

Mathematical Model of Gas Exchange for Modified Atmosphere Packaging Containing Pak-choi

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Abstract: Respiration became the dominant aspects of metabolism after vegetables were harvested. The main factors affecting respiration are temperature and gas concentration of the storage environment. It is a major challenge that how to choose a plastic film with appropriate permeability coefficient for specific varieties vegetables in specific temperature. Therefore, it is the key of modified atmosphere packaging technology of vegetables that to establish mathematical model of gas exchange for modified atmosphere packaging (MAP). Based on the dynamic equilibrium theory of MAP, the variation laws of respiration rates were studied with the dynamic changes of O_2 and CO_2 concentration within packages at $10^\circ C$ and $20^\circ C$ respectively. The optimal simulated function expression was established. The experimental data were analyzed with SPSS for windows statistical software. The mathematical model of gas exchange within close packages was developed when the modified atmosphere packaging for Pak-choi was designed. The theoretical basis for getting a right way to choose packaging materials for MAP and predicting the gas mass concentrations inside the packages were provided. The correctness of model was verified by MAP experiments containing Pak-choi.

Keywords: Pak-choi; modified atmosphere packaging; respiration rate; gas exchange; mathematical model

1. Introduction

The Pak-choi is a kind of popular vegetables. It has nutritional and commercial importance in terms of its special functional composition content and consumption demand. However, it is very liable to spoilage under improper storage conditions. Some of the important factors which influence the storage life and quality deterioration of Pak-choi including the loss of water and high respiration and metabolism. A modified atmosphere packaging (MAP) in combination with low temperature storage is a promising and inexpensive way to improve the shelf life of vegetables^[1]. MAP may create an atmosphere richer in CO_2 and poorer in O_2 which can reduce the respiration rates and physiological changes of fresh produce^[2]. LDPE, PP film are the most widely used MAP packaging materials, but the permeability parameters of the same kinds of film is varied based on the film thickness and the storage temperature. How to choose the plastic film of appropriate permeability coefficient for specific varieties of vegetables at a particular temperature is a major problem placed in front of people. In reality, the selections of film's type and thickness were often based on the experience and estimation of workers, it will need a long experimental period, high costs and the effect of packing is not necessarily ideal. Therefore, the development and establishment of mathematical model of gas exchange within close packages is the key to MAP technology.

In this paper, based on the dynamic equilibrium theory of MAP, the variation laws of respiration rates were studied with the dynamic changes of O_2 and CO_2 concentration within packages at $10^\circ C$ and $20^\circ C$ respectively.

The mathematical model of gas exchange within close packages was developed, it will be helpful in predicting temporal changes of gas concentrations and optimizing the design of MAP systems.

2. Materials and methods

2.1. Fresh produce for experiment

The Pak-choi were provided by a peasant household vegetables farmland in the suburb of Tianjin. Single one has about 10 slices leaves, request that the Pak-choi were harvested at 4:00 AM-5:00 AM, having no yellow leaf and did not soak in water, having no any morbid harm, having no obvious mechanical hurts, the color and luster were fresh.

2.2. Determination of the volume of vegetables

The fresh Pak-choi was put into a wide mouth brown glass bottle of 3300ml singly, and 1000ml water were injected into the bottle in advance. At the same time the fresh Pak-choi should be wrapped tightly using preservative film in order to avoid the influence of water on the vegetables. The level of water will be raised, this part of the volume of water was measured by a graduated cylinder of 100ml, and the sum of several measurement was the volume of vegetables^[3].

2.3. The experiment of the effects of gas concentrations on the respiration rates of Pak-choi

The fresh vegetables for experiment were divided into group A and group B. Group A: $10^\circ C$ condition, the Pak-choi which average weight of 190.0g, and volume

of 543ml was placed in a wide mouth brown glass bottle of 3300ml, and sealed with a rubber stopper that has a hole which aperture is 3mm, and it was sealed by a silicone insole which diameter is 8mm. Group B: 20 °C condition, the Pak-chio which average weight of 188.2 g and volume of 538ml was placed in the same bottle. Finally, bottles of group A and group B were placed in a temperature humidity chamber. The O₂, CO₂ gas concentrations were measured at regular intervals with a headspace gas analyser CheckMate9900 from PBI Dansasor, Denmark (Fig.1).



Fig.1. The CheckMate 9900 instrument

Each measurement repeated three times, and calculated the average value. Because the containers with different gas volume and temperature, the duration of the process was different. The data were processed using SPSS for Windows software, and the fitting curve equation of [O₂]_i = f₁(t), [CO₂]_i = f₂(t) were obtained^{[4][5]}. Respiration rates were calculated by Eqs(1) and Eqs (2)^[6].

$$R_{O_2} = \frac{([O_2]_o - [O_2]_i) \times (V - V_v)}{100 \times W \cdot t} \quad (1)$$

$$R_{CO_2} = \frac{([CO_2]_i - [CO_2]_o) \times (V - V_v)}{100 \times W \cdot t} \quad (2)$$

Where R_{O₂} is the vegetable O₂ consumption (ml • kg⁻¹ • h⁻¹), R_{CO₂} is the vegetable CO₂ production (ml • kg⁻¹ • h⁻¹), [O₂]_o, [CO₂]_o are gas mass concentrations (partial pressures) of O₂ and CO₂ in air respectively (%), [O₂]_i, [CO₂]_i are gas mass concentrations (partial pressures) of O₂ and CO₂ within the package respectively after sealed t hours(%), V is the volume of bottle (ml), V_v is the volume of vegetables (ml), W is the weight of vegetables (kg), t is the closed time (h).

3. Results and Discussion

3.1. The establishment of mathematical model of gas concentrations as a function of time in closed system

In group A and group B, O₂ concentration decreased non-linearly with the growth of the processing time, but CO₂ concentration increased non-linearly in contrast, and the change degree at 20°C is larger than 10°C. The fitting curves processed using SPSS for Windows soft-

ware of O₂, CO₂ concentrations changed with time are shown in Fig.2 and Fig.3.

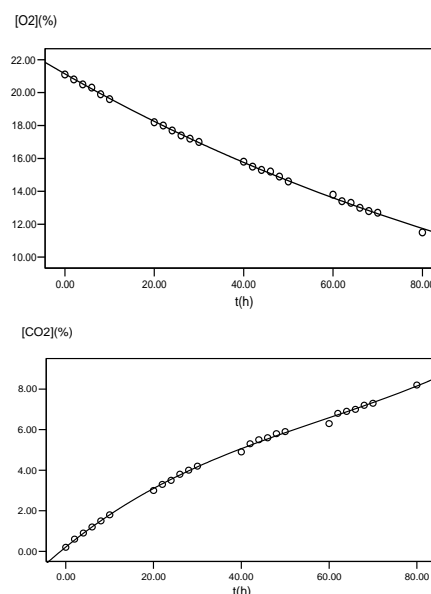


Fig.2. O₂, CO₂ concentrations as a function of time (Group A)
o-experimental data, - fitting curve

The approximation functions were constructed by processing the experimental data with Spss for windows statistical software to express the general trends and characteristics of sample data. The regression equations of each fitted curve are given in Table 1. The results showed: the variation laws of O₂ concentrations changed with time can be fitted by a logarithmic model, the

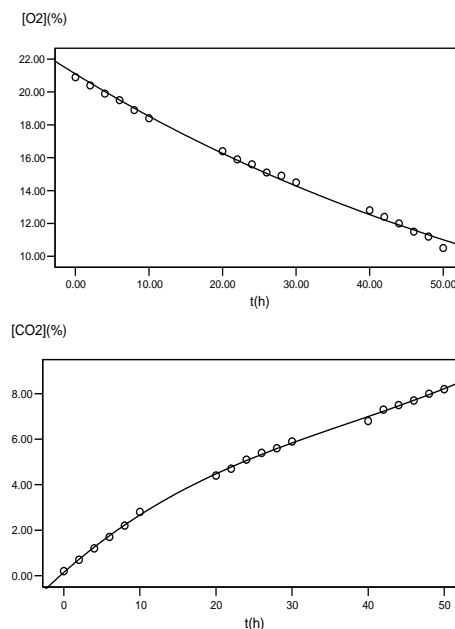


Fig.3. O₂, CO₂ concentrations as a function of time (Group B)
o-experimental data, - fitting curve

Table 1. The equation of O₂, CO₂ concentrations (%) as a function of time t (h)

Group	O ₂ Concentration (%)	CO ₂ Concentration (%)
A	$[O_2]_i = 21.1e^{-0.0073t}$ ($r^2=0.999$)	$[CO_2]_i = 0.2 + 0.17t - 0.0015t^2 + 6.8 \times 10^{-6}t^3$ ($r^2=0.998$)
B	$[O_2]_i = 21.1e^{-0.013t}$ ($r^2=0.999$)	$[CO_2]_i = 0.2 + 0.28t - 0.004t^2 + 3.2 \times 10^{-5}t^3$ ($r^2=0.996$)

r:related coefficient

variation laws of CO₂ concentrations changed with time can be fitted by a cubic polynomial model. The least square method was used in Curve fitting, that is to obtain the model parameters by contrasting the minimal mean squared deviation (MSD) of measured value with fitting value, and then to obtain the optimum functional equation^[7].

3.3. The establishment of mathematical model of respiration rates as a function of O₂ concentrations

The O₂ concentrations are the dominant factors of respiration rate of vegetables in storage conditions. The respiration rates R_{O₂}, R_{CO₂} at different time can be calculated with derivating the equations which were gotten from solving the regression equations in Table 1 into Eqs (1) and (2) respectively. The fitting curves processed using SPSS for Windows software of respiration rates R_{O₂}, R_{CO₂} changed with O₂ concentrations are shown in Fig.4 and Fig.5.

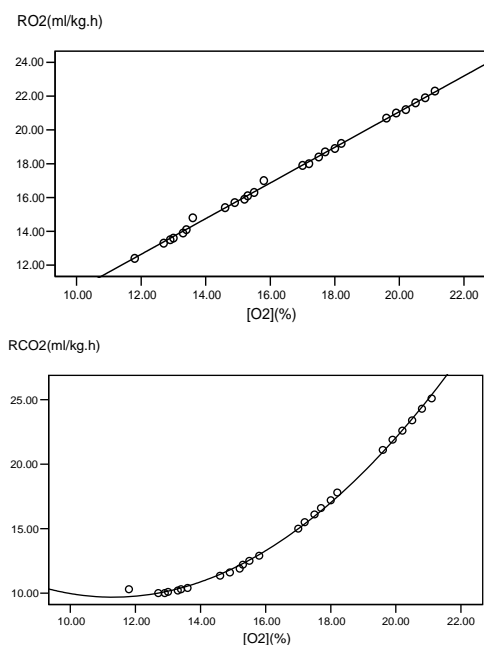


Fig.4. R_{O₂}, R_{CO₂} as a function of O₂ concentrations (Group A)
o-experimental data, - fitting curve

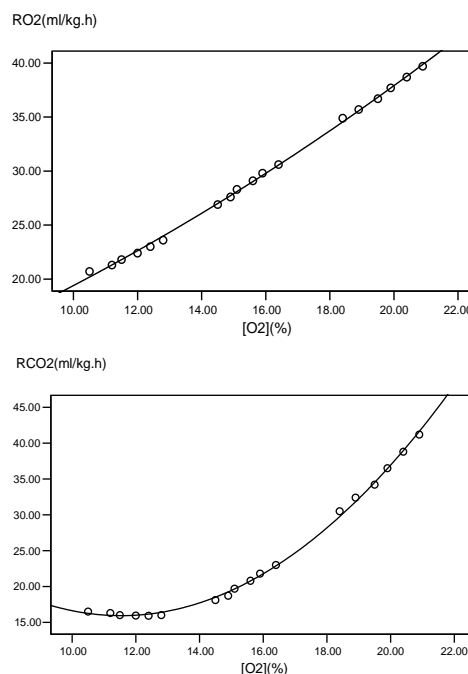


Fig.5. R_{O₂}, R_{CO₂} as a function of O₂ concentrations (Group B)
o-experimental data, - fitting curve

Table 2. The equation of R_{O₂}, R_{CO₂} as a function of O₂ concentration

Group	R _{O₂} =f([O ₂] _i)	R _{CO₂} =f([O ₂] _i)
A	$R_{O_2} = -0.012 + 1.05[O_2]_i$ ($r^2=0.998$)	$R_{CO_2} = 30.6 - 3.70[O_2]_i + 0.16[O_2]_i^2$ ($r^2=0.999$)
B	$R_{O_2} = 6.84 + 0.96[O_2]_i + 0.03[O_2]_i^2$ ($r^2=0.999$)	$R_{CO_2} = 54.9 - 6.77[O_2]_i + 0.29[O_2]_i^2$ ($r^2=0.998$)

The experimental data were processed with Spss for windows statistical software. The results showed: the respiration rates R_{O₂}, R_{CO₂} increased with the growth of O₂ concentrations in both group A and group B. In group A, the variation laws of respiration rates R_{O₂} changed with O₂ concentrations can be fitted by a linear model, and the variation laws of respiration rates R_{CO₂} changed with O₂ concentrations can be fitted by a quadratic model. In group B, the variation laws of respiration rates R_{O₂}, R_{CO₂} changed with O₂ concentrations can be fitted by a quadratic model. The regression equations of each fitted curve are given in Table 2.

3.4. The establishment of mathematical model of gas exchange for MAP containing Pak-choi

The gas exchange in MAP systems can be seen as a dynamic process. The gas concentrations inside the package are determined by two main processes: O₂ consumption and CO₂ evolution caused by produce respiration and permeation of gases through the plastic film.

The process of gas diffusion through the film was determined by Fick's law. If the package is placed in air, the transient variations of the concentrations of O₂ and CO₂ can be expressed by Eqs (3) and (4)^[8]:

$$\frac{d[O_2]_i}{dt} = -\frac{R_{O_2}W}{V} + \frac{P_{O_2}A([O_2]_o - [O_2]_i)}{LV} p_{atm} \quad (3)$$

$$\frac{d[CO_2]_i}{dt} = \frac{R_{CO_2}W}{V} - \frac{P_{CO_2}A([CO_2]_i - [CO_2]_o)}{LV} p_{atm} \quad (4)$$

Where R_{O₂}, R_{CO₂}, W, [O₂]_o, [CO₂]_o, [O₂]_i, [CO₂]_i represent the same meaning and units of eqs (1) and (2), L is the thickness of film (μm), P_{O₂}, P_{CO₂} are film permeabilities for O₂ and CO₂ (ml • μm/m² • h • bar), A is surface area of packing bag(m²), V is the free volume in packing bag (ml), P_{atm} is atmospheric pressure (P_{atm}=1).

Solving the regression equations in Table 2 into Eqs (3) and Eqs (4) respectively, the mathematical model of gas exchange for MAP containing Pak-choi at 10°C can be described by Eqs (5) and (6). The model can be established by the same way at 20°C.

$$\frac{d[O_2]_i}{dt} = -\frac{W}{V}(-0.012 + 1.05[O_2]_i) + \frac{P_{O_2}A([O_2]_o - [O_2]_i)}{LV} p_{atm} \quad (5)$$

$$\frac{d[CO_2]_i}{dt} = \frac{W}{V}(30.6 - 3.7[O_2]_i + 0.16[CO_2]_i^2) - \frac{P_{CO_2}A([CO_2]_i - [CO_2]_o)}{LV} p_{atm} \quad (6)$$

Where the parameters are same as Eqs (3) and (4).

If the ideal storage conditions were known, the gas exchange model could be helpful in the design of MAP systems to evaluate film permeabilities. The equilibrium concentrations of O₂ and CO₂ inside the packages can also be predicted with Eqs (5) and (6) once the package materials are selected. The desired equilibrium gas concentrations can be achieved by adjusting the data of film specification or produce weight with the help of the predictive model.

The correctness of model was verified by MAP experiments containing Pak-choi at 10°C using four kinds of films which permeabilities were tested at advance (Table 3). Before the experiment, the ideal film permeabilities can be evaluated by the model. It was demonstrated with the calculation for O₂ permeability, the ideal equilibrium concentrations were 5% for O₂ and 5% for CO₂, the film permeabilities could be evaluated as the result of P_{O₂}(e) using Eqs (5) under the conditions A=0.06m², W=0.08kg, the results showed in table 3. Compared with P_{O₂}(e) and the real value P_{O₂}(r), it is found that the film O₂ permeability suitable for Pak-choi under such condition might be PP. The calculated method of evaluated film permeabilities P_{CO₂}(e) is the same as P_{O₂}(e). Changes of gas concentrations in different film packages by experiment are shown in Fig.6, the equilibrium concentrations of O₂ and CO₂ inside the PP films was the nearest to the ideal value, the correctness of model was verified.

Table 3. The evaluated film permeabilities P_{O₂}(e) compared with the real value P_{O₂}(r) (mL • μm/m² • d • bar) (10°C)

Film	L(μm)	P _{O₂} (r)	P _{O₂} (e)	P _{O₂} (r)/P _{O₂} (e)
LDPE1	28.7	115259	30078	3.8
LDPE2	39.9	99191	41815	2.4
HDPE	34.7	57741	36366	1.6
PP	49.6	41615	51980	0.8

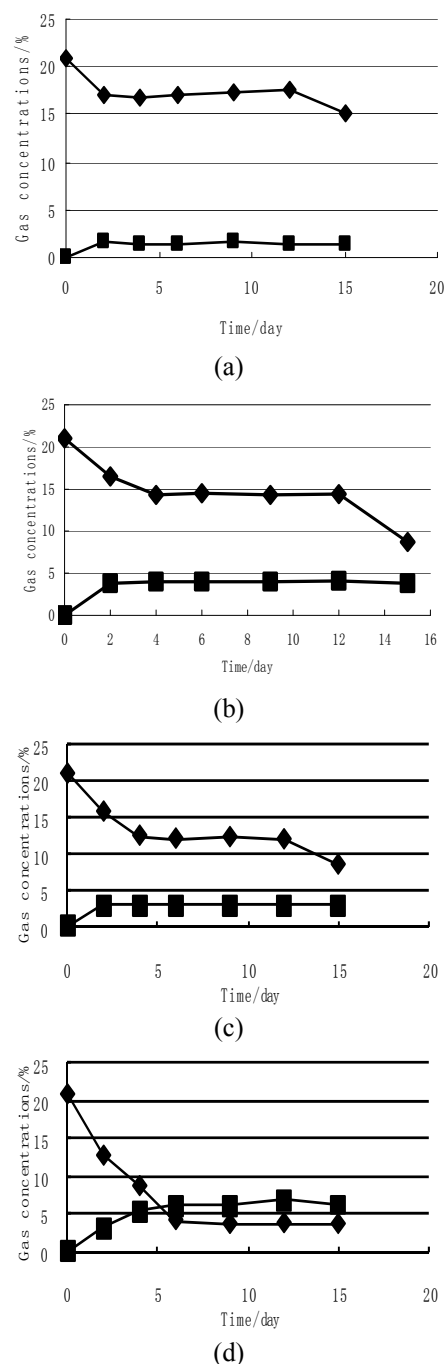


Fig .6. Changes of gas concentrations in different film packages
(a)LDPE1 (b)LDPE2 (c) HDPE (d)PP
◆-O₂ concentrations、■- CO₂ concentrations

4. Conclusion

By using an appropriate film at low temperature storage condition, the ratio of CO_2 to O_2 will continuously adjust itself by the interaction of the Pak-choi respiration and gas diffusion through the packaging film. The key of application of MAP technology successfully is to select a film of suitable permeability which can develop an optimum equilibrium modified atmosphere within the package in a short time and keep the state for a long time. In this paper, the mathematical model of gas exchange within close packages was developed on the basis of the characteristics of respiration when the MAP containing Pak-choi was designed. The theoretical basis for getting a right way to choose packaging materials for MAP and predicting the gas mass concentrations inside the packages were provided.

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