface area (m²), L is thickness of the package (m), $[O_2]_{ip}$ is the partial pressure of O₂ inside the package (kPa), $[O_2]_{op}$ is the partial pressure of O₂ outside the package (kPa), $[CO_2]_{ip}$ is the partial pressure of CO₂ inside the package (kPa), and $[CO_2]_{op}$ is the partial pressure of CO₂ outside the package (kPa).

Oxygen consumption by tomatoes in a modified atmosphere package (C_{O_2} , mol · h⁻¹) was calculated by multiplying the O₂ consumption rate (RR_{O_2} , mol · kg⁻¹ · h⁻¹) by the mass of tomatoes (W_p , kg):

$$C_{O_2} = RR_{O_2} \times W_p \quad (3)$$

The production of CO₂ by tomatoes in a MAP system (Pd_{CO_2} , mol · h⁻¹) was calculated by multiplying the CO₂ production rate (RR_{CO_2} , mol · kg⁻¹ · h⁻¹) by the mass of tomatoes (W_p , kg):

$$Pd_{CO_2} = RR_{CO_2} \times W_p \quad (4)$$

RR_{O_2} and RR_{CO_2} are the respiration rates for O₂ and CO₂, respectively, and are expressed as functions of the O₂ and CO₂ partial pressures inside the package. A simple model to express respiration rate of produce as a function of O₂ and CO₂ is a Michaelis–Menten–type enzyme kinetics equation [10]. In the case of tomatoes, we have considered to describe the rate of O₂ consumption or CO₂ production as a function of O₂ partial pressure inside the package without inhibition by CO₂ as shown in the following equations:

$$RR_{O_2} = \frac{V_{\max 1}[O_2]}{K_{m1} + [O_2]} \quad (5)$$

$$RR_{CO_2} = \frac{V_{\max 2}[O_2]}{K_{m2} + [O_2]} \quad (6)$$

where $V_{\max 1}$ and $V_{\max 2}$ are the maximum respiration rate for O₂ and CO₂ (mol · kg⁻¹ · h⁻¹), respectively, and K_{m1} and K_{m2} are the Michaelis–Menten constant for O₂ and CO₂ (kPa), respectively.

In an unsteady state or transient condition, a model based on the principle of mass balance requires that rate of accumulation of O₂ or CO₂ in the package is equal to the rate of permeation of O₂ or CO₂ into the package plus the rate of generation of O₂ or CO₂ by respiration. Mass balance equations for O₂ and CO₂ can be expressed as follows:

$$\frac{d[O_2]_{ip}}{dt} = \left[\frac{P_{O_2}A}{V_p L} ([O_2]_{op} - [O_2]_{ip}) - \frac{W_p RR_{O_2}}{V_p} \right] \quad (7)$$

$$\frac{d[CO_2]_{ip}}{dt} = \left[\frac{P_{CO_2}A}{V_p L} ([CO_2]_{op} - [CO_2]_{ip}) + \frac{W_p RR_{CO_2}}{V_p} \right] \quad (8)$$

where W_p is mass of tomatoes inside the package (kg) and V_p is free volume of the package (m³). V_p was calculated by subtracting total volume of tomatoes inside the package from total volume of the package. We assume that the free volume of the package is constant. Total volumes of package-I and package-II were 1.05×10^{-3} and 2.40×10^{-3} m³, respectively. Total volume of the packages and total volume of tomatoes were measured by water displacement method, respectively. Equations (7) and (8) are ordinary first-order differential equations. These equations describe the unsteady-state behavior of an MAP system. In order to predict the O₂ and CO₂ partial pressures within a produce package at any time during the period from the start of the experiment to the time a steady-state condition has been achieved, equations (5) and (6) were substituted into equations (7) and (8), respectively, and the equations were then solved simultaneously by the fourth-order Runge-Kutta method using Microsoft Excel software with the initial conditions ($t=0$): $[O_2]_{ip}=21.3$ kPa and $[CO_2]_{ip}=0.0$ kPa. It was also assumed that the package is placed in air, so that $[O_2]_{op}=21.3$ kPa and $[CO_2]_{op}=0.0$ kPa throughout the period of storage. Based on the assumption that gases conform to the Ideal Gas Law, the predicted O₂ and CO₂ within a package at any time were converted from a unit of mol · m⁻³ to a partial pressure (kPa) by multiplying a conversion factor of 8.3143×10^{-3} (T+273.15), where T is in °C (10°C).

In addition, the relation between partial pressure of gases and mole fractions can be expressed by the Ideal Gas Law as described in equation 9.

$$pV = nR(T+273.15) \quad (9)$$

where: R is gas constant (8.3143×10^{-3} m³ · kPa · mol⁻¹ · K⁻¹), p is either partial or total system pressure (kPa), V is volume (m³), n is amount of gas (mol) and T is temperature (°C).

2. Materials and Methods

2.1 Tomatoes

'Maru' tomatoes (*Lycopersicon esculentum*, Mill.) that had been grown in a greenhouse and harvested at the breaker stage to the turning stage of maturity with the mean a^*/b^* ratio of -0.23 to 0.73 were purchased from a commercial grower in Chitose, Hokkaido and used in this experiment. The specific weight of tomatoes was about $991 \text{ kg} \cdot \text{m}^{-3}$. Fruits of uniform shape and size and free from damage and fungal infection were selected.

2.2 Determination of respiration model parameter values

Respiration rate of tomatoes as a function of O_2 concentration was measured at 10°C using the closed system method described by Hagggar et al.[13]. About 0.76 kg of tomatoes (at the breaker stage of maturity) was placed into a desiccator that was tightly closed. The closed desiccator was stored in an incubator at 10°C . The headspace gas was periodically sampled, and the O_2 and CO_2 partial pressures inside the desiccator were analyzed using a gas chromatograph (Shimadzu, GC-14B) equipped with a thermal conductivity detector (TCD) maintained at 50°C and a stainless-steel column (WG-100 SUS O.D. $1/4''$ dia. $\times 1.8 \text{ m}$) at a temperature of 50°C . The carrier gas was helium at a flow rate of $33 \text{ mL} \cdot \text{min}^{-1}$. The headspace analysis was terminated when the O_2 partial pressure level inside the desiccators was less than 2.0 kPa in order to prevent anaerobic respiration. Following the procedure described by Hagggar et al.[13], Yam et al.[14] and Lee et al.[15] with slight modification, the data of O_2 and CO_2 partial pressures inside the desiccator as a function of time were curve-fitted using the software program Kaleidagraph (Synergy

Fig. 1 Plot of actual and predicted O_2 and CO_2 partial pressures inside the closed desiccator during storage at 10°C .

Fig. 2 Experimental package box made of acrylic and covered with LDPE film.

Software, version 3.6) as shown in Fig. 1. Functions for O_2 and CO_2 to fit the data were determined to be

$$[\text{O}_2] = 21.28 - A_1 [1 - \exp(B_1 t - C_1 t^2)] \quad (10)$$

$$[\text{CO}_2] = A_2 [1 - \exp(B_2 t - C_2 t^2)] \quad (11)$$

where $[\text{O}_2]$ and $[\text{CO}_2]$ are the O_2 and CO_2 partial pressures in the sealed desiccators (kPa), respectively, t is the time from sealing the desiccators (h), and A , B , and C are fitting coefficients. The curve-fitting of the data of O_2 and CO_2 partial pressures inside the desiccator as a function of time was developed using the range data of O_2 partial pressure from higher than 2 kPa , because the respiration model used in this study is valid only for aerobic respiration as reported by Lee et al. (1991). In the case of tomatoes, if the O_2 partial pressure inside the package is less than the O_2 tolerance limit (less than 2 kPa), it can cause anaerobic respiration. Equations (10) and (11) were then used to derive the input variables RR_{O_2} and RR_{CO_2} , respectively. The first derivatives of Eqs. (10) and (11) represent the O_2 consumption rate and CO_2 production rate, respectively, at any time. The respiration rate of tomatoes at any time can be calculated using the following equations:

$$RR_{\text{O}_2} = \frac{d[\text{O}_2]}{dt} \left(-\frac{V_d}{W_d} \right) \quad (12)$$

$$RR_{\text{CO}_2} = \frac{d[\text{CO}_2]}{dt} \left(\frac{V_d}{W_d} \right) \quad (13)$$

where W_d is mass of tomatoes inside the desiccator (kg) and V_d is free volume of the desiccator (m^3). V_d was calculated by subtracting total volume of tomatoes inside the desiccator from total volume of the desiccator. Total volume of the desiccator was measured by water displacement method. The first derivatives of O_2 and CO_2 partial pressures were calculated from equations (10) and (11):

$$\frac{d[\text{O}_2]}{dt} = A_1 [B_1 - 2C_1 t] \exp(B_1 t - C_1 t^2) \quad (14)$$

$$\frac{d[\text{CO}_2]}{dt} = -A_2 [B_2 - 2C_2 t] \exp(B_2 t - C_2 t^2) \quad (15)$$

The negative sign in equation (12) indicates that the O_2

partial pressure in the desiccator decreases with time.

Respiration data from the above experiments were used to estimate the respiration model parameters ($V_{\max}$ and K_m) for the following linearized form of Eqs. (5) and (6) by using linear regression.

$$\frac{1}{RR_{O_2}} = \frac{K_{m1}}{V_{\max1}} \frac{1}{[O_2]} + \frac{1}{V_{\max1}} \tag{16}$$

$$\frac{1}{RR_{CO_2}} = \frac{K_{m2}}{V_{\max2}} \frac{1}{[O_2]} + \frac{1}{V_{\max2}} \tag{17}$$

2.3 Modeling of gas composition in a modified atmosphere package of tomatoes

To verify the respiration model parameters and to validate the mathematical model as expressed in Eqs. (7) and (8), the headspace gas composition inside the package model stored at 10°C was monitored as a function of time. Low-density polyethylene (LDPE) film of 2.0×10^{-5} m in thickness was used to package the fruit. Packaging of fruit was conducted by placing the tomatoes into square acrylic boxes with upper sides opened. The open side was then covered with LDPE film to which a silicone rubber septum for gas analysis was attached (Fig. 2). Two types of model package were used in this experiment. One had a film area of 0.01 m^2 and contained about 0.24 kg of tomatoes (consist of 2–3 tomatoes samples) at the breaker stage of maturity, with the total volume and free volume of the package being about 1.05×10^{-3} and $0.81 \times 10^{-3} \text{ m}^3$, respectively (hereafter called model package-I). The other had a film area of 0.02 m^2 and contained about 0.53 kg of tomatoes (consist of 5–6 tomatoes samples) at the turning stage of maturity, with the total volume and free volume of the package being about 2.40×10^{-3} and $1.87 \times 10^{-3} \text{ m}^3$, respectively (hereafter called model package-II). The model packages were stored in an incubator at a temperature of 10°C for 2 weeks. The O_2 and CO_2 concentrations inside the package were periodically analyzed using a gas chromatograph (Shimadzu, GC-14B). The data of O_2 and CO_2 concentrations (%) were then converted to partial pressure by multiplying their respective % values obtained by GC by the total internal pressure at a certain time $(P_T)_t$. A correction for the total internal pressure must be made because the total pressure inside the package was not constant due to the respiratory quotient of tomatoes was not unity and the permeability of LDPE film to CO_2 was larger than those to O_2 . The total internal pressure of the package at a certain time $(P_T)_t$ can be calculated using the following expression [7,16].

$$(P_T)_t = \frac{(\%N_2)_{op}}{(\%N_2)_t} \times 101.311 \tag{18}$$

where $(P_T)_t$ is total internal pressure of the package at a certain time (kPa), $(\%N_2)_{op}$ is the percent nitrogen in the outside of package, and $(\%N_2)_t$ is the percent nitrogen inside the package at a certain time.

The O_2 permeability of the LDPE film at 10°C was determined by the method described by Flodin et al. [17] using a gas chromatograph as described above. The film permeability to O_2 was estimated to be $1.53 \times 10^{-9} \text{ mol} \cdot \text{m} \cdot \text{m}^{-2} \cdot \text{h}^{-1} \cdot \text{kPa}^{-1}$. Based on the data of Yam and Lee [11] and Zagory and Kader [5], it was assumed that the ratio of permeability to CO_2 and permeability to O_2 was about 3.3, and the permeability to CO_2 was therefore estimated to be $5.05 \times 10^{-9} \text{ mol} \cdot \text{m} \cdot \text{m}^{-2} \cdot \text{h}^{-1} \cdot \text{kPa}^{-1}$.

3. Results and Discussion

3.1 Respiration rate of tomatoes in a closed system experiment

Changes in O_2 and CO_2 partial pressures inside the closed desiccator as a function of time are shown in Fig. 2. The O_2 partial pressure decreased and the CO_2 partial pressure increased with time. These data with the O_2 partial pressure ranged from about 2.0 kPa to 21.3 kPa were curve-fitted using the software program KaleidaGraph (Synergy Software, version 3.6) based on equations (10) and (11), and the estimated values of the coefficients (A, B, and C) are shown in Table 1. The coefficient of determination r^2 was 0.998 for O_2 and 0.996 for CO_2 , and the fitted curve almost coincided with experimental data (Fig. 2). Similar results were reported for cauliflower [14] and cut broccoli [10,13].

The respiration rates at each sampling time were calculated by substituting the estimated values of the coefficients into Eqs. (14) and (15) and then substituting the results obtained by using Eqs. (14) and (15), into Eqs. (12) and (13), respectively. The data obtained from Eqs. (12) and (13) were used to estimate the respiration model parameter values ($V_{\max}$ and K_m) of Eqs. (16) and (17) by plotting $1/RR_{O_2}$ and $1/RR_{CO_2}$ versus $1/[O_2]$ using linear regression. $K_m/V_{\max}$ was the slope and $1/V_{\max}$ was the intercept of the plot of Eqs. (16) and (17). The plots of

Table 1 Estimated fitting coefficients for Eqs. (10) and (11) describing the O_2 and CO_2 change-curves for a closed desiccator containing tomatoes at 10°C.

	A	B	C	R ²
[O ₂]	21.144	-0.026334	0.000178	0.998
[CO ₂]	18.430	-0.034065	-0.000134	0.996

Fig. 3 Plot of $1/RR_{O_2}$ versus $1/O_2$. Fig. 4 Plot of $1/RR_{CO_2}$ versus $1/O_2$.

$1/RR_{O_2}$ and $1/RR_{CO_2}$ versus $1/[O_2]$ are shown in Fig. 3 and Fig. 4, respectively. Plotting the data of $1/RR_{O_2}$ and $1/RR_{CO_2}$ versus $1/[O_2]$ was developed using the data of O_2 partial pressure higher than 2.0 kPa to avoid the anaerobic respiration. As shown in those figures, there was strong linearity in the relationships of $1/RR_{O_2}$ and $1/RR_{CO_2}$ with $1/[O_2]$. These results indicate that the respiration model developed is applicable, in agreement with the findings by Lee et al.[10], Hagger et al.[13], and Yam et al.[14] for cut broccoli, cut broccoli, and cauliflower, respectively. The estimated values of parameters from regression analysis were $V_{max} = 7.84 \times 10^{-4} \text{ mol} \cdot \text{kg}^{-1} \cdot \text{h}^{-1}$ and $K_m = 23.0 \text{ kPa}$ for O_2 consumption rate and $V_{max} = 1.13 \times 10^{-3} \text{ mol} \cdot \text{kg}^{-1} \cdot \text{h}^{-1}$ and $K_m = 57.3 \text{ kPa}$ for CO_2 production rate. Using these model parameter values, respiration rates as a function of O_2 inside a permeable package can be predicted by substituting the model parameter values into Eqs. (5) and (6). Based on that equations and the estimated values of parameters indicate that respiration rates increase with the increasing of O_2 partial pressure and decrease with the decreasing O_2 partial pressure.

3.2 Modeling gas composition in a modified atmosphere package

In order to simulate changes in O_2 and CO_2 partial pressures in a MAP system, the respiration model parameters were substituted into Eqs. (7) and (8). Fig. 5 shows the predicted O_2 and CO_2 partial pressures inside the model packages and experiment data. The predicted gases partial pressures inside the model packages agreed well with experiment data. These results support the validity of previous developed models [7–10, 12–13]. In the model package–I, O_2 partial pressure decreased to about 6.1 kPa in 5 days and then an equilibrium partial pressure of O_2 of about 4.0 kPa was maintained for 14 days, while CO_2 partial pressure simultaneously increased to about 9.3 kPa in 4 days, remained at that level for 3 days, and then decreased to about 6.0 kPa over the remainder of the storage period. In the model package–II, O_2 partial pressure decreased to about 4.9 kPa during the first 4 days of storage and then reached an equilibrium of about 3.5 kPa, while CO_2 partial pressure reached an equilibrium of

Fig. 5 Predicted and experimental data for O_2 and CO_2 partial pressures inside packages tomatoes in the case of (I) a model package–I containing 0.241 kg of tomatoes with a film surface area of 0.01 m^2 and free volume of $0.807 \times 10^{-3} \text{ m}^3$ and in the case (II) a model package–II containing 0.542 kg of tomatoes with a film surface area of 0.02 m^2 and free volume of $1.853 \times 10^{-3} \text{ m}^3$.

about 10.9 kPa after 4 days of storage, remained at that level for about 5 days and then decreased to about 7.1 kPa over the remainder of the storage period. The decrease in CO₂ partial pressure may have been caused by an excessively high level of relative humidity inside the package, which could cause dissolution of CO₂ in water because CO₂ has high solubility in water [4,18]. Moreover, at the steady-state partial pressure of CO₂, the partial pressure of O₂ was low (less than 6.0 kPa), a condition in which the respiration process of tomatoes would be inhibited and the evolution rate of CO₂ would thus decrease. On the other hand, the permeation rate of CO₂ through film increases with increasing the partial pressure gradients between the inside and outside of the package. In addition, the film permeability to CO₂ is 3 times larger than that to O₂. Therefore, the production rate of CO₂ was lower than the rate of permeation of CO₂ through the film; so after the equilibrium condition was reached the CO₂ partial pressure tends to decrease.

There was a slight difference between results of prediction of O₂ and CO₂ partial pressures for the two types of model package. The prediction results for model package-I was more accurate than those for model package-II, especially for prediction of CO₂ partial pressure. However, less predictive result was obtained for O₂ partial pressure in model package-I at times higher than 2 days, where the predicted data were less than the experiments data. In addition, the predicted CO₂ partial pressure inside the model package-II tended to higher than the experimental results. This difference might have been due to the difference in degrees of maturity of tomatoes used at the start of the storage period, since it is known that degree of maturity of tomatoes affects their respiration rate and also ripening rate. The degree of maturity of tomatoes used in model package-I was lower than that of tomatoes used in model package-II. Tomatoes in the breaker stage were used for model package-I, while tomatoes in the turning stage were used for model package-II. Therefore, at the start of the storage period, when the oxygen partial pressure inside the package was still high, the respiration rate of tomatoes in model package-II may have been higher than that of tomatoes in model package-I. On the other hand, the degree of maturity of tomatoes used to develop the respiration model was the same as that of tomatoes used in model package-I. When color of tomatoes changes to pink to light red, the respiration rate becomes maximum, a condition called peak climacteric. Therefore, the color of tomatoes after two days of storage in model package-II might have become pink, and the respiration rate

would have increased even though the oxygen partial pressure inside the package decreased to about 11.0 kPa. Therefore, during the period from 3 to 5 days of storage, the experimental data for O₂ were less than the predicted data, and then after 7 days of storage, the predicted data agreed well with the experimental data, while the experimental data for CO₂ were slightly greater than the predicted data during the period from about 2 to 7 days of storage and after 8 days of storage, the experimental data for CO₂ agreed well with the predicted data.

This mathematical model enables prediction of O₂ and CO₂ partial pressures inside a package rapidly by using packaging system variables, including film surface area, tomato weight, free volume, film permeability and tomato respiration. Therefore, this kind of model would be useful for designing an MAP system to determine the most appropriate of design variables that resulted in the most suitable of gases composition inside the package of produce. The O₂ and CO₂ partial pressures inside the package can be predicted previously before storage process is conducted. Therefore, the possibility of injury caused by fermentation or anaerobic respiration during storage in MAP can be minimized.

This model can also be used to analyze the effect of each packaging system variable on changes in O₂ and CO₂ partial pressures inside the package. Dynamic changes in O₂ and CO₂ partial pressures can easily be predicted by using this model. For example, Fig. 6 shows the simulated changes in O₂ and CO₂ partial pressures inside the package based on the effect of packaging ratio (ratio of film surface area to fruit mass). The results show that the smaller the packaging ratio is, the lower is the steady-state O₂ partial pressure and the higher is the steady-state CO₂ partial pressure. A packaging ratio of about 0.0415 (m²·kg⁻¹) or higher resulted in suitable steady-state O₂ partial pressure inside the package for tomatoes with a value higher than 2.0 kPa. Exposure of tomatoes in a modified atmosphere package to an O₂ level below their O₂ tolerance limit (less than 2.0 kPa) may increase anaerobic respiration and the development of off-flavors due to accumulation of ethanol and acetaldehyde [2,5].

The respiration model developed in this study was based on enzyme kinetics without inhibition by CO₂, and the effect of CO₂ on O₂ consumption rate was not taken into account. On the other hand, the estimated values of parameter models of RR_{O_2} were derived from O₂ depletion data collected in a desiccator in which CO₂ was allowed to accumulate using the method developed by Hagger et al.[13]. However, the model developed in this study

Fig. 6 Simulation of the effects of packaging ratio (A/W , $\text{m}^2 \cdot \text{kg}^{-1}$) on changes in O_2 and CO_2 partial pressures inside the package.

enabled accurate prediction of changes in O_2 and CO_2 partial pressures inside the package, indicating that the effect of CO_2 on respiration rate of tomatoes was negligible, in agreement with previous results reported by Henig and Gilbert[8], Gong and Corey[19], and Jaime et al.[20]. Henig and Gilbert[8] reported that the rate of reduction in O_2 consumption rate was very small despite the accumulation of CO_2 inside the package. In addition, Lee et al.[10] reported that a respiration model based on enzyme kinetics without inhibition by CO_2 could be used to predict transient and equilibrium gas concentrations inside permeable packages of fresh produce.

4. Conclusions

Application of a respiration model based on enzyme kinetics using a Michaelis-Menten-type equation without inhibition by CO_2 and a simple mathematical model for a MAP system enabled prediction of changes in O_2 and CO_2 partial pressures inside a permeable package of tomatoes. The predicted results agreed well with the experimental data, indicating that the model is valid. However, there was a slight difference between the results of prediction of O_2

and CO_2 partial pressures in two model packages. This difference might have been caused by the difference in maturity stages of tomatoes used in the two model packages. This model would be useful for designing an MAP system to select the most appropriate variables design that resulting in the most suitable gas composition for the packaged produce. Therefore, the possibility of injury caused by fermentation or anaerobic respiration due to inappropriate in selection of variables design can be minimized. This model can also be used to analyze the effect of each packaging system variable, such as packaging ratio and film permeability, on changes in O_2 and CO_2 partial pressures inside the package.

References

- 1) C.C. Yang, M.S. Chinnan; Modeling of color development of tomatoes in modified atmosphere storage. *J. Amer. Soc. Hort. Sci.*, **119** (3), 546–550 (1994).
- 2) J.D. Geeson, K.M. Browne, K. Maddison, J. Shepherd, F. Guaraldi; Modified atmosphere packaging to extend the shelf life of tomatoes. *J. Food Technol.*, **20**, 339–349 (1985).
- 3) S. Nakhasi, D. Schlimme, T. Solomos; Storage potential of tomatoes harvested at the breaker stage using modified atmosphere packaging. *J. Food Sci.*, **56**, 55–59 (1991).
- 4) Suparlan, K. Itoh; Combined effects of hot water treatment (HWT) and modified atmosphere packaging (MAP) on quality of tomatoes. *Packaging Tech. and Sci.*, **16**, 171–178 (2003).
- 5) D. Zagory, A.A. Kader; Modified atmosphere packaging of fresh produce. *Food Technol.*, **42** (9), 70–77 (1988).
- 6) Suparlan, J. Himoto, K. Itoh; Effects of modified atmosphere and storage temperature on the quality of tomatoes. *J. Fac. Agr. Hokkaido Univ.*, **70**, 19–27 (2000).
- 7) M. Zhu, C.L. Chu, S.L. Wang, R.W. Lencki; Predicting oxygen and carbon dioxide partial pressures within modified atmosphere packages of cut rutabaga. *J. Food Sci.*, **67**, 714–720 (2002).
- 8) Y. S. Henig, S.G. Gilbert; Computer analysis of the variables affecting respiration and quality of produce packaged in polymeric films. *J. Food Sci.*, **40**, 1033–1035 (1975).
- 9) K. Hayakawa, Y.S. Henig, S.G. Gilbert; Formulae for predicting gas exchange of fresh produce in polymeric film package. *J. Food Sci.*, **40**, 186–191 (1975).
- 10) D.S. Lee, P.E. Hagggar, J. Lee, K.L. Yam; Model for fresh produce respiration in modified atmospheres based on principles of enzyme kinetics. *J. Food Sci.*, **56** (6), 1580–

- 1585 (1991).
- 11) K.L. Yam, D.S. Lee; "Design of modified atmosphere packaging for fresh produce". In M.L. Rooney ed., *Active food packaging*. 1st ed., Blackie Academic & Professional, Chapman & Hall. Glasgow. 1995, p 55–73.
 - 12) Y. Song, N. Vorsa, K.L. Yam; Modeling respiration-transpiration in a modified atmosphere packaging system containing blueberry. *J. Food Eng.*, **53**, 103–109 (2002).
 - 13) P.E. Hagggar, D.S. Lee, K.L. Yam; Application of an enzyme kinetics based respiration model to closed system experiments for fresh produce. *J. Food Process Eng.*, **15**, 143–147 (1992).
 - 14) K.L. Yam, P.E. Hagggar, D.S. Lee; Modeling respiration of low CO₂ tolerance produce using a closed system experiment. *Foods and Biotech.*, **2** (1), 22–25 (1993).
 - 15) D.S. Lee, Y. Song, K.L. Yam; Application of an enzyme kinetics based respiration model to permeable system experiment of fresh produce. *J. Food Eng.*, **27**, 297–310 (1996).
 - 16) L. Moyls, R. Hocking, T. Beveridge, G. Timbers; Exponential decay method for determining gas transmission rate of films. *Trans ASAE*, **35** (4), 1259–1265 (1992).
 - 17) C. Flodin, J.H. Bower, B.D. Patterson; Oxygen permeance: a method applied to modified atmosphere packages containing fresh plant foods. *Packaging Technol. and Sci.*, **12**, 185–191 (1999).
 - 18) P. Renault, M. Souty, Y. Chambroy; Gas exchange in modified atmosphere packaging. 1: A new theoretical approach for micro-perforated packs. *International J. Food Sci. and Technol.* **29**, 365–378 (1994).
 - 19) S. Gong, K.A. Corey; Predicting steady-state oxygen concentrations in modified-atmosphere packages of tomatoes. *J. Amer. Soc. Hort. Sci.*, **119** (3), 546–550 (1994).
 - 20) P. Jaime, M.L. Salvador, R. Oria; Respiration rate of sweet cherries: "Burlat", "Sunburst" and "Sweetheart" cultivars. *J. Food Sci.*, **40**, 186–191 (2001).

◇◇◇ 和文要約 ◇◇◇

トマトの MA 包装内における酸素と二酸化炭素濃度の変化予測

Suparlan, 伊藤和彦

北海道大学大学院農学研究科生物生産工学講座

農産物加工工学研究室

トマトを 10℃で MA 包装貯蔵した場合の包装内の酸素濃度と二酸化炭素濃度の変化を予測するモデルを作成した。このモデルは簡単な数学モデルと酵素反応速度論に基づく呼吸モデルを用いて作成した。トマトの呼吸モデルは閉鎖系で CO₂ による呼吸作用の抑制がないことを前提として、Michaelis-Menten 式を利用して作成した。パラメータとしてフィルムの酸素および二酸化炭素透過率、フィルム表面積、包装内空気量、トマトの質量、トマトの呼吸速度を用いた。数学モデル式は Runge-Kutta 法を利用して解き、作成したモデルの有効性を 2 種類の実験を行なって検証した。1 つは約

0.24 kg の試料を入れた容器内の上部を表面積 0.01 m² のフィルムで覆い、他の実験は試料約 0.55 kg を用い、表面積 0.02 m² のフィルムで覆い、容器内の酸素および二酸化炭素濃度の経時変化を測定し予測値との比較を行なった。その結果、モデルは容器内の酸素・二酸化炭素濃度の予測に有効であることを明らかにした。本研究で検討した簡単な呼吸モデルは、トマトの MA 包装に応用することが可能であることが明らかになり、これを利用することにより、嫌気呼吸によるトマトの品質低下を防ぐ最適包装貯蔵条件を予測することが可能であると考えられる。