## Technical paper

# Predicting Gas Concentrations of Welsh Onion in Polymeric Film Packaging and Shipping Containers

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A theoretical model of the atmosphere within polymeric film and shipping containers was developed and validated by experiments with or without Welsh onion (*Allium fistulosum L*.). There were three processes in the model: respiration of fresh vegetables, permeability of gas in polymeric film and permeability of gas in the shipping container. The respiration rate of Welsh onion was expressed in a multiple regression equation. When empty packages were used, changes in carbon dioxide ( $CO_2$ ) and oxygen ( $O_2$ ) concentrations inside the unperforated polypropylene (OPP) film packaging and expanded polystyrene (EPS) containers agreed very well with the simulated data. These results indicate the suitability of the proposed model. Changes in  $CO_2$  and  $O_2$  concentrations in the EPS container were approximated when Welsh onion was placed in the film package. The predicted  $CO_2$  and  $O_2$  concentrations in the OPP film differed slightly from the experimental data obtained with a maximum of 1.5% and 1.2%, respectively, but gas correlated significantly with the model. Therefore, the simulation model may be useful for fresh vegetables wrapped with polymeric film and then encased in shipping containers.

Keywords: modified atmosphere packaging, theoretical model, respiration rate, gas permeability, Welsh onion

Modified atmosphere packaging (MAP), taking into account the respiration rate of fresh vegetables and gas permeation of polymeric film, is a common technique for maintaining the quality of fresh fruits and vegetables (Kader et al., 1989). In addition, corrugated shipping containers with polyethylene laminated liners and expanded polystyrene (EPS) containers have helped to extend the shelf life of vegetables (Yoza et al., 1993; Ibaraki et al., 1995). However, in most cases the combination of polymeric film and shipping containers for MAP was chosen empirically. The respiration rate of fresh vegetables during shipping is influenced by temperature, vibration of transporting vehicle, and concentration of oxygen (O<sub>2</sub>) and carbon dioxide (CO<sub>2</sub>) (Kader, 1987; Nakamura et al., 1986). Therefore, inappropriately designed packaging may induce objectionable odors in the vegetables due to anaerobic respiration, or may otherwise induce yellowing or decrease the content of chemical components (Lipton & Harris 1974; Charles & Roger, 1991). Thus it is necessary to properly design MAP expressly for fresh vegetables. To this end, a variety of studies, including one on the respiration rates of fresh vegetables, permeability of film and container, and a beneficial atmosphere are needed. A mathematical model for simulating the change of gas in MAP may help to predict the periodical changes. Mathematical models have been used widely to predict the gas composition of the atmosphere surrounding vegetables wrapped with polymeric film (Hayakawa et al., 1975; Shiina et al., 1988; Cameron et al., 1989, 1994; Fishman et al., 1995) or in shipping containers with polyethylene laminated liners (Uchino et al., 1996). However, most previous attempts to predict gas

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composition concentrated on an analysis of the atmosphere, either that which surrounded the vegetables in the polymeric film, or that which was in the container.

The main objective of this work was to predict the gas composition and permeability surrounding vegetables packaged with polymeric film while in shipping containers, in an actual shipment with or without Welsh onions.

#### Mathematical Model for the Packaging System

Figure 1 presents a model illustrating Welsh onion packaged with polymeric film while in a shipping container. The volume of  $CO_2$  in the atmosphere within the unperforated polymeric film package containing fresh vegetable  $[V_{1C} \text{ (ml)}]$  is determined by two processes:  $CO_2$  evolution by respiration of Welsh onion [R (ml)] and the amount of permeation of  $CO_2$  through the film package  $[PM_{1C} \text{ (ml)}]$ . Therefore, change in  $CO_2$  of the film package is approximated by the following equation:

$$V_{1C}(t+dt) = V_{1C}(t) + dR + dPM_{1C}.$$
 (1)

Changes in  $CO_2$  evolution using Welsh onion, and the amount of  $CO_2$  permeation through the package within a short time dt (h) are respectively given as:

$$dR = \frac{r}{44} \cdot \alpha \cdot W \cdot dt , \qquad (2)$$

$$dPM_{1C} = \frac{K_{1C}}{24} \cdot A_1 \cdot (P_{2C} - P_{1C}) \cdot dt, \qquad (3)$$

where

*r*=respiration rate of onion (mgCO<sub>2</sub>·kg<sup>-1</sup>·h<sup>-1</sup>),  $\alpha$ =capacity ratio of CO<sub>2</sub> at 15°C (ml·mM<sup>-1</sup>), *W*=weight of onion (kg),

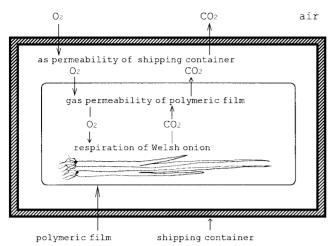


Fig. 1. Schematic model of Welsh onion and its environment illustrating two levels of barriers to gas change.

 $K_{1C}$ =permeability of CO<sub>2</sub> in the film package (ml·m<sup>-2</sup>·day<sup>-1</sup>· atm<sup>-1</sup>),

 $A_1$  = effective area of the film package (m<sup>2</sup>),

 $P_{1C}$ ,  $P_{2C}$ =partial pressures of CO<sub>2</sub> in the film package and shipping container, respectively (atm).

The volume of  $O_2$  inside the film package is similarly determined by the  $O_2$  consumption by onion and permeation of  $O_2$ . Therefore, change in  $O_2$  of the package  $[V_{10} \text{ (ml)}]$  is approximated by the following equation:

$$V_{10}(t+dt) = V_{10}(t) - \frac{dR}{rq} + dPM_{10} , \qquad (4)$$

(5)

where

rq = respiration quotient (-)

 $PM_{10}$  = amount of O<sub>2</sub> emitted through the package (ml).

The volume of  $N_2$  inside the film package is determined only by permeation of  $N_2$ . Thus, the change in volume of nitrogen ( $N_2$ ) within the package [ $V_{1N}$  (ml)] is approximated by the following equation:

$$V_{1N}(t+dt) = V_{1N}(t) + dPM_{1N}$$

where

 $PM_{1N}$ =amount of N<sub>2</sub> emitted through the film package (ml).

The volume of CO<sub>2</sub> inside the container, but outside the film package [ $V_{2C}$  (ml)] is determined by permeation through both the polymeric package [ $PM_{1C}$  (ml)] and the container [ $PM_{2C}$  (ml)]. Therefore, change in CO<sub>2</sub> inside the container is approximated by the following equation:

$$V_{2C}(t+dt) = V_{2C}(t) - n \cdot dPM_{1C} + dPM_{2C}, \qquad (6)$$

$$dPM_{2C} = \frac{\kappa_{2C}}{24} \cdot A_2 \cdot (P_C - P_{2C}) \cdot dt , \qquad (7)$$

where

*n*=number of film packages in shipping container,

 $K_{2C}$ =permeability of CO<sub>2</sub> of shipping container (ml·m<sup>-2</sup>·day<sup>-1</sup>· atm<sup>-1</sup>),

 $A_2$ =effective area of shipping container (m<sup>2</sup>),

 $P_{\rm C}$ =partial pressure of CO<sub>2</sub> in air (atm).

Changes in volume of  $O_2 [V_{20} (ml)]$  and  $N_2 [V_{2N} (ml)]$  inside the container are approximated by the following equations, similarly:

$$V_{20}(t+dt) = V_{20}(t) - n \cdot dPM_{10} + dPM_{20}, \qquad (8)$$

$$V_{2N}(t+dt) = V_{2N}(t) - n \cdot dPM_{1N} + dPM_{2N}, \qquad (9)$$

where

 $PM_{20}$ ,  $PM_{2N}$ =the amount of O<sub>2</sub> and N<sub>2</sub> emitted through the shipping container, respectively (ml).

#### **Materials and Methods**

*Materials* Welsh onions were obtained from unheated greenhouses in Fukuoka, Japan. Only undamaged onions were used.

Unperforated OPP film packages and an EPS containers were used for this experiment. Both were the types used for the actual shipment of Welsh onions. The effective area and volume of the film package was  $0.093 \text{ m}^2$  and 700 ml, respectively, and that of the EPS container was  $0.54 \text{ m}^2$  and 22,440 ml, respectively.

Respiration rate of Welsh onion The Welsh onions (100 g) were placed in a 1600 ml cylindrical container (acrylic resin) at 15°C. Various gas mixtures were flowed through the containers for 18 h at a rate of 7000 ml/h. The containers were then plugged tightly with rubber stoppers, and the atmosphere inside the plugged container was analyzed regularly for O<sub>2</sub> and CO<sub>2</sub> concentrations using gas chromatography (Shimadzu gas chromatograph: thermoconductivity detector, column: Porapak N, 3 mm i.d.×1 m+Molecular sieve, 3 mm i.d.×3 m and column oven temperature: 65°C). Respiration rate of the onions was calculated from changes in the concentration of CO<sub>2</sub>. The respiration rate [r (mgCO<sub>2</sub> ·kg<sup>-1</sup>·h<sup>-1</sup>·atm<sup>-1</sup>)] as a function of both the O<sub>2</sub> and CO<sub>2</sub> concentration was evaluated by multiple regression analysis. Thirty-six gas mixtures were tested.

*Measurement of gas permeability* Gas permeability of unperforated OPP film and EPS containers was determined at 15°C by the simple pouch method described in Ohta *et al.* (1991). This method was employed for  $CO_2$ ,  $O_2$  and  $N_2$  to measure the gas concentration in the film package or container periodically using gas chromatography. This experiment was repeated four times.

Measurement of gas compositions in film packages and EPS container Firstly, to check the theoretical predictions of atmosphere changes in film packages and shipping containers, empty packages were used. OPP film packages were sealed completely without Welsh onion. The initial volume in each package was 800 ml, and 20 of these empty packages were packed in one EPS container, after which the lid was placed on the container and secured with tape.

The next experiment was to simulate the actual shipment of Welsh onions. A bunch of onions (100 g) was sealed completely in 20 OPP film packages, 700 ml per package, and then placed in the container. These containers were stored at 15°C.

The gas composition of the atmosphere inside the film packages, and outside the packages but inside the container, was periodically determined by gas chromatography.

*Computer simulation* Computer simulation of changes in gas composition in the OPP film package and the EPS container were carried out under the conditions described previously. The weight of one bunch of onions was 100 g, specific gravity was  $0.33 \text{ g}\cdot\text{cm}^{-3}$ , volume of the film package was 700 ml (800 ml for empty package test), and pressure in the package and container was 1 atm. Twenty film packages were packed in the EPS container. The results of the simulation were compared with experimental data while the numerical calculations were performed on a computer.

### **Results and Discussion**

Respiration rate of Welsh onion for various gas mixtures was estimated as follows:

$$r=30.40-2.06\times[CO_2]+0.57\times[O_2].$$
 (10)

The coefficient of multiple correlation was 0.92. The respiration quotient was 0.92. Figure 2 shows the relationship between measured and calculated respiration rate. Values from the multiple regression analysis approximated measured values (R=0.92). For predicting the respiration rate of a fresh vegetable as a function of O<sub>2</sub> and CO<sub>2</sub>, Yang and Chinnan (1988) used a quadratic function to correlate rate with storage time. Cameron et al. (1989) attempted to determine the  $O_2$  consumption of tomato as a function of O<sub>2</sub> concentration using an exponential type equation. All these attempts were empirical approaches. To determine the respiration rate theoretically, Lee et al. (1991) used enzyme kinetics (Michaelis-Menten type equation) to correlate the respiration rate with the  $O_2$  and  $CO_2$  concentration. However, it is unnatural to express the respiration rate for multiple enzymes as a simplistic Michaelis-Menten type enzyme. Therefore, the respiration rate of cut Welsh onion was expressed by multiple regression analysis because of the approximate fit between the measured and calculated values.

Gas permeability coefficients for the OPP film and EPS are shown in Table 1. It was found that the  $CO_2$  and  $O_2$  permeability coefficients of the OPP film were in agreement with those proposed by Ohta *et al.* (1991), while the  $CO_2$  permeability coefficient of the EPS container was 12 times that of the OPP film. The difference in  $CO_2$ ,  $O_2$  and  $N_2$  permeability coefficients of the EPS container was not significant. Those of EPS were higher than those of the corrugated shipping container with a polyethylene laminated liner (Uchino *et al.*, 1996).

Experimental and simulated data changes over time for CO<sub>2</sub>

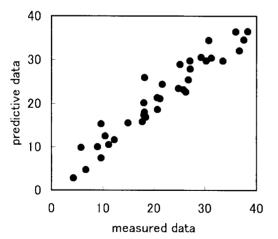
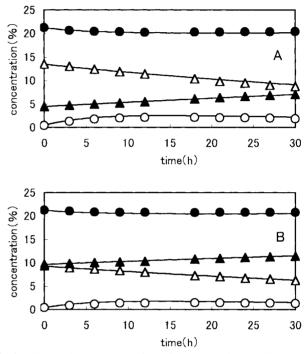


Fig. 2. Correlation between experimental and predictive values of respiration rate of Welsh onion  $(mgCO_2 \cdot kg^{-1} \cdot h^{-1})$ .

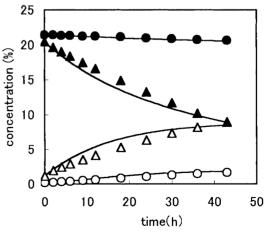
Table 1. Gas permeability of OPP film packaging and EPS containers at  $15^{\circ}$ C.

Property	Thickness (mm)	Permeability (ml·m <sup>-2</sup> ·day <sup>-1</sup> ·atm <sup>-1</sup> )		
		CO <sub>2</sub>	O <sub>2</sub>	$N_2$
OPP film	0.025	3570	1137	678
EPS container	18.0	42,955	47,089	45,673

and  $O_2$  observed in the OPP film package and EPS container (without Welsh onion) are shown in Fig.3. In this experiment, there was no addition of  $CO_2$  or reduction of  $O_2$  owing to respiration. So, the experimental  $CO_2$  concentrations inside the OPP film package decreased constantly while these  $O_2$  concentration increased constantly. When the initial concentrations inside the OPP film package were 13.5 and 4.5%, respectively (Fig. 3-A), the experimental and simulated  $CO_2$  concentrations inside the



**Fig. 3.** Changes in gas concentrations of CO<sub>2</sub> and O<sub>2</sub> in OPP film package (without Welsh onion) and EPS container at 15°C. A: Initial CO<sub>2</sub> and O<sub>2</sub> concentrations in film package are 13.5% and 4.5% respectively. B: Initial CO<sub>2</sub> and O<sub>2</sub> concentrations in film are 9.8% and 9.3%, respectively.  $\triangle$ : experimental data of CO<sub>2</sub> concentrations in OPP film package.  $\triangle$ : experimental data of O<sub>2</sub> concentrations in OPP film package.  $\bigcirc$ : experimental data of CO<sub>2</sub> concentrations in OPP film package.  $\bigcirc$ : experimental data of CO<sub>2</sub> concentrations in OPP film package.  $\bigcirc$ : experimental data of CO<sub>2</sub> concentrations in EPS container.



**Fig. 4.** Changes in gas concentrations of  $CO_2$  and  $O_2$  in OPP film and EPS container of Welsh onion at 15°C. 100 g of Welsh onion was sealed completely with unperforated OPP film. The number of film packages in an EPS container was 20. Initial volume of film package was 700 ml. Symbols are the same as in Fig.3.

package also decreased constantly. Similarly,  $O_2$  concentrations were constantly increased. The maximum differences between experimental and simulated data of  $CO_2$  and  $O_2$  were 0.4% and 0.1%, respectively. Moreover, the maximum experimental  $CO_2$  concentration inside the EPS container was 2.1% (initial  $CO_2$  concentration, 0.4%), while the minimum  $O_2$  concentration was 20.2% (initial  $O_2$  concentration, 21.3%) with the simulated value of  $CO_2$  and  $O_2$  at 2.5 and 20.1%, respectively. When the initial  $CO_2$  and  $O_2$  concentrations inside the OPP film package were 13.5 and 4.5%, respectively (Fig. 3-B), the experimental values agreed very well with the simulated values. This indicates the suitability of the proposed model.

Experimental and simulated data for the OPP film package and the EPS container with Welsh onions are shown in Fig. 4. The experimental value for  $CO_2$  concentration inside the EPS increased to 1.7%, while that for O<sub>2</sub> concentration decreased to 1.0%. These values agreed well with the predicted data. On the other hand, the experimental data for CO<sub>2</sub> and O<sub>2</sub> concentration inside the OPP film package approximated the simulated data. Simulated CO<sub>2</sub> concentration increased gradually, but the experimental CO<sub>2</sub> concentration only slowly increased. Thus, the maximum difference between experimental and simulated data was 1.5%. Similarly, the maximum difference between predicted and experimental data was 1.2%. These slight differences may be caused by individual variation respiration. However, these experimental and simulated gas concentrations correlated significantly (at the 99.9% level) with correlation coefficients of 0.989. Therefore, the simulation model may be useful for fresh vegetables wrapped in polymeric film and enclosed inside a shipping container.

#### Nomenclatures

- $V_{1C}$ ,  $V_{1O}$  and  $V_{1N}$ : the volume of CO<sub>2</sub>, O<sub>2</sub> and N<sub>2</sub> in the atmosphere in an unperforated polymeric film package, respectively (ml)
- $V_{2C}$ ,  $V_{2O}$  and  $V_{2N}$ : the volume of CO<sub>2</sub>, O<sub>2</sub> and N<sub>2</sub> in the atmosphere in the container, respectively (ml)
- $PM_{1C}$ ,  $PM_{1O}$  and  $PM_{1N}$ : the amount of permeation of CO<sub>2</sub>, O<sub>2</sub> and N<sub>2</sub> through the film package, respectively (ml)
- $PM_{2C}$ ,  $PM_{2O}$  and  $PM_{2N}$ : the amount of permeation of CO<sub>2</sub>, O<sub>2</sub> and N<sub>2</sub> through the container, respectively (ml)
- $R: CO_2$  evolution by respiration of Welsh onion (ml)
- *r*: the respiration rate of Welsh onion (mgCO<sub>2</sub>·kg<sup>-1</sup>·h<sup>-1</sup>)
- *rq*: the respiration quotient (-)
- $\alpha$ : the capacity ratio of CO<sub>2</sub> at 15°C (ml·mM<sup>-1</sup>)
- W: the weight of Welsh onion (kg)
- $K_{1C}$  and  $K_{2C}$ : the permeability of CO<sub>2</sub> of film package and container, respectively (ml·m<sup>-2</sup>·day<sup>-1</sup>·atm<sup>-1</sup>)

 $A_1$  and  $A_2$ : the effective area of film package and container (m<sup>2</sup>)

 $P_{1C}$ ,  $P_{2C}$  and  $P_{C}$ : partial pressure of CO<sub>2</sub> in film package, container and air, respectively (atm)

*n*: the number of film packages in a shipping container(-)

t: time (h)

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