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Modeling Fresh Produce Respiration and Designing Modified Atmosphere Package

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Abstract The method to characterize the fresh produce respiration was presented with possible application of modified atmosphere package design. Particularly the respiration model based on enzyme kinetics was introduced as function of oxygen and carbon dioxide concentrations. The method to estimate the equilibrated package atmosphere for any package conditions was presented by incorporation of O_2 and CO_2 permeabilities of the packaging film. Temperature dependences for fresh produce respiration and gas permeation were given by Arrhenius equation and then used to analyze the effect of temperature on the package atmosphere. An example analysis was presented for better understanding of the concept.

Key Words Respiration measurement, Kinetics, Packaging atmosphere, Temperature dependence

Introduction

Modified atmosphere packaging (MAP) for fresh produce is a tool relying on modification of internal package atmosphere by produce respiration and package permeation. The resultant effect of attained modified atmosphere (MA) is to keep the fresh produce freshness and extend the produce shelf life. The MA of reduced O_2 and elevated CO_2 concentrations inside the permeable plastic package works to reduce respiration rate, ethylene production and softening of the texture. An MA optimal specifically for the commodity is created and maintained by an intricate interplay between the respiration of the produce and the gas permeation of the package (Yam and Lee, 1995). Therefore understanding the respiration characteristics and permeation property of the package layer is essential for proper design of fresh produce MAP design.

As a design factor for MAP of fresh produce, respiration of the fresh produce produces carbon dioxide and consumes oxygen:

$$C_6H_{12}O_6(s) + 6O_2(g) \rightarrow 6CO_2(g) + 6H_20(l) + 2{,}816 \text{ kJ} \quad (1)$$

The respiration process of fresh produce thus works to increase the internal CO_2 concentration and decrease the O_2 concentration. Even though water vapor is produced from the respiration process with heat generation, it is not usually considered in designing the MAP. In most circumstances of fresh produce MAP, the humidity inside the package is saturated with little possibility of control by package film: most plastic package films have low water vapor permeability to keep the internal headspace humidity at saturation level (Song et al., 2001); high saturated humidity is not so deleterious and may usually be assumed good for produce quality, even though sometimes lower humidity may be desirable for some commodities.

Respiration is also an indication of the rate of catabolic changes and quality deterioration: the higher the respiration rate, the faster the quality deterioration with shorter storage life. The condition to reduce respiration in aerobic range is the target of MAP design. Thus, information on the respiration is required for designing storage and package of fresh produce. Storage and packaging to keep freshness can be helped from the overall picture on respiration. The variables affecting respiration rate need to be identified and quantified in their influence. The internal factors such as commodity, maturity and harvest time and external factors such as temperature and gas concentration of atmosphere are the variables to be considered in the study of the respiration (Kader, 1987). Modeling of respiration deals with mathematical presentation of respiration rate responding to these variables. Even though all these factors are desired to be quantified in respiration modeling, currently gas composition and temperature are the main variables to be considered in the respiration model. Sometimes time after harvest has been considered in the empirical respiration model (Yang and Chinnan, 1988), which has not been accepted widely. Therefore this paper reviews the effect of gas composition and temperature on the respiration in viewpoint of fresh produce package design.

Measurement and Modeling of Respiration

The produce respiration rate can be measured by the open, closed or permeable system. Fig. 1 shows the schematic prin-

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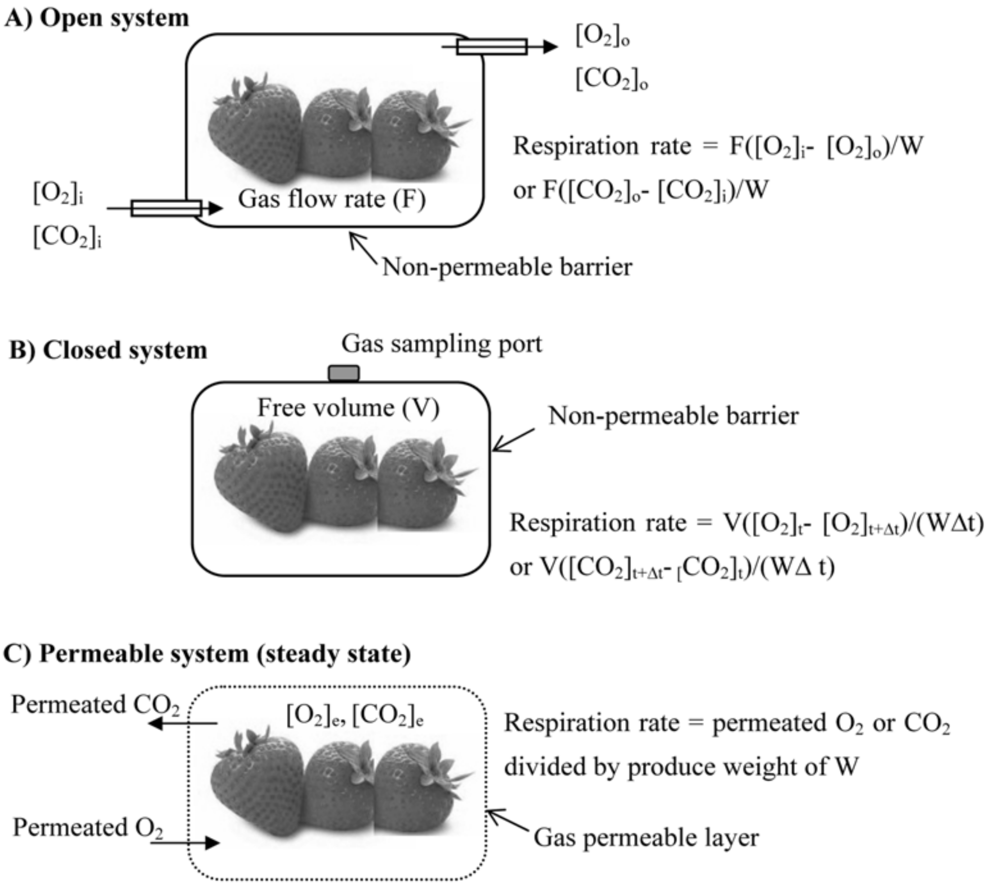

Fig. 1. Schematic diagram for measuring respiration of fresh produce (weight: W).

ciple of respiration measurement by different methods. The open system method involves storing the produce in a barrier box or bottle that has an inlet port and outlet port through which a pre-mix gas passes (Fig. 1A). Respiration rate is calculated by the product of flow rate and gas (O_2 or CO_2) concentration difference between inlet and outlet divided by produce weight. For example, guess that inlet gas of 10% O_2 and 10% CO_2 changes to that of 9.5% O_2 and 10.4% CO_2 at flow rate of 60 mL min^{-1} in a jar containing 0.3 kg produce. The O_2 consumption rate under this gas condition is given by $\frac{(10-9.5)}{100}\times\frac{60}{0.3}$ = 1.0 mL min^{-1} kg^{-1} = 60 mL h^{-1} kg^{-1}. The CO_2 evolution rate is $\frac{(10.4-10)}{100}\times\frac{60}{0.3}$ =0.8 mL min^{-1} kg^{-1}=48 mL h^{-1} kg^{-1}.

The disadvantage of this method is that it works only with produce of high respiration, and much time and labor are required for obtaining data with many different jars. Another point to be considered in the open system method is humidity of the inlet gas: saturated humidity of the inlet gas controlled in O_2 and CO_2 concentrations is desired; if the dry inlet gas is applied, calibration in flow rate is required for moisture saturation through the gas flow in the jar. Another difficulty of open system method is use of concentration difference in respiration calculation, which propagates or amplifies with the concentration measurement errors.

The closed system method involves monitoring the O_2 and CO_2 concentrations as a function of time inside a hermetically closed barrier jar containing the produce (Fig. 1B). Respiration rate is obtained by product of free volume and gas concentration change rate divided by produce weight. For example, guess that a closed jar containing 0.3 kg produce in 400 mL free volume of air (20.9% O_2 and 0.00% CO_2) results in 19.8% O_2 and 1.0% CO_2 after 2 hours. The O_2 consumption rate is given by $\frac{(20.9-19.8)}{100\times 2}\times\frac{400}{0.3}$=7.3 mL h^{-1} kg^{-1}. The CO_2 evolution rate is $\frac{(1.0-0.00)}{100\times 2}\times\frac{400}{0.3}$=6.7 mL h^{-1} kg^{-1}. This method is suitable for produce with very low respiration rates, but the data obtained cannot represent a certain set of gas composition. The same problem of using concentration difference in respiration calculation observed in the open system still exists for closed system, and a mathematical function to describe the change of gas concentration through the time is often used to smooth out the curve of concentration profile, which contributes to reducing the fluctuation error and obtaining the stable respiration pattern.

The permeable system is similar to the closed system except that a permeable package is used instead of a closed jar. Its advantage is that the experimental conditions are closer to real packaging situation, and the time and labor of conducting experiments could be less than for the open and the closed systems providing that the researcher has an intelligent guess of what permeable packages to use. The permeable system can be divided into unsteady state method and steady state one (Lee et al., 1995). Fig. 1C explains the steady state version of the permeable system method. When steady state is arrived for a set of package conditions, the respiration of the produce in the permeable package is calculated as follows:

$$r_{O_2} = \frac{SP_{O_2}(0.21 - [O_2]_e/100)p}{WL} \quad (2)$$

$$r_{CO_2} = \frac{SP_{CO_2}([CO_2]_e/100 - 0.0)p}{WL} \quad (3)$$

where r_{O_2} and r_{CO_2} are respective respiration in O_2 consumption and CO_2 evolution (mL kg^{-1} h^{-1}), S is package film area (m^2), P_{O2} and P_{CO2} are film permeability to O_2 and CO_2 gases (mL mm h^{-1} m^{-2} atm^{-1}), respectively, p is atmospheric pressure (atm), $[O_2]_e$ and $[CO_2]_e$ are the equilibrated oxygen and carbon dioxide concentrations (%), respectively, W is produce weight (kg), and L is film thickness (mm).

As an example, 0.08 m^2 plastic film package of 0.11 kg produce maintains the 1.5% O_2 and 4.2% CO_2 at equilibrium. The film has thickness of 20 mm, and respective O_2 and CO_2 permeability of 3,000 and 13,000 mL mm m^{-2} h^{-1} atm^{-1}. The r_{O_2} and r_{CO_2} are given as follows:

$$r_{O_2} = \frac{0.08 \times 3000 \times (0.21 - 1.5/100)}{0.11 \times 20} = 21.3 \text{ mL kg}^{-1} \text{ h}^{-1}$$

$$r_{CO_2} = \frac{0.08 \times 13000 \times (4.2/100 - 0.0)}{0.11 \times 20} = 19.9 \text{ mL kg}^{-1} \text{ h}^{-1}$$

Mathematical model describing respiration as function of environmental variables is very useful for designing the fresh produce MAP. An enzyme kinetics type respiration model has been developed to describe the respiration rate of fresh produce as a function of O_2 and CO_2 concentrations (Lee et al., 1991), and is widely being used by many researchers in designing MAP of many fresh commodities. The model describes the rate of respiration as function of O_2 and CO_2 concentrations by Equation 4:

$$r = \frac{V_m[O_2]}{K_m + (1 + [CO_2]/K_i)[O_2]} \quad (4)$$

where r is respiration rate in O_2 consumption or CO_2 production (mL kg^{-1} h^{-1} or mg kg^{-1} h^{-1}) at oxygen concentration $[O_2]$ (%) and carbon dioxide concentration $[CO_2]$ (%), and V_m, K_m and K_i are parameters. The model has been shown to be useful for measuring respiration of fresh produce by the open, closed and permeable systems (Haggar et al., 1992; Lee et al., 1991; Lee et al., 1995).

Because closed system method is widely used for characterizing the fresh produce respiration due to its simplicity in experiment, an example of closed system data is given to show an easy way of respiration modeling (Table 1). As mentioned before, mathematical functions are used to smooth out the gas concentration change data obtained in closed system experiment. Many nonlinear functions have been used for describing the gas composition changes through time and obtaining the derivatives to be used for calculating respiration rates (Cameron et al., 1989; Haggar et al., 1992; Mahajan and Goswami, 2001). In this study, for simplicity the quadratic equation with coefficients of a, b and c (Equation 5) was fitted to the data of gas concentration vs. time t (h) in Table 1 as shown in Fig. 2 (Jacxsens et al., 1999).

$$[O_2] \text{ or } [CO_2] = at^2 + bt + c \quad (5)$$

Table 1. A set of O_2 and CO_2 concentration data for a glass jar (free volume: 899 mL) containing 0.101 kg soybean sprouts at 5°C

Time (h)	O_2 (%)	CO_2 (%)	r_{O2} (mL kg^{-1} h^{-1})	r_{CO2} (mL kg^{-1} h^{-1})
0	0.03	20.9	32.74	14.54
4.667	1.387	18.369	31.30	14.26
9.167	2.144	16.511	29.91	13.98
19.45	3.665	13.231	26.73	13.34
27.1	4.711	11.316	24.37	12.87
34.017	5.713	9.573	22.23	12.45
44.017	6.938	7.627	19.14	11.83
50.6	7.478	6.456	17.11	11.43
57.133	8.522	5.206	15.09	11.02
68.1	9.871	3.273	11.70	10.35
75.767	10.934	2.201	9.34	9.88
81.217	11.497	1.615	7.65	9.54

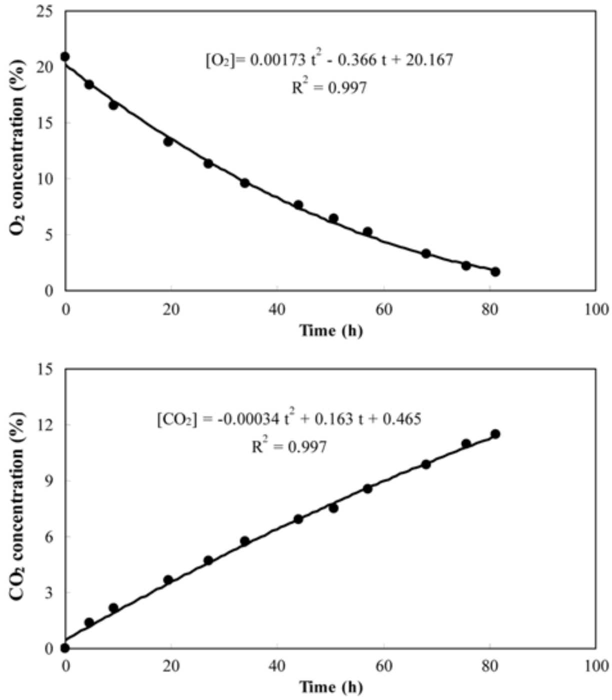

Fig. 2. 2nd order polynomial fitted to the gas concentration data set in Table 1.

Now the respiration rate at each time can be calculated by using a derivative of those functions:

$$r_{O2} = -\frac{d[O_2]}{100dt}\left(\frac{V}{W}\right) \tag{6}$$

$$r_{CO_2} = \frac{d[CO_2]}{100dt}\left(\frac{V}{W}\right) \tag{7}$$

The derivatives for O_2 and CO_2 concentrations in the example of Fig. 2 can be obtained as follows:

$$\frac{d[O_2]}{dt} = 0.00346t - 0.366 \tag{8}$$

$$\frac{d[CO_2]}{dt} = -0.00068t + 0.163 \tag{9}$$

The respiration rates at each time obtained by the procedure described above are also given in Table 1. If we fit Equation 10 linearized from Equation 4 to the gas composition and respiration data, the model parameters of V_m, K_m and K_i can be obtained as given in Table 2.

$$\frac{1}{r} = \frac{1}{V_m} + \frac{K_m}{V_m}\frac{1}{[O_2]} + \frac{1}{K_iV_m}[CO_2] \tag{10}$$

Thus it was shown that simple closed system experiment can be used for determining the respiration model parameters, which would be useful in designing the fresh produce MAP.

Another important external variable affecting respiration is temperature. Mostly the effect of temperature on respiration is described by Arrhenius equation:

$$r = r_o \exp\left(\frac{-E_a}{RT}\right) \tag{11}$$

where E_a is activation energy (J mol^{-1}), R is gas constant (8.314 J K^{-1} mol^{-1}), T is absolute temperature (K) and r_o is a constant (mL kg^{-1} h^{-1} or mg kg^{-1} h^{-1}). Generally Equation 11 holds for any gas composition where aerobic respiration is maintained. The activation energy for the respiration rate ranges usually from 30 to 80 kJ mol^{-1} . Mahajan and Goswami (2001) recently reported that Arrhenius equation can be used for describing the temperature dependence of respiration model parameters: V_m, K_m and K_i for apple respiration (Equation 4) could be presented by Arrhenius equation; V_m and K_m showed positive activation energy meaning temperature dependent increase while K_i had negative value of activation energy (decrease with temperature). This type of relationship would simplify the process of MAP design of fresh produce, which will be shown by an example below. However, from the author's experience these simple functional relationships can not work for most produces and thus are suggested to be carefully used for the cases confirmed.

Construction and Solution of Package Design Problem

Design process of fresh produce MAP starts from finding ranges of optimum gas composition to preserve the quality at best conditions available (Fig. 3). For some commodities, modified or controlled atmosphere does not help keep the freshness quality and extend the shelf life: in this case, the MAP does not have any benefit and is not tried. However, many commodities can be benefited from proper choice of gas composition in preserving the freshness. For these commodities, it is necessary to establish the optimum gas composition range under tolerable storage temperature conditions. Temperature should be in a range to help delay senescence and ripening process even though some tolerant range may be allowed or experienced in distribution and storage. Also the

Table 2. Respiration model parameters obtained from closed system analysis for the data set in Table 1

Respiration expression	V_m (mL kg^{-1} h^{-1})	K_m (% O_2)	K_i (% CO_2)	R^2
r_{O2}	16.4	0.59	24.49	0.990
r_{CO2}	58.95	9.32	8.59	0.998

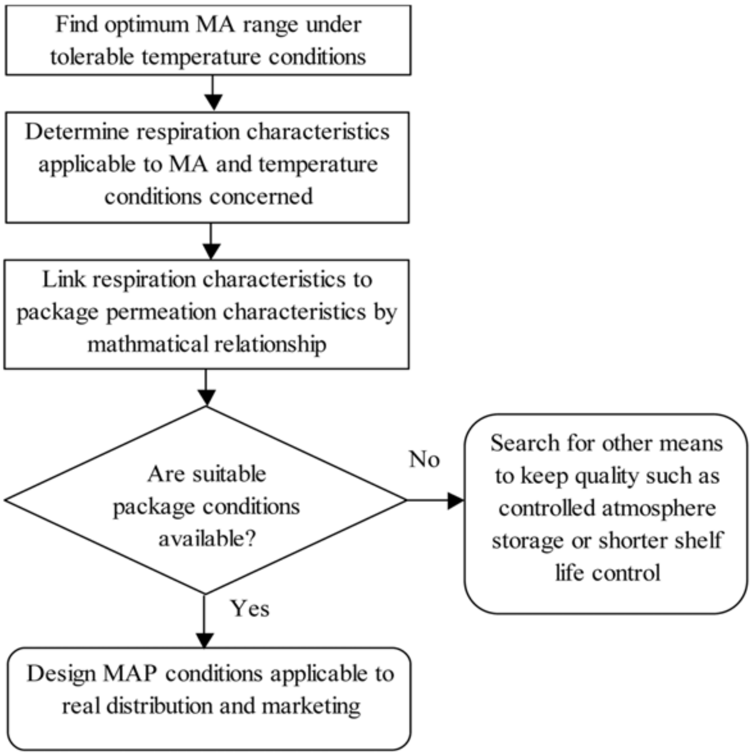

Fig. 3. Strategy of designing MAP of fresh produce.

considered temperature should not below that causing chilling injury above freezing temperature. O_2 and CO_2 concentration outside the optimal window may not give any positive MA effect on the produce quality or, may even cause deleterious physiological damage on the produce: the symptoms undesirable include formation of alcohols and aldehydes, off-flavor development, and internal tissue breakdown. Table 3 shows some examples of the optimum atmosphere and tolerance limit to low O_2 and high CO_2.

The next step of MAP design step is to combine the respiration model with permeation characteristics, which makes it possible to estimate package atmosphere for any design variables (Fig. 3). Equations 12 and 13 proposed by Hayakawa et al. (1975) are widely used to estimate time-dependent O_2 and CO_2 concentrations of fresh produce MAP.

$$\frac{d[O_2]}{dt} = 100\left\{\frac{SP_{O_2}(0.21-[O_2]/100)p}{VL} - \frac{Wr_{O_2}}{V}\right\} \tag{12}$$

$$\frac{d[CO_2]}{dt} = 100\left\{\frac{SP_{CO_2}(0.00-[CO_2]/100)p}{VL} + \frac{Wr_{CO_2}}{V}\right\} \tag{13}$$

where V is the free volume of the package (mL).
The differential Equations 12 and 13 are the mass balance equations taking into account the respiration of the fresh produce and permeation of the plastic film. In case that volume change needs to be considered, the similar equations for calculating volume of O_2, CO_2 and N_2 can be formulated with addition of N_2 balance equation (Talasila and Cameron, 1997). These kinds of differential equations can be easily solved by plugging them into mathematical computer software such as MathCad® or Mathematica®.

Main interests of most MAP design, however, are on the equilibrated atmosphere of O_2 and CO_2 concentrations as function of package variables, which would be solved based on the assumption of $d[O_2]/dt = 0$ and $d[CO_2]/dt = 0$ for Equations 12 and 13, respectively: the derivative terms in Equations 12 and 13 on left sides cancel out. If enzyme kinetics based respiration model is applied to describe the respiration characteristics of fresh produce, Equations 14 and 15 are obtained with substitution of r_{O_2} and r_{CO_2} by Equation 4.

$$\frac{SP_{O_2}(0.21-[O_2]_e/100)p}{L} = W\frac{V_{mo}[O_2]}{K_{mo}+(1+[CO_2]_e/K_{io})[O_2]_e} \tag{14}$$

$$\frac{SP_{CO_2}([CO_2]_e/100-0.00)p}{L} = W\frac{V_{mc}[O_2]_e}{K_{mc}+(1+[CO_2]_e/K_{ic})[O_2]_e} \tag{15}$$

where V_{mo}, K_{mo} and K_{io} are V_m, K_m and K_i for O_2 consumption, respectively, and V_{mc}, K_{mc} and K_{ic} are the parameters for CO_2 production, respectively.

The simultaneous algebraic Equations 14 and 15 are easily solved numerically by using mathematics software (e.g. Math-

Table 3. Optimum modified atmosphere and tolerance limit to low O_2 and high CO_2 for some fresh fruits and vegetables

Commodity	Temperature (°C)	Optimum gas composition		Tolerance limit	
		O_2 (%)	CO_2 (%)	Minimum O_2 (%)	Maximum CO_2 (%)
Apple	0	3	3	1	5
Banana	13	2	5	1	8
Broccoli	0	2-5	10		
Cabbage	0	1-2	5-10		
Celery	0	1-4	3		
Cucumber	8	1-4	5		
Garlic	-0.5-0	2	3-6		
Green onion	0	2-5	5-10		
Green pepper	8	3-5	5		
Lettuce	0	2-5	0	4	
Mushroom	0	1-2	10-15	0.5	
Orange	1	15	0	5	5
Peach	0	1-2	5	0.25	6
Pear	0	2-4	1	2	2
Persimmon	0	3-5	5-8	3	10
Pineapple	7	2-5	0		
Strawberry	0	4-10	0-20	1	
Tomato	13	3-5	0	2	2

Adapted from Park *et al*. (2000).

Cad® or Mathematica®) and are very useful to calculate the equilibrium O_2 and CO_2 concentrations ($[O_2]_e$ and $[CO_2]_e$) at constant temperatures. Effect of package variables such as surface area, film thickness and gas permeabilities can easily analyzed by solving those equations. Produce weight and respiration model parameters constitute the variables of the produce. Through repetitive solution for many different conditions, optimum package conditions can be found. If suitable conditions for the commodity can not be found from iterative calculation, other means for keeping the freshness should be looked for (Fig. 3).

In Equations 14 and 15 the environmental variable of temperature is implicitly embedded as temperature effect on gas permeabilities and respiration. If Arrhenius equation for gas permeation and respiration model parameters is valid, Equations 14 and 15 can be used to estimate package atmosphere for any given temperatures. Temperature dependence of gas permeability is explained by Arrhenius equation for most plastic films (Yam and Lee, 1995):

$$P_i = P_{i,o}\exp\left(\frac{-E_{a,i}}{RT}\right) \tag{16}$$

where P_i is permeability of i gas (mL μm h^{-1} m^{-2} atm^{-1}), $P_{i,e}$ is preexponetial factor of i gas permeability (mL μm h^{-1} m^{-2} atm^{-1}), and $E_{a,i}$ is activation energy for i gas permeation.

If respiration model parameters follows Arrhenius equation relationship (Equation 17) as reported by Mahajan and Goswami (Mahajan and Goswami, 2001), all those functions can be incorporated into Equations 14 and 15 to result in Equations 18 and 19.

$$k_p = k_{p,o}\exp\left(\frac{-E_{a,p}}{RT}\right) \tag{17}$$

where k_p is V_m, K_m or K_i at temperature T in absolute scale, and $k_{p,o}$ and $E_{a,p}$ are , respectively, preexpoential factor and activation energy for V_m, K_m or K_i.

$$\frac{SP_{O_2,O}\exp\left(\frac{-E_{a,O_2}}{RT}\right)(0.21-[O_2]/100)p}{L} = W\frac{V_{mo,o}\exp\left(\frac{-E_{a,Vmo}}{RT}\right)[O_2]}{K_{mo,o}\exp\left(\frac{-E_{a,Kmo}}{RT}\right)+\left(1+[CO_2]\exp\left(\frac{E_{a,Kio}}{RT}\right)/K_{io,o}\right)[O_2]} \tag{18}$$

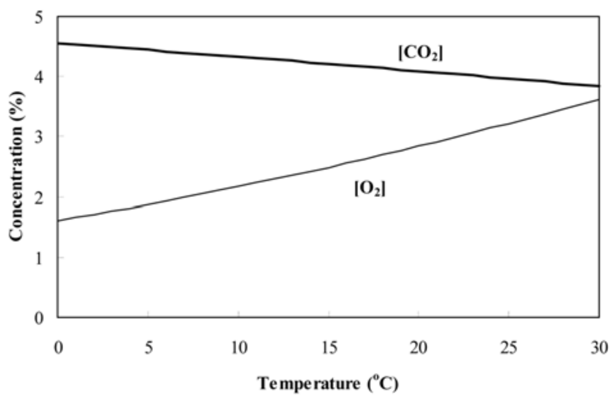

Fig. 4. Equilibrated internal atmosphere of an apple package at different temperatures.

Table 4. Arrhenius equation parameters for film gas permeation and produce respiration model parameters

Parameter	Preexponential factor	Activation energy (J/mol)
P_{O2} (mL mm h^{-1} m^{-2} atm^{-1})	1.049×10^9	30200
P_{CO2} (mL mm h^{-1} m^{-2} atm^{-1})	5.144×10^9	31100
V_m for O_2 consumption (mL kg^{-1} h^{-1})	4.3×10^6	19150
V_m for CO_2 evolution (mL kg^{-1} h^{-1})	1.9×10^5	21080
K_m for O_2 consumption (% O_2)	1.3×10^4	18030
K_m for CO_2 evolution (% O_2)	1.1×10^3	10350
K_i for O_2 consumption (% CO_2)	1.8×10^{-3}	−20290
K_i for CO_2 evolution (% CO_2)	1.9×10^{-2}	−15250

Film permeabilities are from Yam and Lee (1995); respiration model parameters are from Mahajan and Goswami (2001).

$$\frac{SP_{CO_2,O}\exp\left(\frac{-E_{a,CO_2}}{RT}\right)(0.00-[CO_2]/100)p}{L} = W\frac{V_{mc,o}\exp\left(\frac{-E_{a,Vmc}}{RT}\right)[O_2]}{K_{mc,o}\exp\left(\frac{-E_{a,Vmc}}{RT}\right)+\left(1+[CO_2]\exp\left(\frac{E_{a,Kic}}{RT}\right)/K_{ic,o}\right)[O_2]} \quad (19)$$

Knowing all the Arrhenius equation parameters, equilibrated package atmosphere can be easily estimated. An example solution is given in Fig. 4 for a 30 μm thick LDPE film package with 0.06 m^2 surface area, containing 0.25 kg of apple whose respiration characteristics are given in Table 4. The package conditions is somehow similar to those of Jurin and Karel (1963), who developed as the first time the method to estimate package atmosphere systematically. It is noted that gas volume change with temperature is not considered in these equations. The effect to be explained by ideal gas law is not great for usual temperature range of MAP application and can be cancelled on both sides of the equations, which can justify this approach. In this case of the apple package, temperature rise increases the oxygen concentration slightly and reduces the carbon dioxide concentration very slightly (Fig. 4): the change of package atmosphere with temperature is not great enough to affect the effectiveness of MAP significantly. It is noted that the activation energies for gas permeation are a little higher than those of produce respiration, which does not induce the endangered high CO_2 and low O_2 concentrations with increased temperature. This example shows that beneficial MA conditions can be achieved for the package even under fluctuating temperature conditions. The method presented here would constitute a more versatile and convenient way to design fresh produce MAP than that working for a constant temperature condition. However, hurdle to this method is the paucity of temperature dependent respiration kinetics.

Conclusions

Fresh produce respiration model based on enzyme kinetics can be characterized by open, closed and permeable experimental systems. The respiration behaviour of fresh produce as function of O_2 and CO_2 concentrations, can be combined with film gas permeation to predict the package atmosphere, which is useful for designing the package. The model parameters for gas permeation and produce respiration given in Arrhenius relationship make it possible to easily estimate the equilibrated package atmosphere at any temperatures.

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