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CARBON DIOXIDE INJURY PREDICTION MODEL FOR FRESH-CUT APPLES

– Research paper –

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Abstract: Carbon dioxide (CO_2) injury is one of the key cause affecting the sales of fresh-cut apples during the sales period. The method to warn the time till occurring CO_2 injury would be convenient for businesses and consumers, but so far, no one has paid attention. This research aimed to study the change rule of the mechanism of carbon dioxide injury of fresh-cut apples treated with high CO_2 concentration. The experiment was conducted at 5, 15, 25 and 35°C for 4 days. Every twelve hours, the fresh-cut apple was analyzed by measuring the changes of firmness, soluble solids concentration, browning index and sensory evaluation. The results showed that sensory scores, firmness and soluble solids concentration decreased over time, while the browning index of freshly cut apple increased rapidly with time. Based on the dynamic model of the browning index, with the CO_2 Injury warning model of ready-to-eat apples treated with high CO_2 concentration was determined.

Keywords: High carbon dioxide, Carbon dioxide injury, Fresh-cut apple, Injury prediction model

INTRODUCTION

Minimally processed fresh-cut apples is one of the most convenient fruit grown in the world and is very popular among consumers (Putnik et al., 2017). Recently, the sales market of fresh-cut apples has grown rapidly due to the advantages of fresh-cut apples such as freshness, convenience and profuse nutrition (Oliveira et al., 2015a; Siddiq et al., 2013). However, minimal processing usually involves grading, cleaning, sorting, peeling, cutting, final packaging, which leads to a shelf life of less than two weeks for these products. For consumers and sellers, the shelf life is not long enough, so it is often to use some fresh-keeping methods (Lee et al., 1995; Montero-Calderon et al., 2011). Therefore, an essential problem in the fresh-cut apple industry is to insure the nutrition and health of food for consumers during the extended shelf life (Oms-Oliu et al., 2011).

Controlled atmosphere (CA), which includes low concentrations of oxygen and carbon dioxide above the concentration of carbon dioxide in the air, is a technology for long-term preservation of whole and ready-to-eat fruits and vegetables (Both et al., 2018). However, some studies have found apples are damaged by carbon dioxide during CA preservation (Deell et al., 2016; Fawbush et al., 2008). External damage of carbon dioxide occurs during the initial storage period (Watkins et al., 1997). The pathological changes are obvious with yellowish-brown and collapsed wrinkles (Colgan et al., 1999). Once fresh-cut apple produces external diseases caused by CO_2 injury, it will lose its commercial value (Cortellino et al., 2015). Some people have done similar work in other food products, but there is less research on this aspect of ready-to-eat apples (Yunfeng, et al., 2019; Qian, et al., 2014). Therefore, an analysis of fresh-cut apples shelf life is required.

The most obvious characteristics of CO_2 injure are flesh browning, brown spots, depressions and so on (Burmeister et al., 1995). Therefore, browning of apple slices is a major problem affecting the processing of sliced apple (Cortellino, et al., 2016; Huque et al., 2013). Moreover, perishable food such as precut fresh apple becomes soft, off-flavored and loses vitamins causing damage which is considered unmarketable and undesirable to consumers. In order to amplify the harm of carbon dioxide, the food product damage will be stored in unnormal CA established. In this paper, the Arrhenius approach is used to know the

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quality trend of ready-to-eat apple slices with storage time and temperature, where this linear equation is considered appropriate for use under CA condition.

MATERIALS AND METHODS

2.1. Preparation of fresh apple slices

Apples (Fuji) were purchased from a wholesale mart of agricultural products and stored at 2 ℃. Choose apples with good appearance and even size. Fresh apples were soaked in 200 mL/L sodium hypochlorite solution for 5 minutes and then washed with sterile water. Then apples were peeled, cored and cut into 8 parts with uniform size. The cut apples were soaked in a 1.5% Vc solution for 5 minutes and then dried quickly to produce fresh-cut apples. All tools in contact with apple were flushed with tap water and soaked with 75% alcohol before use. Afterward, samples were kept at 5kPa O_2 + 95kPa CO_2 (in the same glass jars) at 5 ℃, 15 ℃, 25℃ and 35 ℃, respectively, and the treatment was recorded as 0 d. The sample was measured every 12 hours for 4 days.

2.2. Indicator detection

(1) The browning index (BI) was used to characterize the degree of browning of apple slices. The color of the flesh was measured by CR-10 fully automatic color difference meter (Keshengxing, Instrument Inc., HANGZHOU, China.), and the brightness, red-greenness and yellow-blueness of the apple pulp were characterized by L*, a*, b* values. Then calculate the BI value according to the following formula :

$$BI = \frac{100 \times (x - 0.31)}{0.172} \tag{1}$$

where:

$$x = \frac{(a^* + 1.75 \times L^*)}{(5.645 \times L^* + a^* - 3.023 \times b^*)} \tag{2}$$

(2) The measurement of soluble solids concentration was carried out using a sugar meter (PAL-1; ATAGO Inc., TIANJIN, Japan). Weigh 10 grams of pulp and grind it in a mortar. After it was ground, put it into gauze and squeeze it out. The effluent juice was dripped into the sugar meter that has been zeroed, and the reading was finally made.

(3)Firmness was assessed using a hardometer (FHR-5, Bamboo Village Electrical Machinery Manufacturing Institute, Japan). The value obtained by penetrating the apple to a depth of 1 mm was measured.

(4)A group of people was invited to perform a sensory evaluation of each processed fruit sample. Freshly cut apples were comprehensively evaluated according to color, crispness, flavor and appearance. The total score is 9 points, of which 1~4 is unacceptable, 4~6 is normal, and 6~9 is excellent.

2.3. Modeling of CO_2 injury prediction in apples slices

Based on the corresponding zero-order and first-order reaction equations shown in the following two formulas, the relevant parameters are fitted, and the magnitude of correlation coefficient R^2 of the two formulas is compared. Furthermore the kinetics equation is determined.

$$f(t) = f(t_0) - kt \tag{3}$$

$$f(t) = f(t_0) \cdot \exp(-kt) \tag{4}$$

where:

f(t)= A value at end of storage

f(t₀) = A value at the beginning of storage

k = Quality degradation constant

t = Storage time，d

The zero-order and first-order kinetic models as shown in the following figure can be obtained by incorporating the reaction rate values obtained at different temperatures into the Arrhenius equation.

$$f(t) = f(t_0) - A \cdot \exp\left(\frac{-Ea}{R \cdot T}\right) \tag{5}$$

$$f(t) = f(t_0) \cdot \exp\left[A \cdot \exp\left[\frac{-Ea}{R \cdot T}\right] \cdot (-t)\right] \tag{6}$$

where：

Ea = Activation energy，kJ/mol；

A = Pre-exponential factors；

R = Deal gas constant，8.314 J/(mol • K)

T = Absolute temperature，K

The correlation analysis between each index and sensory evaluation was carried out to find out the key index which could best characterize the CO_2 injury of fresh-cut apples. The injury warning equation was established according to the following formula：

$$SL = t_s - t_d \tag{7}$$

where:

SL = Remaining shelf life of fresh-cut apples，d；

t_s = Time of injury symptoms，d；
t_d = Storage days，d
Model validation is necessary. Relative errors are calculated according to the following formulas：

$$P = PV - MV / MV \times 100\% \quad (8)$$

where:
P = Relative errors
PV = Predicted value
MV = Measured value

2.4. Statistical analysis
Data was collated and plotted using Microsoft Excel 2010 software. All data were statistically processed using SPSS 17.0 statistical software ($p<0.05$).

RESULTS AND DISCUSSION

3.1 Changes in browning index of freshly cut apple
For fresh-cut products, color is the most intuitive nature for consumers to measure the freshness of products. Fruit with good color is attractive to consumers. The BI value can be used to describe the browning of fresh-cut apples in order to characterize the quality changes of fresh-cut apples during storage (Altisent et al., 2014). Figure1 shows the significant promoting effect of temperature on the deterioration of apple pieces due to CO_2 injury ($P<0.05$). The higher the storage temperature, the shorter the time to reach the end of browning. Moreover, the shelf life of ready-to-eat apples at 5℃ is two days longer than at 35℃. On the second day, the BI value of freshly flesh of apple stored at 35 ℃ was 31.4% lower than that of fresh-cut apples saved in 5 ℃, which is caused by the destruction of the relevant defense mechanisms due to high temperatures (Liang et al., 2016) (Shaham et al., 2003).

3.2 Changes of soluble solids content
The content of soluble solids (SSC) is an index of fruit nutrition, which determines sweetness, maturity, and price of fruits. Figure 2 shows that the higher the temperature, the faster the consumption of soluble solids in apples ($P<0.01$). With the increase of time, the SSC decreased slowly. On the second day, at 5 ℃, 15 ℃, 25 ℃ and 35 ℃, SSC were 13.1%, 12.1%, 11.5% and 10.8%, respectively, which were 11.49%, 18.24%, 22.30% and 27.03% lower than the initial value. The decrease of SSC may be due to the oxidative decomposition of intracellular sugar by respiration (Mackenzie et al., 2011).

3.3. Hardness change of cut apple
Fruit hardness plays an important role in affecting taste and juiciness. And hardness is closely related to the shelf life of ready-to-eat fruits, because proper hardness not only gives fresh-cut apples a good taste, but also makes fresh-cut apples resist adversity to maintain their own good quality. The result shows that the temperature had a significant effect ($p \leq 0.01$) on the firmness of the fruit.

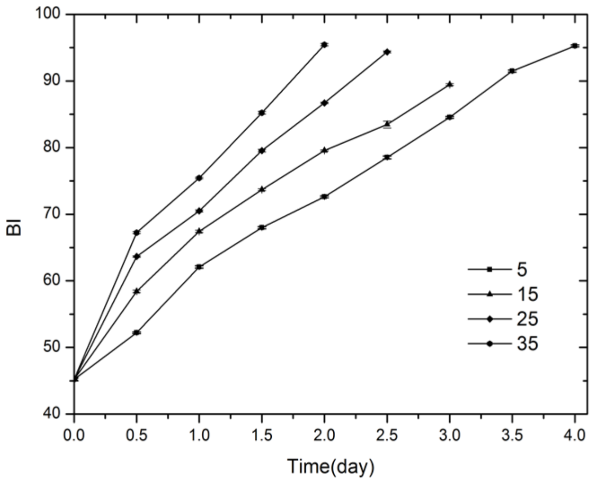

Figure 1. Changes in browning index of fresh-cut apple

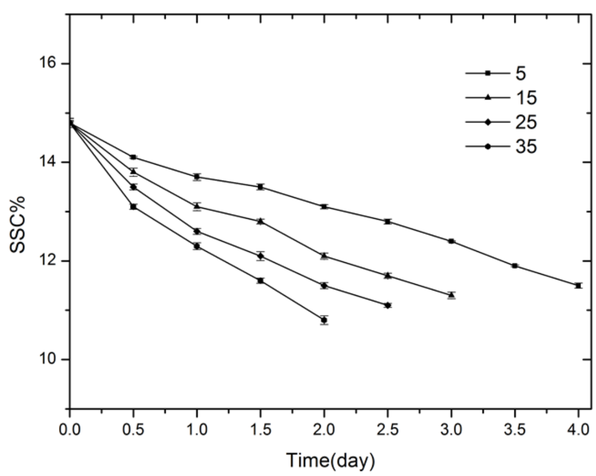

Figure 2. Changes of soluble solids content in fresh-cut apples

As shown in Figure 3, the hardness of the fru gradually decreases with time. And the hardness c apples at low temperatures is always higher than a high temperatures. On the second day, firmnes value of pulp of apple stored at 35 °C was 26.6% lower than that of freshly cut apples saved in 5 ° (Paajanen et al., 2017).

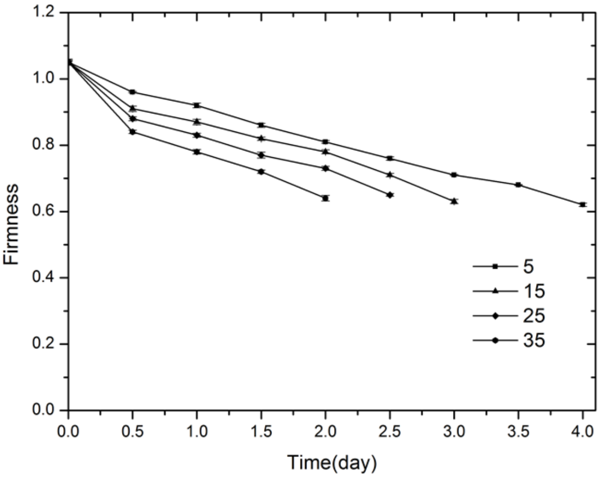

Figure 3. Firmness change of fresh-cut apple

3.4 Sensory analysis of apple slices

Under CA storage conditions, Fuji apples are mor prone to external CO_2 injure than other varieties c apples (Gapper, et al., 2013). Fresh-cut apples wer easily damaged by carbon dioxide as apple slice exposed to high carbon dioxide concentration fc storage, which caused serious browning on th surface of the sarcocarp. Figure 4 shows that sensory scores of apple brownies decrease with the length of storage time at all three storage temperatures, and gradually losing its edible value ($P < 0.05$).

Fresh-cut apples stored at 35 °C had serious browning on the second day, while fresh-cut apples stored at 5°C did not reach the end of shelf life until the fourth day. The results in Figure 4 show that the low temperature storage has a stronger inhibitory effect on apple browning than high temperature storage in high concentration carbon dioxide treatment.

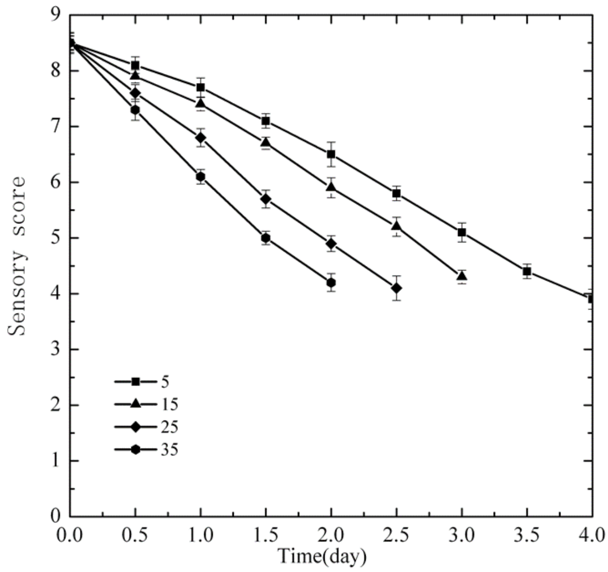

Figure 4. Changes in sensory score of fresh-cut apple

3.5. Kinetic fitting analysis

The zero-order kinetics model at each temperature can be obtained by linearly fitting the change values of each index at each temperature with the storage time. The first-order kinetic model can be obtained by linearly fitting each index with the logarithm and the storage time. By comparing the fitting coefficients of the two models, a dynamic equation with a high fitting coefficient is selected as the dynamic model of the index. Therefore, in Table 1, we can easily conclude that the browning index is suitable for establishing zero order dynamic model, and the hardness and soluble solids content are suitable for establishing first-order kinetic model. Arrhenius equation can be used to effectively describe the linear relationship between reaction rate constant and temperature, and the activation energy Ea and pre-exponential coefficient A required for the reaction can be calculated. Table 2 shows the calculation results.

In Table 3, A zero-order dynamic model of the browning index and a first-order dynamic model of hardness and soluble solids content of fresh-cut apples were established.

3.6. Establishment of CO_2 injury prediction Model for Fresh-cut apples

At present, the evaluation of food quality mostly depends on sensory evaluation. Sensory evaluation, as a method of evaluating food, has the characteristics of intuition, simplicity and convenience. However, sensory evaluation as a method of relying on professional evaluation is not only incapable of being used in a large amount, but also subject to the subjective factors of the evaluator. Therefore, the quality of apple pieces was measured by other methods, and results were compared with the sensory evaluation to find a method that can replace the sensory evaluation. The sensory score of fresh-cut apples has a certain relationship with each index and can be expressed by the Pearson correlation coefficient r. According to Table 4, the correlation coefficients between different indicators and sensory evaluation at different temperatures are all above 0.96, which indicates that these indicators are significantly associated with sensory scores, and the sigma |r| is 3.917, 3.904 and 3.924 respectively.

The linear increase in the BI value allows us to build models to warn of occurring CO_2 injury due to browning index measurement is non-destructive and convenient. The CO_2 injury prediction model equation of fresh-cut apples:

$$SL = \frac{f(t_s) - f(t)}{10748.27 \times \exp(-1894.4 / T)} \quad (9)$$

where:

$f(t_s)$ = Browning index of apples stored at t time

$f(t)$ = Initial browning index

After obtaining the early warning equation of browning index when fresh-cut apples are damaged by carbon dioxide, it is necessary to further confirm the critical value of the damage of fresh-cut apples. Table 5 shows the browning index and sensory evaluation of CO_2 injury at four temperatures, and the critical BI of fresh-cut apples with carbon dioxide damage is 93.624.

Table 1. Kinetic Regression Rate Constants K and Determinant Factor R2

Index	Temperature (℃)	Zero order		First order	
		Rate constant k	Decisive factor R^2	Rate constant k	Decisive factor R^2
BI	5	12.447	0.9916	0.1808	0.9639
	15	13.923	0.961	0.209	0.9131
	25	18.609	0.9659	0.2701	0.9139
	35	23.689	0.9597	0.3462	0.9058
$\sum R^2$			3.8782		3.6967
Firmness	5	0.1027	0.9913	0.1261	0.9965
	15	0.125	0.9665	0.1416	0.9649
	25	0.1434	0.9367	0.1733	0.9623
	35	0.188	0.9174	0.2289	0.9513
$\sum R^2$			3.8119		3.875
SSC	5	0.77	0.9894	0.059	0.9891
	15	1.1214	0.9738	0.0871	0.9839
	25	1.4286	0.9539	0.112	0.97
	35	1.9	0.9613	0.1504	0.977
$\sum R^2$			3.8784		3.92

Note: the regression coefficient of the equation is greater than 0.9, indicating that the equation is very significant

Table 2. Model fitting parameter values

Index	dynamic mode	A/(mL/kg·h)	Ea/(kJ/mol)	R^2
BI	Zero Order	10748.27	15750.04	0.9646
Firmness	First Order	53.47	14096.39	0.9562
SSC	First Order	757.94	21828.41	0.9951

Table 3. Quality Decay Dynamics Equations

Index	Dynamic model	Dynamics Equations
BI	Zero Order	$f(t) = 45.218 + 10748.27 \times \exp\left(\frac{-1894.4}{T}\right) \times t$
Firmness	First Order	$f(t) = 1.05 \times \exp\left[-53.469 \times \exp\left(\frac{-1695.5}{T}\right) \times t\right]$
SSC	First Order	$f(t) = 14.8 \times \exp\left[-180.314 \times \exp\left(\frac{-2231.80}{T}\right) \times t\right]$

Table 4. Relevance Analysis

Temperature	5°C	15°C	25°C	35°C	∑|r|
BI	-0.986**	-0.963**	-0.983**	-0.985**	3.917
Firmness	0.995**	0.976**	0.967**	0.966**	3.904
SSC	0.988**	0.973**	0.976**	0.987**	3.924

Table 5. Confirmation of Critical Browning Index Value

Index	5°C	15°C	25°C	35°C	average value
Sensory evaluation	3.9	4.3	4.1	4.2	4.125
BI	95.243	89.456	94.356	95.442	93.624

The critical browning value is brought into the formula (8), and the early warning equation of the fresh-cut apple CO_2 injury is finally obtained :

$$SL = \frac{93.62 - f(t)}{10748.27 \times \exp(-1894.4/T)} \quad (10)$$

According to the prediction model equation, the shelf life value of ready to eat apple at 10°C and 20°C storage condition in the validation group was calculated, which is CO_2 injury prediction value. Comparing the predicted value with the measured value, it was found that the average relative error of apple slices stored in 10°C and 20 °Cis 3.3% and 4.8%, respectively, less than 10%, which indicates that the CO_2 injury prediction model established based on the change of browning index can be used to predict shelf life.

Table 6. Relative Error Value of Model

Temperature (°C)	PV/d	MV/d	Relative Error (%)
10	3.6	3.5	3.3
20	2.8	3.0	4.8

CONCLUSIONS

In this paper, the changes in the firmness, soluble solids concentration, browning index and sensory evaluation of freshly cut apples were studied under different storage temperatures. Then a zero-order dynamic model of browning index and a first-order dynamic model of hardness and soluble solids content of cut apples were established. At the same time, based on the kinetic model, with the CO_2 injury warning model of fresh-cut apples treated with high carbon dioxide concentration was determined:, the coefficient R^2 of the fitting curve of the predicted value and the measured value is 0.9646, and the average relative error P is 4.05% and less than 10%, which indicated that the CO_2 injury prediction model based on the change of browning index is feasible

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