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Model of gas exchange dynamics for modified-atmosphere packages containing fresh produce

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Abstract: A model for modified-atmosphere packaging (MAP) systems containing fruits and vegetables was developed. The computer simulation was performed to predict the gas mass concentrations inside the packages and was successfully verified by experiments with yellow peaches at 5, 15 and 25 ℃ using two types of packaging films. A Michaelis-Menten type respiration model with noncompetitive inhibition mechanism due to CO_2 was adopted while the respiration rates were measured with an improved permeable system method suitable for either steady or unsteady state. The applicability of the model in the design of MAP systems was demonstrated with a calculation to evaluate film specification and equilibrium concentrations of O_2 and CO_2 in the package containing yellow peaches.

Key words: gas exchange dynamics; modified-atmosphere package; respiration rate; yellow peach

Temperature control and modification of atmosphere are effective ways in keeping the quality of fresh fruits and vegetables. A modified-atmosphere packaging (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. Improper control of gas concentrations may lead to undesirable results such as anaerobic respiration and accelerated physiological decay[1]. A desired package atmosphere depends on the balance between the gas diffusion and the produce respiration. Theoretical analysis of in-package atmosphere dynamics will be helpful in predicting temporal changes of gas concentrations and optimizing the design of MAP systems.

Several attempts have been made to model gas exchange in MAP systems. Many models were of empirical equations[2-4], while most of them concentrated on the analyses under steady state[5-8]. Fishman et al.[9] applied a model for the transient period by adding an approximate treatment to it and verified it with red bell peppers as a non-climacteric commodity. Hertog et al.[10] proposed a generic model based on a simplified interpretation of biochemical mechanisms of produce. Song et al.[1] established a respiration-transpiration model in which the physiological behavior of produce was included and tested on blueberries.

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Our objective is to develop a dynamic model of gas exchange for MAP systems which is based on the biophysical mechanism of produce respiration and gas diffusion. The model equations were solved numerically to predict the in-package concentrations of O_2 and CO_2 and were verified by the experimental values of yellow peaches as the climacteric commodity. A calculation was performed to evaluate the appropriate film and equilibrium gas concentrations inside a model package containing yellow peaches. The respiration rates were expressed with a Michaelis-Menten type model based on enzyme kinetics while an improved permeable system method was adopted which enabled the model to be suitable in both steady and unsteady state.

1 Model Development

1.1 Gas exchange model

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: O_2 consumption and CO_2 evolution caused by produce respiration and permeation of gases through the plastic film. The produce respiration is known to depend on the concentrations of O_2 and CO_2 at a certain storage temperature[11]. 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 O_2 and CO_2 can be expressed by mass balance equations (1) and (2):

$$\frac{d\rho_{O_2}}{dt} = (100)\frac{\frac{A}{L}\bar{P}_o P_{atm}\left(0.209 - \frac{\rho_{O_2}}{100}\right) - Wr_o}{V} \quad (1)$$

$$\frac{d\rho_{CO_2}}{dt} = (100)\frac{\frac{A}{L}\bar{P}_c P_{atm}\left(0.0003 - \frac{\rho_{CO_2}}{100}\right) + Wr_c}{V} \quad (2)$$

If the headspace of the package is charged with air, the initial conditions become Eqs. (3) and (4):

$$\rho_{O_2} = 20.9 \qquad t = 0 \quad (3)$$

$$\rho_{CO_2} = 0.03 \qquad t = 0 \quad (4)$$

where ρ_{O_2}, ρ_{CO_2} are gas mass concentrations (partial pressures) of O_2 and CO_2 within the package respectively (%); dt is the time interval (h); A is the surface area of packing bag (m^2); L is the thickness of packing film (m); $\bar{P}_o$, $\bar{P}_c$ are film permeabilities for O_2 and CO_2 (mL·m/(m^2·h·Pa)); P_{atm} is the atmospheric pressure(101 325 Pa); W is the produce weight (kg); r_o, r_c are the rates of O_2 consumption and CO_2 evolution (mL/(kg·h)); V is the free volume (mL).

If the gas equilibrium in an MAP system is reached, then $\frac{d\rho_{O_2}}{dt} = 0$, $\frac{d\rho_{CO_2}}{dt} = 0$. Eqs. (1) and (2) can be converted into Eqs. (5) and (6):

$$\frac{A}{L}\bar{P}_o P_{atm}\left(0.209 - \frac{\rho_{O_2}}{100}\right) - Wr_o = 0 \quad (5)$$

$$\frac{A}{L}\bar{P}_c P_{atm}\left(0.0003 - \frac{\rho_{CO_2}}{100}\right) + Wr_c = 0 \quad (6)$$

The variation of gas volume within permeable packages after a certain time interval can be described by Eqs. (7) to (10):

$$dV_o = \frac{A}{L}\bar{P}_o P_{atm}\left(0.209 - \frac{\rho_{O_2}}{100}\right) - Wr_o dt \quad (7)$$

$$dV_c = \frac{A}{L}\bar{P}_c P_{atm}\left(0.0003 - \frac{\rho_{CO_2}}{100}\right) + Wr_c dt \quad (8)$$

$$dV_n = \frac{A}{L}\bar{P}_n P_{atm}\left(0.78 - \frac{\rho_{N_2}}{100}\right)dt \quad (9)$$

$$dV = dV_o + dV_c + dV_n \quad (10)$$

where dV_o, dV_c, dV_n, dV are variations of O_2, CO_2, N_2 and total volume within packages after a certain time interval (mL); $\bar{P}_n$ is the film permeability for N_2 (mL·m/(m^2·h·Pa)); ρ_{N_2} is the concentrations of N_2 within the package (%).

The concentrations of O_2, CO_2 and N_2 inside the packages after dt time are given in Eqs. (11) to (13):

$$\frac{\rho'_{O_2}}{100} = \frac{V\frac{\rho_{O_2}}{100} + dV_o}{V + dV} \quad (11)$$

$$\frac{\rho'_{CO_2}}{100} = \frac{V\frac{\rho_{CO_2}}{100} + dV_c}{V + dV} \quad (12)$$

$$\frac{\rho'_{N_2}}{100} = \frac{V\frac{\rho_{N_2}}{100} + dV_n}{V + dV} \quad (13)$$

where ρ'_{O_2}, ρ'_{CO_2}, ρ'_{N_2} are the concentrations of O_2, CO_2 and N_2 within packages after a certain time interval (%).

1.2 Respiration model

Respiration is an enzyme-mediated process. It is suggested that the principles of enzyme kinetics might be applied to model the respiration of produce[12, 13]. Lee et al. [11] treated the effect of CO_2 as uncompetitive inhibition on respiration and presented a Michaelis-Menten type respiration model based on enzyme kinetics. The model is valid only for aerobic conditions which can be given in Eq. (14) or in its linearized form Eq. (15):

$$r = \frac{V_m \rho_{O_2}}{K_m + \left(1 + \frac{\rho_{CO_2}}{K_i}\right)\rho_{O_2}} \quad (14)$$

$$\frac{1}{r} = \frac{1}{V_m} + \frac{K_m}{V_m}\frac{1}{\rho_{O_2}} + \frac{1}{K_i V_m}\rho_{CO_2} \quad (15)$$

where r is the respiration rate in O_2 consumption or in CO_2 evolution (mL/(kg·h)), V_m is the maximum respiration rate (mL/(kg·h)), K_m is the Michaelis-Menten constant (% O_2), and K_i is the inhibition constant (% CO_2).

2 Experimental Method

2.1 Fresh produce and package materials

"Jinxiu" yellow peaches of about eighty percent maturity were obtained from the terminal market in Guangming town, Shanghai, China. The average weight per fruit is 240.5 g. Fruits were sorted for physical damage and stored in refrigerators set at the experimental temperatures for 24 h before being tested. Two kinds of LDPE films with the thickness of 0.045 mm and 0.03 mm named as film A and film B respectively were used to construct the plastic bags in the experiments.

2.2 Gas analysis

Gas analysis was performed using the GC－9800TF gas chromatograph (Kechuang Ltd., Shanghai, China).

2.3 Respiration rates determination

The respiration rates were measured with a permeable system[13]. Peaches were packaged singly in plastic bags (20 cm × 15 cm rectangular in shape, surface area 0.06 m^2) constructed with film A. After being vacuumed and sealed, the packages were injected with 600 mL air through leakproofing pieces attached to the bags and were stored in refrigerators at 0, 5, 10, 15 and 25 ℃. Gas samples drawn from the packages were analyzed for O_2 and CO_2 concentrations at intervals of 4 h with the gas chromatograph. Sampling continued until the O_2 level inside the packages reached 2% and/or the CO_2 level reached 15%. Two replicates were used for each condition.

The partial pressures of O_2, CO_2 and N_2 inside the packages were calculated by Eqs. (7) to (10) with a series of given respiration rates r_o and r_c. The real respiration rates were determined by comparing the calculated values of partial pressure with the measured values using the least square method[14]. The calculation was done using a computer program developed with C language. The data of respiration rates were used to estimate the parameters V_m, K_m and K_i of respiration model Eq. (15) by multiple linear regression analysis performed with the statistical software SAS (SAS Institute, 1999). By considering produce respiration and film permeability simultaneously, this method could be used to determine the respiration rates for fresh produce in the whole storage period including steady or unsteady state. The film permeabilities at experimental temperatures were determined with the method of gas injection and were calculated using the procedure introduced above.

2.4 Model verification

The applicability of the gas exchange model to predict O_2 and CO_2 concentrations in MAP systems at different storage conditions was tested with yellow peaches by comparing the predicted with measured values of gas concentrations as a function of time inside the packages. Peaches were packaged in plastic bags (18 cm × 25 cm rectangular in shape, surface area 0.09 m^2) constructed with film B. Every bag contained two fruits and was charged with 600 mL air before being stored in refrigerators set at 5 ℃ and 25 ℃. 1 mL headspace samples were taken periodically through a silicone sampling port for gas chromatograph analysis. The measured data obtained using film A at 5 ℃ and 15 ℃ and film B at 5 ℃ and 25 ℃ were adopted to verify the model. The respiration rates at experimental temperatures were determined with Eq. (15) as the method mentioned above. The predicted values of gas concentrations were obtained by solving Eqs. (1) and (2) using the Euler polygon method with the mathematical software Mathematica.

3 Results and Discussion

3.1 Parameter values of respiration model

The respiration rates of yellow peaches obtained from the permeable system experiments at 0, 5, 10, 15 and 25 ℃ were used to fit the respiration model Eq. (15). The estimated values of the parameters are presented in Tab. 1.

Tab. 1 Estimated values for V_m, K_m and K_i determined by multiple linear regression

Temperature/℃	Parameter estimates for r_o model				Parameter estimates for r_c model			
	V_m	K_m	K_i	R^2	V_m	K_m	K_i	R^2
0	3.12	1.38	141.12	0.996	2.71	0.39	17.04	0.999
5	15.50	7.02	69.18	0.991	14.43	8.03	57.50	0.998
10	19.01	1.59	11.73	0.990	16.47	0.71	19.65	0.992
15	22.71	7.63	14.42	0.991	17.90	6.07	14.35	0.991
25	28.26	0.15	16.53	0.995	21.09	0.10	52.32	0.956

3.2 Verification of gas exchange model

The gas exchange model was verified by the experiments with yellow peaches using film A at 5 ℃, 15 ℃ and film B at 5 ℃, 25 ℃. The permeabilities of the film measured with the gas injection method at experimental temperatures are given in Tab. 2. Eqs. (1) and (2) could be solved numerically according to the film permeabilities and parameters of the respiration model determined above. Fig. 1 shows the comparison of the measured and predicted concentrations of O_2 and CO_2 as a function of time in the packages using film A (LDPE film, thickness 0.045 mm, surface area 0.06 m^2, single fruit per package) at 5 ℃ and 15 ℃. Fig. 2 shows the gas concentrations as a function of time in the packages using film B (LDPE film, thickness 0.03 mm, surface area 0.09 m^2, double fruits per package) at 5 ℃ and 25 ℃. The symbols are experimental values and the solid lines are predictions with Eqs. (1) and (2).

Tab. 2 Permeability data for film A and film B

Film	Temperature/℃	Permeability/(mL·m·(m^2·h·Pa)$^{-1}$)	
		O_2	CO_2
Film A	5	2.01×10^{-8}	8.32×10^{-8}
	15	3.56×10^{-8}	1.43×10^{-7}
Film B	5	3.12×10^{-8}	1.07×10^{-7}
	25	1.04×10^{-7}	3.20×10^{-7}

A good agreement was observed between the simulated and experimental values. Due to the higher respiration rates of yellow peaches at 15 ℃ and 25 ℃, the O_2 concentration inside the bags constructed with either film A or film B dropped rapidly comparing with the condition under 5 ℃. The change trend of O_2 and CO_2 concentrations in both model packages decreased with increasing CO_2 from which the inhibition effect of high CO_2 concentration on respiration was shown.

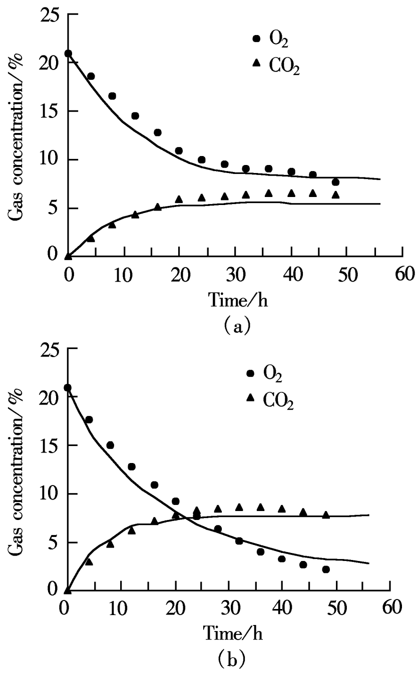

Fig. 1 Gas concentrations as a function of time in the packages using film A. (a) 5 ℃; (b) 15 ℃

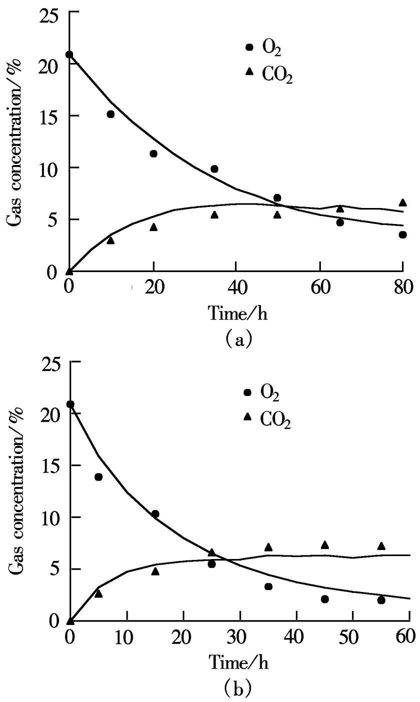

Fig. 2 Gas concentrations as a function of time in the packages using film B. (a) 5 ℃; (b) 25 ℃

3.3 Demonstration of gas exchange model for MAP system design

The gas exchange model developed could be helpful in the design of MAP systems to evaluate film permeabilities and equilibrium gas components within packages. It was demonstrated with the following calculation for a model package containing yellow peaches at 0 ℃. The gas concentrations suitable for yellow peaches were 2% to 5% for O_2 and 3% to 10% for CO_2[15], while the data of 2% O_2 and 5% CO_2 could be chosen as the desired condition for the calculation. Eqs. (16) and (17) show respiration equations for yellow peaches at 0 ℃ according to the discussion above. The film permeabilities could be evaluated as the result of 1.13×10^{-8} mL·m/(m^2·h·Pa) for P_o and 4.34×10^{-8} mL·m/(m^2·h·Pa) for P_c using Eqs. (5), (6), (16) and (17) under the conditions $A = 0.09$ m^2, $L = 0.045$ mm, $W = 0.24$ kg. The appropriate packaging film could be chosen according to Tab. 3[16]. It is found that the film suitable for yellow peaches under such condition might be LDPE.

$$r_o = \frac{15.50\rho_{O_2}}{7.02 + \left(1 + \frac{\rho_{CO_2}}{69.18}\right)\rho_{O_2}} \tag{16}$$

$$r_c = \frac{14.43\rho_{O_2}}{8.03 + \left(1 + \frac{\rho_{CO_2}}{57.50}\right)\rho_{O_2}} \tag{17}$$

Tab. 3 Permeabilities for O_2 and CO_2 of some common films

Film	Permeability/(mL·m·(m^2·h·Pa)$^{-1}$)		Selectivity
	O_2	CO_2	
Silicone rubber	2.75×10^{-6}	1.79×10^{-5}	6.5
LDPE (0.992 g/mL)	3.01×10^{-8}	2.03×10^{-7}	6.7
HDPE(0.964 g/mL)	3.84×10^{-10}	1.86×10^{-9}	4.8
Polybutadiene	2.10×10^{-7}	1.93×10^{-6}	9.2
PVC-RMF	5.76×10^{-8}	3.51×10^{-7}	6.1
Mylar	3.61×10^{-10}	1.23×10^{-9}	3.4
Nylon	2.04×10^{-10}	9.62×10^{-10}	4.7
Saran	1.14×10^{-11}	1.17×10^{-10}	10.2

The equilibrium concentrations of O_2 and CO_2 inside the packages can also be predicted with Eqs. (5), (6), (16) and (17) 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.

4 Conclusion

MAP combined with cold storage may help to extend the storage life of fresh produce. A desired package atmosphere depends on the balance between the gas diffusion and the produce respiration. The parameters of the Michaelis-Menten type respiration equations based on enzyme kinetics were estimated using a permeable system while produce respiration and film permeability were considered simultaneously. The gas exchange model validated with these parameters could be used for either steady or unsteady state to choose film specifications and package dimensions as well as to predict the steady-state concentrations of O_2 and CO_2, which would provide a desired gas concentration in modified-atmosphere packages. The applicability of the model was verified by experiments with yellow peaches at 5, 15 and 25 ℃ using different packaging films. A good agreement was shown between the predicted and experimental values.

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果蔬 MAP 包装的气体交换动力学模型

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摘要:建立了一个自发气调包装(MAP)系统的气体交换动力学模型,运用计算机模拟预测包装内气体质量浓度,并以上海市特产"锦绣黄桃"为研究对象,采用 2 种包装薄膜,在 5,15 和 25 ℃下进行了实验验证,实验结果证明了模拟计算结果的正确性.同时还建立了 Michaelis-Menten 型呼吸速率模型,该模型将 CO_2 看作 O_2 的非竞争性抑制剂.呼吸速率测定采用改进的渗透系统法,该方法既适用于平衡状态,也适用于非平衡状态.应用气体交换模型对装有黄桃的 MAP 系统进行了设计计算,给出了薄膜特性和包装内 O_2 和 CO_2 的平衡浓度.

关键词:气体交换动力学;自发气调包装;呼吸速率;黄桃
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