ABSTRACT

In this study, pickles were used as the research objects, the shelf life of the pickles during storage at different temperatures (25℃, 30℃ or 37℃) was studied, the changes of sensory quality and the total number of colonies during storage were determined. The results showed that the sensory score declined with storage time increased, the higher the storage temperature, the greater the rate of change; with the increased of storage time, the total number of colonies increased, the higher the storage temperature, the higher the rate of change, this conformed to the first-order kinetics model. Kinetic model of the total number of colonies was established, through the analysis, obtained an Arrhenius equation and the first-order (chemical reaction), the correlation coefficient of which were greater than 0.9, showing a high goodness of fit; and a shelf life prediction kinetic model was obtained as follows: y = 224.73 e^{-0.0791 x} (R^2 = 0.9999). Experiments showed that the kinetics model of pickles quality changes had a high fitting accuracy, it can exhibit a good reliability in predicting the shelf life of pickles.

Keywords: pickles; the shelf life; prediction model

INTRODUCTION

Pickles, which are vegetables that were preserved in salt to save and sauce, they have strong salty and can be long-term preservation. They not only can be used to eat directly accompany a meal, but also can be as raw materials for the cooking. In recent years, salted food has developed rapidly in our country, the variety and quantity of salted food increased sharply each year. In the process of food processing and storage, the groups of food had different degrees of damage with the storage conditions changed of temperature and humidity. Dynamic model[1-3] can be used to reflect that the loss rate of food components at different conditions of temperature and humidity, to provide theoretical basis for optimizing the technology of processing and storage [4].Given the study of the quality change rule and the shelf life[5] of pickled products in the market circulation and storage process are still weak, this experiment by studying the pickles at different temperatures, their sensory quality and the total number of colonies changes along with the storage time, on the basis to build the shelf life prediction model, it aimed to improve the safety for people eating pickle products and to meet more and more attention of food safety consciousness.

EXPERIMENTAL SECTION

Materials and reagents: Homemade pickles; Plate count AGAR mediums were purchased from Beijing bridge technology co., LTD. (Beijing China); Sodium chloride (AR) was purchased from Beifangtianyi of Beijing chemical reagent factory (Beijing China).
Methods
Experiment process: Salted turnip, cleaned and shaped, desalinated to increase brittleness, squeezed to dehydration, packaged by vacuum, last, finished products.

Pickle sensory score: This study consists of 10 professional personnel to sensory evaluation on pickles refer to table 1, sensory quality [6] includes three aspects: the taste, smell, color and luster. If comprehensive score was below 60 points, thought that the sample was metamorphism and remaining shelf life of pickles was zero.

<table>
<thead>
<tr>
<th>Indicators</th>
<th>Levels</th>
</tr>
</thead>
<tbody>
<tr>
<td>Color and luster</td>
<td>Smooth and bright, keep the original color</td>
</tr>
<tr>
<td></td>
<td>(30 to 40 points)</td>
</tr>
<tr>
<td></td>
<td>Color and luster is darker, more smooth and</td>
</tr>
<tr>
<td></td>
<td>bright (20 – 30 points)</td>
</tr>
<tr>
<td></td>
<td>Dark color and light (below 20 points)</td>
</tr>
<tr>
<td>Smell</td>
<td>The inherent fragrance, no peculiar smell</td>
</tr>
<tr>
<td></td>
<td>(20 – 30 points)</td>
</tr>
<tr>
<td></td>
<td>The inherent fragrance partial light</td>
</tr>
<tr>
<td></td>
<td>(10 – 20 points)</td>
</tr>
<tr>
<td></td>
<td>Fragrance is not obvious, have peculiar</td>
</tr>
<tr>
<td></td>
<td>smell (below 20 points)</td>
</tr>
<tr>
<td>Taste</td>
<td>Buttery chewiness, flavor scent</td>
</tr>
<tr>
<td></td>
<td>(20 – 30 points)</td>
</tr>
<tr>
<td></td>
<td>Good chewiness, the lower scent</td>
</tr>
<tr>
<td></td>
<td>(10 – 20 points)</td>
</tr>
<tr>
<td></td>
<td>Poor chewing and the poor taste</td>
</tr>
<tr>
<td></td>
<td>(below 20 points)</td>
</tr>
</tbody>
</table>

The determination of the total number of colonies: refer to national food safety standard of China: Food microbiological examination, Aerobic plate count.

Establish shelf life prediction model (ASLT accelerated life test) [7]:
Pickle samples were divided into three groups, which were placed respectively at the constant temperature condition of 25 ℃, 30 ℃ and 37 ℃, after 1 d, 8 d, 15 d and 22 d, determined the total number of colonies, did three sets of parallel and took the average values as the test results. According to the test results, the mathematical model of quality change and shelf life prediction model [8, 9] of the pickle products were established in the process of storage.

Validation and evaluation of shelf life prediction model:
Compare the shelf life measured value and predicted value by the shelf life prediction model of pickle products, to evaluate the accuracy of the shelf life prediction model and calculate the relative error.

RESULTS AND DISCUSSION

The relationship of the quality score and shelf life of pickles at different storage temperatures:
The changes of pickles sensory score during storage were shown in figure 1, pickles sensory score had a downward trend during the whole process of storage, the higher the storage temperature, the faster sensory score down. Quality loss were mainly in the color, smell and taste during storage. On the 1d, sensory score was 100 points, quality was excellent. According to pickle quality criteria, when sensory score was 60 points, pickles were placed at the condition of constant temperature storage of 25 ℃, after 32 d, the total number of colonies were 38000 CFU/g; at the condition of constant temperature of 30 ℃, after 20 d, the total number of colonies were 37810 CFU/g; at the condition of constant temperature of 37 ℃, after 11 d, the total number of colonies were 38100 CFU/g.

Due to the influence of various physical, chemical and microbiological during storage [10], the food quality was worsen gradually, when they reached the level of sensory that refused by consumers, they were called the rotten foods. On this basis, we can determine the end of their shelf life according to pickles of sensory evaluation. At different storage temperatures, when the pickles sensory score was 60 points, the average number of colonies was 37970 CFU/g.
The changes of the pickle total number of colonies during storage

As shown in figure 2, with the storage time increased, the total number of colonies gradually increased, with the temperature increased, the growth rate of the total number of colonies speeded up. The pickles total number of colonies had a slower growth at the 25 °C to cultivate, the storage effect was best; the pickles total number of colonies at 30 °C to cultivate growth faster than 25 °C, the storage effect was better. The total number of colonies grew rapidly at 30 °C to cultivate and storage effect was general.

Dynamic model of the pickles total number of colonies during storage [11]:

Chemical reaction kinetics model has been widely applied in many fields. In the process of food processing and storage, most quality changes related to food are following the zero order or first order reaction model, the first order reaction kinetics model is widely used. The relationship between reaction rate constant and temperature is usually described with Arrhenius equation. Dynamic model of the pickles total number of colonies in the storage process was analyzed with exponential equation, obtained the regression equations that were shown in table 2.

Table 2: Regression equation of the pickles total number of colonies with the changed of time at different storage temperatures

<table>
<thead>
<tr>
<th>Storage temperature</th>
<th>Regression equation</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>y=54.51e^{0.2089x}</td>
<td>0.9106</td>
</tr>
<tr>
<td>30</td>
<td>y=62.298e^{0.32x}</td>
<td>0.9644</td>
</tr>
<tr>
<td>37</td>
<td>y=52.595e^{0.4613x}</td>
<td>0.9375</td>
</tr>
</tbody>
</table>

As you can see by the related index, regression coefficients of three equations were greater than 0.9, showed the index of regression equation had a better fitting with change trend of the pickles total number of colonies, which
could accurately predict the changes of the pickles total number of colonies and provide accurate data and verify basis for constructing related mathematical model. Describe the changes rule of the pickles total number of colonies in the process of storage, storage dynamics model parameters were shown in table 3.

The formula of kinetics model for first order chemical reaction: \( N = N_0 e^{K_n t} \)

Where \( N \) is the total number of colonies; \( N_0 \) is the minimum standard of colony detection; \( K_n \) is the rate constant of bacterial growth; \( t \) is the storage time, d.

### Table 3 Dynamic model parameters of the changes of the pickles total number of colonies

<table>
<thead>
<tr>
<th>Storage temperature / °C</th>
<th>The initial total number of colonies / (CFU / g)</th>
<th>The growth rate constant / ( K_n )</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>56</td>
<td>0.2039</td>
</tr>
<tr>
<td>30</td>
<td>56</td>
<td>0.3200</td>
</tr>
<tr>
<td>37</td>
<td>56</td>
<td>0.4613</td>
</tr>
</tbody>
</table>

From table 3, \( K_n \) was obtained by figuring from figure 2 and the data in table 2 and combining the first order chemical kinetics model. The experimental data and analysis results showed that temperature had a great influence on growth rate constant of the colony, with the increased of storage temperature, colony growth rate constant increased. \( K_n \) was microbial growth rate constant which was a function of temperature, through using Arrhenius equation: \( K_n = K_{n0} e^{-\frac{E}{RT}} \)

where \( K_{n0} \) is the regression coefficient; \( E \) is the activation energy / (J/mol); \( R \) is gas constant, (\( R = 8.314 \) J/mol). \( T \) is kelvin temperature/K.

Take logarithm on both sides, obtained: \( \ln K_n = \ln K_{n0} - \frac{E}{RT} \).

In table 3, \( K_n \) was taken logarithm and did Arrhenius curves for \( 1 / T \), the results shown in figure 3.

As shown in figure 3, \( K_n \) was taken logarithm and did Arrhenius curves for \( 1 / T \), which had a good linear relationship \( (R^2 = 0.9981) \). The linear equation was that: \( \ln K_n = -62.977 \frac{1}{T} + 0.939 \)

Through the above analysis and calculated, obtained mathematical model that change of the pickles total number of colonies in the process of storage, and the model was:

\( N = N_0 e^{K_n t} \), \( K_n = 1.482 e^{1.1} e^{-\frac{67667}{RT}} \)

where \( N \) is the total number of colonies/(CFU/g); \( N_0 \) is the initial total colony/ (CFU/g); \( K_n \) is bacterial growth rate constant; \( t \) is storage time/d; \( R \) is gas constant \( R \), (\( R = 8.314 \) J/mol). \( T \) is kelvin temperature/K.

**Establish the shelf life of prediction model:**

When remaining shelf life of pickles was zero, through calculating the pickles average number of colonies at different storage temperature conditions, which were 37970 CFU/g, by calculating, obtained the shelf life of the pickles total number of colonies, the shelf life and the average shelf life of the index at different temperatures were
shown in table 4.

<table>
<thead>
<tr>
<th>Storage temperature/℃</th>
<th>The shelf life /d</th>
<th>The total number of colony</th>
<th>The sensory score</th>
<th>the average shelf life /d</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>32</td>
<td>32</td>
<td>32</td>
<td>32</td>
</tr>
<tr>
<td>30</td>
<td>20</td>
<td>20</td>
<td>20</td>
<td>20</td>
</tr>
<tr>
<td>37</td>
<td>14</td>
<td>11</td>
<td>12</td>
<td>12</td>
</tr>
</tbody>
</table>

Dates from table 4 can see that difference between the shelf life of colonies total value as a judge and the pickles average shelf life was not big, it can better reflect the pickles quality changes. Pickles products shelf life prediction model was established according to the shelf life obtained from the total number of colonies as shown in figure 4.

![Figure 4: Prediction model of pickle shelf life](image)

**Table 5 the comparison of the predicted values and the measured values of pickles shelf life during different temperatures**

<table>
<thead>
<tr>
<th>Storage temperature/℃</th>
<th>The predicted values of the shelf life /d</th>
<th>The measured of the shelf life /d</th>
<th>The relative error /%</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>31.10</td>
<td>32</td>
<td>2.90</td>
</tr>
<tr>
<td>30</td>
<td>20.94</td>
<td>20</td>
<td>4.70</td>
</tr>
<tr>
<td>37</td>
<td>12.04</td>
<td>12</td>
<td>0.33</td>
</tr>
</tbody>
</table>

Validation and evaluation of shelf life prediction model:

Pickles were placed at storage conditions of 25 °C, 30 °C, and 37 °C, used shelf life measured values to verify the shelf life model. Compared the pickles shelf life measured values, the predicted values by the shelf life prediction model and the relative error [12], the results were shown in table 5.

**CONCLUSION**

During storage at different temperatures, the sensory score of pickles declined with storage time increased, the higher the storage temperature, the greater the rate of change; the total number of colonies increased with storage time increased, the higher the storage temperature, the higher the rate of change, this conformed to the first-order kinetics model. The experimental results showed that regression coefficients of Arrhenius equation and first chemical reaction of the pickles total number of colonies changes were greater than 0.9, showing a high goodness of fit, and it can better reflect the total number of colonies with the changed of storage temperature and time in the process of pickles storage.

Establish shelf life prediction model of pickle products: $y = 224.73 e^{0.0791x}$ ($R^2 = 0.9999$), and verified that the relative error between the shelf life predicted and the measured values was within 5%, so it can forecast pickles shelf life according to the total number of colonies value.

**REFERENCES**

[4]. W Tian; Y Xu, Food Science, 2000(9), 14-18.
[5]. Y Cao; L Lu; X Xiong, Food research and development, 2009, 30(5), 165-168.
[8]. X Yu; X Che; L Zhang, Food research and development, 2007, 28(3), 84-87.