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Kinetics of relative electrical conductivity and correlation with gas composition in modified atmosphere packaged bayberries (*Myrica rubra* Siebold and Zuccarini)

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Abstract

Modified atmosphere package (MAP) was employed to store the perishable Chinese bayberry (*Myrica rubra*) at temperatures of 2°C, 8°C and 15°C. Electrolyte leakage from plasma could make the flesh collapse rapidly and appear to be unsavory, which may be evaluated in terms of relative electrical conductivity (REC). REC and gas composition in the headspace were measured during storage. The kinetic parameters of REC were determined, including reaction order, reaction rate constant and activation energy. An integrated model was developed to predict the REC, which reflects the cell membrane permeability, within the temperature range from 2°C to 15°C. It was found that the degree of maturity had no significant influence on gas composition in the headspace ($P \geqslant 0.05$) by one-factor ANOVA analysis using SAS personal computer software. Correlation between REC and gas composition was not significant ($P > 0.05$) by Pearson correlation analysis.

Keywords: Electrical conductivity; Gas composition; Modified atmosphere package (MAP); Kinetics; Bayberry (*Myrica rubra* Siebold and Zuccarini)

1. Introduction

Bayberry (*Myrica rubra* Siebold and Zuccarini), or *Yangmei* in Chinese Mandarin Pinyin, is indigenous to China. It has been cultivated more than 2000 years and the annual output is about 30,0000 tons. The mature berry from mid-June to early July with dark red or purple red is 1–1.5 to 3 cm in diameter. High sugar content with moderate acids in its abundant juice makes the fruit a delicious taste. Its flesh can also be processed into sweets, jam, juice and wine, or canned in syrup.

The literature detailed in the postharvest storage of bayberry is little in the world except for that in Chinese. It is the difficulty of keeping red bayberry with acceptable quality that makes it a known cherished fruit. After harvest, the bayberry would quickly turn discolored on the 2nd day and unsavory on the 3rd day under normal air conditions (Xi, Zheng, Ying, Ying, & Chen, 1994). The effect of vibration stress during transportation on respiratory reaction and cell membrane permeability was significantly positive and detrimental to the quality of bayberry, with respiration rate and relative electrical conductivity (REC) rising (Ying, Chen, Xi, & Zheng, 1993). Xi et al. (1994) reported that the REC increased in the duration of storage at temperatures of 1°C, 11°C and 21°C, but the kinetics was not studied in detail. Chen, Ying, and Qian (1994) analysed the textural changes of stored bayberries, finding that the stress yield point of bayberries descended with the storage time and developing a regressive equation. For the first time Hu, Yu, and Chen (2001) reported that the bayberries appeared to be climacteric-like based on the characteristics of

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ethylene emission; however, more study pertaining to physiological mechanism is needed to corroborate it. It was not until 2001 that the controlled atmosphere was employed and the physiological changes were investigated during bayberry storage. Controlled atmosphere storage could effectively reduce the respiration rate, membrane lipid peroxidation in terms of malondialdehyde and the activities of a series of metabolic enzymes such as superoxide dismutase, ascorbate peroxidase and glutathione reductase (Xi, Luo, Cheng, Xu, & Wang, 2001). The aerobic fungi could also be effectively inhibited by controlled atmosphere, although an equilibrium gas composition was needed to inactivate the anaerobic microorganism (Qi, Wang, Liang, Zhou, & Chai, 2003).

However, research on modified atmosphere package (MAP) for the bayberry has been reported little, although the MAP method is convenient and the cost is lower than CA. The MAP was used to store bayberries at different degree of maturity in this study, with cell membrane permeability in terms of REC and the gas composition in headspace of the package investigated. High conductivity is indicative of leakage of intracellular ions and, therefore, damage to membranes (Ade-Omowaye, Taiwo, Eshtiaghi, Angersbach, & Knorr, 2003). Electrical conductivity can be used effectively as a physical maturity index and a suitable index of storage quality, in addition to its convenience for measurement (Montoya, De La Plaza, & López-Rodriguez, 1994a, b).

Since bayberry has a large specific surface area and no obvious cuticle, it is easy for the fruit to result in severe solute release from the flesh and deterioration in quality quickly in the postharvest stage. Electrolyte leakage is an important and effective quality index especially for bayberry (Xi et al., 1993). The reason that REC instead of electrical conductivity was used to evaluate the storage quality was that REC could be more consistent, accurate and irrespective of some extrinsic factors that might affect the results during measurement, because the sampled bayberries selected for measurement were not consistent in weight and morphology, etc. The objectives of this research were to establish kinetic models of electrolyte leakage which may facilitate the storage design and shelf-life prediction, and to determine if the gas composition of oxygen and carbon dioxide in the headspace of package correlates with the electrolyte leakage or, rather, if other factors like gas composition affect REC significantly besides the temperature, which may ease the selection and usage of the storage methods to preserve the bayberry well and cost-effectively. The differences in gas composition between degrees of maturity were determined to prove if the different matured bayberry could be treated in same storage design to a limited extent at lower temperatures.

2. Materials and methods

2.1. Materials and packaging

The bayberry harvested in Cixi County, Zhejiang Province, China, on June 14, 2003, was transported to the Laboratory of Cold Chain Research at Shanghai Jiao Tong University within 3 h. The fresh fruit was immediately cooled at 2°C for 12 h, and covered by plastic material to avoid dehydration. After precooling the fruits were classified into two groups based on the degree of maturity: sevenfold mature bayberry and the ninefold mature one, namely, the light red bayberry and the dark red one according to the appearance.

Both the light red and dark red bayberry were packed in MAP using the 30 μm-thick low-density polyethylene (LDPE) film (Ancheng Plastic Material Co., Limited, Shanghai, China) and stored at 2°C, 8°C, 15°C and a control at 2°C under normal atmosphere. The LDPE film was $17 \times 25\,cm^2$ in size and heat-sealed to avoid gas leakage. Each package weighed about 190 ± 5 g.

2.2. Relative electrical conductivity

It is possible that during storage, plasma membrane of the cell would tend to be unstable and consequently lead to electrolyte leakage. Electrical conductivity of the bayberry under storage was assayed using a digital conductometer (DDB-6200, Shanghai Leici Apparatus, Shanghai, China) with a DJS-1 conductivity immersion electrode. Four bayberries from each storage sample were rinsed with distilled water and filter paper was used to lightly wipe the fruit in order to remove the water remaining on the pulp. Then the fruits were immersed in a 250 ml beaker with 100 ml distilled water for 1 h. Afterwards, the conductometer was used to measure the fruits and then the beaker was immediately immersed in the boiling water at 100°C for 5 min, followed by cooling the beaker until it reached room temperature under normal condition. Then the total electrical conductivity was re-assayed and recorded. All the measurements were repeated three times. The percent value of REC was calculated as electrolyte leakage by dividing the absolute value of the electrical conductivity (S/m) of the first measured by the total conductivity after water bathing.

2.3. Variation of gas composition

Three replicates of gas composition in the headspace of LDPE packages were measured using the O_2/CO_2 analyzer (CheckMate 9900, PBI Dansensor, Denmark). The Scotch high strength adhesive septum was stuck on the package. Through the septum the needle was pressed into the package. After the analyzer stabilized the concentrations of O_2 and CO_2 and N_2 inside the package were displayed on the screen. The septum should not be removed till the end of experiment to avoid massive gas leaking. The concentration (mol/L) of oxygen and carbon dioxide was calculated at standard temperature and pressure to make the data comparable.

2.4. Kinetic models of REC

The kinetic models of REC for different temperatures were obtained by graphical determination. The rate of change in REC during storage can be modeled as

$$\frac{dE}{dt} = kE^n, \quad (1)$$

where E is the REC (percent), t the time (day), k the reaction rate constant (day^{-1}) and n the kinetic order of the reaction (Labuza & Riboh, 1982). The model is positive because the ions are the product of electrolyte leakage instead of the substrate. The rate constant is temperature dependent and follows the Arrhenius equation (Lau, Tang, & Swanson, 2000)

$$k = k_{ref} \exp\left(-\frac{E_A}{R}\left(\frac{1}{T} - \frac{1}{T_{ref}}\right)\right), \quad (2)$$

where k is the reaction rate constant or the frequency factor (day^{-1}), E_A the activation energy (J/mol K), R the universal gas constant (8.314 J/mol K), T the absolute temperature (K) and k_{ref} is the reaction rate constant (day^{-1}) at the reference temperature (T_{ref}). The reference temperature selected for this study was 8.5°C, the mean temperature of 2°C and 15°C. Substituting Eq. (2) into Eq. (1) yields

$$\frac{dE}{dt} = k_{ref} \exp\left(-\frac{E_A}{R}\left(\frac{1}{T} - \frac{1}{T_{ref}}\right)\right)E^n. \quad (3)$$

Integrating Eq. (3) yields

$$\int_{E_0}^{E(t)} \frac{dE}{E^n} = \int_0^t k_{ref} \exp\left(-\frac{E_A}{R}\left(\frac{1}{T} - \frac{1}{T_{ref}}\right)\right) dt. \quad (4)$$

Another equation will be developed, given that the electrolyte leakage is the first-order reaction

$$E(t) = E_0 \exp\left(\int_0^t k_{ref} \exp\left(-\frac{E_A}{R}\left(\frac{1}{T} - \frac{1}{T_{ref}}\right)\right) dt\right), \quad (5)$$

where E_0 is the initial REC. Eq. (5) can be used to predict the REC after a certain period of MAP treatment at different temperatures (Lau & Tang, 2002).

3. Results and discussions

3.1. Relative electrical conductivity

The REC of both light red and dark red bayberries increased during MAP storage at each temperature (Figs. 1and 2). Moreover, it was also apparent that the

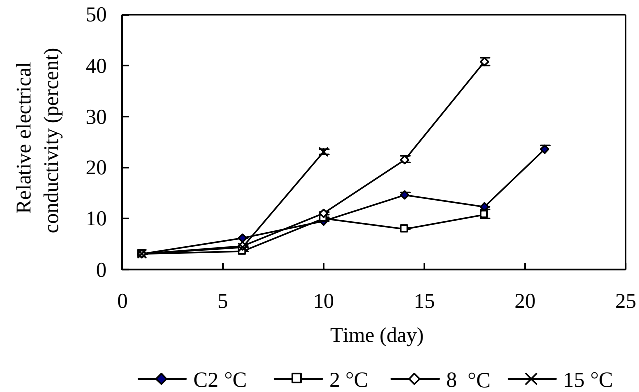

Fig. 1. Relative electrical conductivities of light red bayberries treated with MAP at different temperatures. “C”refers to the control.

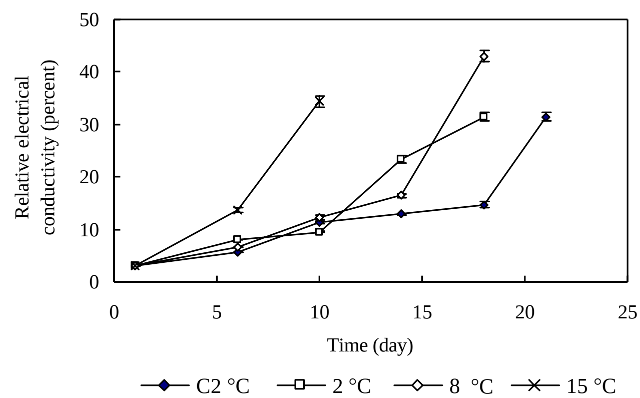

Fig. 2. Relative electrical conductivities of dark red bayberries treated with MAP at different temperatures. “C” refers to the control.

REC generally increased with the storage temperature, corresponding to the increase in the electrolyte leakage from the cells of bayberries. At the same temperature of 2°C, the REC of the controlled light red bayberries was generally higher than that of MAP bayberries (Fig. 1), while for dark red bayberries, the REC of the controlled bayberries was lower than that of the MAP ones (Fig. 2). It was on the 21st day for the control at 2°C, 18th day for MAP at 2°C and 8°C and 10th day for MAP at 15°C, respectively, that the pulp of bayberry decayed and softened too seriously to be capable of continuing the assay. Therefore, the experiments had to be terminated at the corresponding time.

The results of reaction order from graphical determination were summarized in Table 1. All the r^2 values of each respective reaction order of electrolyte leakage for both light red and dark red bayberries were obtained, indicating that the first order was the most workable for the kinetic models (Figs. 3 and 4). The reaction rate constants were calculated from the slope of Ln(REC) vs. time using linear regression analysis. Xi et al. (1994) studied the changes of REC of bayberry stored at temperatures of 1°C, 11°C and 21°C under normal

Table 1
Approximation of the order of relative electrical conductivity by examining the r^2 from plots of zero-, half-, first- and second-order reactions

Temperature (°C)	0 order, E vs. time		0.5 order, $E^{0.5}$ vs. time		1st order, $\ln E$ vs. time		2nd order, $1/E$ vs. time	
	Light red	Dark red	Light red	Dark red	Light red	Dark red	Light red	Dark red
C2	0.84	0.79	0.90	0.90	0.92	0.94	0.81	0.84
2	0.78	0.91	0.80	0.96	0.81	0.97	0.82	0.82
8	0.86	0.78	0.94	0.91	0.98	0.98	0.93	0.87
15	0.75	0.94	0.79	0.99	0.84	0.99	0.94	0.90

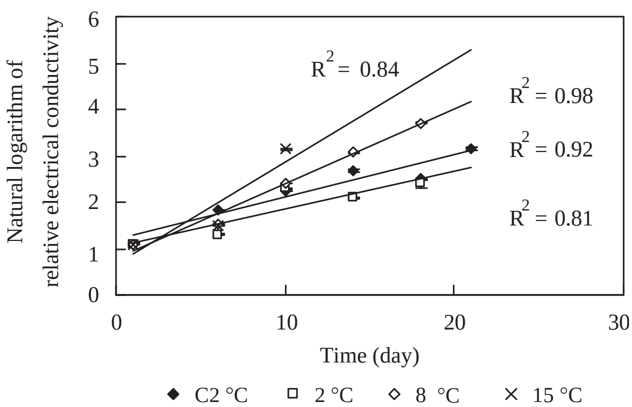

Fig. 3. Linear regression of Ln(REC) to time for light red bayberry. "C" refers to the control.

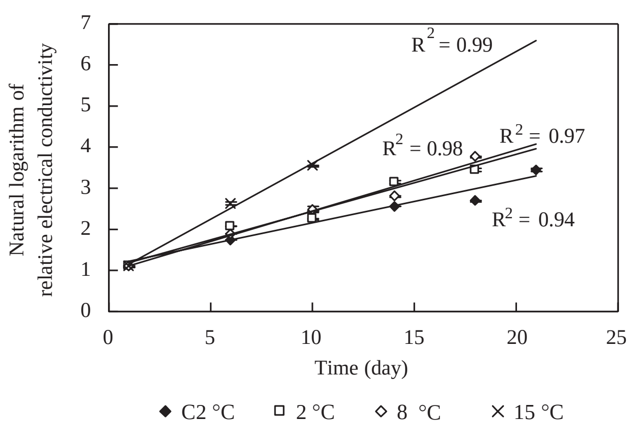

Fig. 4. Linear regression of Ln(REC) to time for dark red bayberry. "C" refers to the control.

atmosphere, finding that REC followed a linear regression but the correlation coefficients (r^2) were not very high, i.e. 0.89 for all three temperatures. The possibility of other reaction order was not studied further. The slopes of the regression increased with temperatures rising, indicating that the reaction rate constants was speeded up by higher temperatures, which was in a good agreement with this study. Listed in Table 2 were reaction rate constants based on the first-order kinetic equation, from which it could be seen obviously that the reaction rate constant was temperature dependent and

Table 2
Reaction rate constants (day^{-1}) of light and dark red bayberries

Temperature (°C)	Light red	Dark red
C2	0.0917 ± 0.0019	0.1050 ± 0.0016
2	0.0804 ± 0.0042	0.1379 ± 0.0022
8	0.1603 ± 0.0016	0.1484 ± 0.0017
15	0.2206 ± 0.0032	0.2725 ± 0.0044

increased apparently with the temperature, conforming to the principles of the kinetic mechanism. Furthermore, the reaction rate constants of dark red bayberries in a series of different temperatures were significantly higher than that of light red bayberries. The differences in rate constant might have resulted from the unstability of cell membrane of dark red bayberries because of a much more severe senescence compared with that of light red bayberries.

The activation energies (E_A) of the electrolyte leakage in bayberries were calculated based on the Arrhenius relationship described by Eq. (3). The activation energies for both light red and dark red bayberries were 50.77 and 34.95 kJ/mol, respectively. It might have resulted from the differences in microstructure of cell membranes. In the dark red bayberries, the cell membranes appeared to be more permeable for ions to outside plasma than light red ones because of senescence, considering that activation energy for ionic permeation through membrane was sample-specific despite temperature independence. Less energy was required for a unit mole of ions to permeate through membrane of dark red bayberries when compared with light red ones.

In the temperature range from 2°C to 15°C, Eq. (5) can be used to predict the REC as a function of time, with the initial REC (E_0) being 3 percent for both dark and light red bayberries, reference reaction rate constants (K_{ref}) being 0.145 day^{-1} for light red and 0.180 day^{-1} for dark red, respectively. The predictive model would be more effective for the quality control and storage design if a limitation of REC defining the maximum value of acceptable quality was provided. Xi et al. (1993) reported that the storage life of bayberry could amount to 9–12 days when treated at 0–2°C. On the tenth day, in the present study, the values of REC were 9.92 and 9.51 percent under MAP at 2°C, which may be proposed for the maximum value of acceptable quality for light red and dark red bayberries, respectively.

3.2. Variation of gas composition

Increasing temperature induced high-level carbon dioxide and decreased oxygen content in the headspace of MAPs both for light red and dark red bayberries (Figs. 5 and 6). At same temperature, the values of gas composition were analysed using Statistical Analysis System (SAS 8.2, SAS Institute Inc., USA). The one-factor ANOVA was carried out to determine the effect of maturity degree on electrolyte leakage, i.e. to determine if differences in oxygen or carbon dioxide concentration between maturity degrees, namely between light red and dark red bayberries, was significant. The initial values of the first assay were excluded because these values had not been affected by MAP. It was found that the oxygen concentrations between light red and dark red bayberries at temperatures of 2°C, 8°C and 15°C were not significantly different ($P \geqslant 0.05$), and the carbon dioxide concentrations between light red and dark red at 2°C and 8°C were not significantly different either ($P \geqslant 0.05$) while at 15°C they did have significant differences ($P < 0.05$). The results suggested that the respiration of bayberry at different maturity was in the same pattern at lower temperatures from 2°C to 8°C, i.e. ripening stage exerted little influence on bayberry's respiration pattern. But at higher temperature such as 15°C it was not the same way (Fig. 6). The inconsistency in significance between oxygen and carbon dioxide at same temperature of 15°C might be attributed to the physiological anomaly at high temperature.

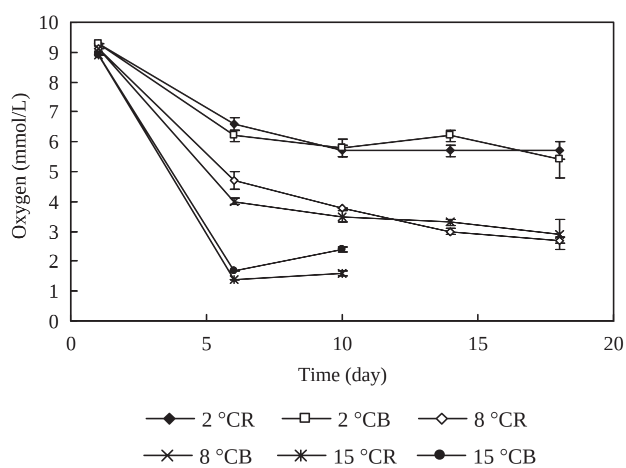

Fig. 5. Oxygen concentration in headspace of MA packages. "R" refers to light red bayberry while "B" to dark red.

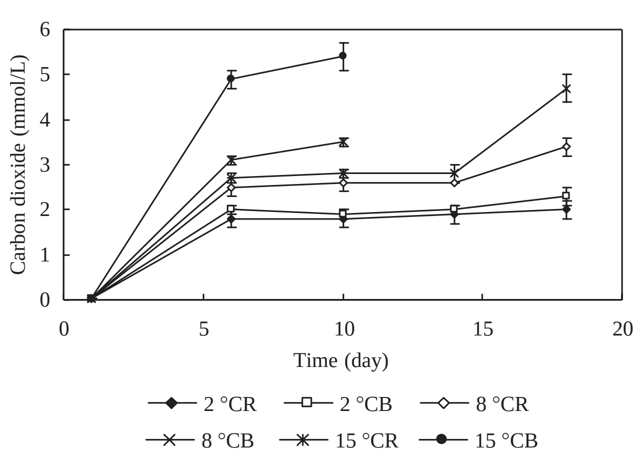

Fig. 6. Carbon dioxide concentration in headspace of MA packages. "R" refers to light red bayberry while "B" to dark red.

3.3. Correlation between REC and gas composition

Pearson correlation analysis was performed with SAS personal computer software to determine the correlation coefficient between values of oxygen, carbon dioxide concentration and REC. Oxygen concentration significantly correlated with carbon dioxide ($P < 0.05$), while the concentration of oxygen and carbon dioxide did not correlate with REC ($P > 0.05$). It suggested that neither oxygen nor carbon dioxide do have direct impact on cell membrane permeability physiologically and vice versa.

4. Conclusions

The relative electrical conductivity of bayberry increased with increasing temperatures from 2°C to 15°C during storage under modified atmosphere. The REC follows the first-order reaction with reaction rate constants being calculated and the reaction energies being 50.77 and 34.95 kJ/mol for light red and dark red bayberries, respectively. A predictive model (Eq. (5)) has been developed to facilitate the MA storage design and prolonging shelf-life, with reference reaction rate constants (K_{ref}) being 0.145 day^{-1} for light red and 0.180 day^{-1} for dark red and the initial REC (E_0) being 3 percent for both light and dark. The maximum values of acceptable REC as a quality index was proposed as 9.92 and 9.51 percent for light red and dark red bayberries, respectively.

Degree of the maturity exerts little influence on respiration pattern of bayberry under modified atmosphere at lower temperatures from 2°C to 8°C, implying that the bayberry can be treated in same package design regardless of the maturity degree at lower temperatures. Gas composition in headspace of package has no direct impact on relative electrical conductivity. It suggests that temperature is the more important factor to control the storage quality of bayberry than gas composition.

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