The Degradation Kinetics Model of Apricot during HA Drying

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Abstract. The browning index and carotenoid studies were carried out during HA drying process. The effects of different HA drying temperature (40 °C, 50 °C, 60 °C, 40 °C (10 h) → 60 °C (end), 50 °C (10 h) → 60 °C (end), 40 °C (10 h) → 50 °C (10 h) → 60 °C (end)) and air velocities (2 m/s, 3 m/s, 4 m/s) on colour and carotenoid of apricot were studied. Meanwhile, a HA drying degradation model was established. The test showed that the BI value increased and carotenoid content reduced with the passing of the processing time during the drying process. The browning action during the HA drying process was fit according to the zero and first-order reaction model. Furthermore, the activation energy was obtained by the Arrhenius equation, which was 17.59 kJ/mol. This research provided the theoretical basis for the quality control of dried apricot slice.

1. Introduction

Apricot (Prunus armeniaca L.) is native from Xinjiang of China, and Xinjiang is the leading world producer (about 132.54 Mt in 2013). In China, the most widely produced types are Saimaiti, Juana, Sailaikejialali and Xiaobai types. Pleasant aroma is the main reason why can it be consumed around the world. However, apricots have a short harvest season and a 5-7 days of storage [1]. In order to supply the good apricots to consumers for long time, drying is the most effective method, before desorption there has many different commercially used drying techniques drying methods, for example, sun, hot air and microwaves.

Togrul and Oguz Bozkir both studied drying process through different air temperatures and velocities and developed mathematical modeling, the difference was dry apricots whether washed for washed [2, 3]. Meanwhile, colour plays an important role on apricot drying [4], thus Ihsan reported the effect of hot-air drying and sun drying on color values of Hacihaliloglu apricots in Turkey [5]. Ali studied effects of Various Sulphuring Methods and Storage Temperatures on the color change of dried Apricots [6]. However, no one combined drying craft and color change, set up the connection between them and modeling to explain the reason that apricot become browning during drying.

Knowledge on kinetics of colour changes is essential to predict browning degree during all kinds of processing. The most used kinetic models and parameter estimates, for fruits and vegetables degradation of colour, are presented in Table 1. Almost fruits and vegetables are well described by first-order models (Eq. (4)).
Table 1 kinetic model for degradation of colour

| Product            | Temperature range(℃) | kinetic models   | k       | Ea   | Reference          |
|--------------------|----------------------|------------------|---------|------|--------------------|
| Green chilli puree | 60-90                | first order      | 0.049   | 11.4 | Jasim A. [7]       |
| Date paste         | 70–120°C             | first order      | 65.17   |      | Jasim A. [8]       |
| Peach puree        | 110-135              | first order      | 107     |      | I.M.L.B.A. et al.  [9] |
| canned fresh green peas | 120-131         | first order      | 5.48×10⁻⁴ | 89.37 | Raul. L. G. [10] |
| Tomato paste       | 70-100               | biphasic first order | 7.67×10⁻³ | 48.2 | Barreiro J. A. [11] |
| Peas               | 70-90                | first order      | 0.009×10⁻⁵ | 76.3 | Steet J. A. [12] |
| pumpkin            | 75-95                | first order      | 0.27    | 86.2 | Goncalves E.M. [13] |

However, no detailed studies concerning the colour change kinetics of apricot have yet been performed. The aims of this study were to determine the kinetics of apricot colour degradation during drying. The results will help to define optimal hot-air drying conditions for maximum quality retention, that will certainly be important for apricot products development.

2. Materials and Methods

2.1. Material and equipment

2.1.1. Material. Apricot (Prunus armeniaca L.) used in this study was obtained in a local market of Urumqi, Xinjiang, China. Actually, it did not have any external defect. The mean diameter of the samples was about 2.3 cm and the mean weight was 13.2 g. Before the experiments, initial moisture content of the apricot was measured immediately using the AOAC [14] treatment by putting the apricot in an air circulating oven for 6 h at 105 ℃. The content was 81.2% (w.b) and the whole samples were stored at 4±0.5 ℃ before being used in the experiments.

The hot air drying experiments were performed in internal recycling air-drying equipment (Figure 1, tray dryer, self-made). This equipment included drying part, tray, frame and control and collection of temperature and humidity. During operation, the drying room was heated by electrically heated wire. When the room temperature reached the initial temperature, samples in the dryer was carried to start the control program. When the room temperature exceeded the initial temperature, the electrically heated wire was stopped till the end of the drying.
1. Frame 2. Materiel 3. Tray 4. Wet exhaust fan 5. Internal recycling fan 6. Drying chamber 7. Temperature and humidity sensor 8. Control box 9. Electric heating wire

**Figure 1.** Schematic diagram of internal recycling air-drying equipment

2.1.2. **Methods.** Then the equipment was opened. When the room temperature reached the initial temperature (Tab.2) or air velocities (Tab.2), samples were distributed uniformly on a tray in the hot air for the drying experiments. During the first 50 h, the L, a and b values was determined for 10 h each. After 50 h, the L, a and b values was determined for 2 h each. The test was stopped until the relative moisture content of the apricot under 15%. Each experiment was replicated for three times.

| No. | HA temperature(°C) | air velocities(m/s) |
|-----|---------------------|---------------------|
| 1   | 40°C                | 2                   |
| 2   | 40°C                | 3                   |
| 3   | 40°C                | 4                   |
| 4   | 50°C                | 3                   |
| 5   | 60°C                | 3                   |
| 6   | 40°C(10h)—60°C(until end) | 3         |
| 7   | 50°C(10h)—60°C(until end) | 3         |
| 8   | 40°C(10h)—50°C(10h)—60°C(until end) | 3    |

*“until End”: means the total hours of the relative moisture content of apricot research 15% - the rest parts hours*

2.1.3. **Colour measurement.** Sample colour was measured before and during the drying process through a CR-10 colorimeter (Konica Minolta, Japan). The colour values were expressed as L (ness or brightness/darkness), a (redness/greenness) and b (yellowness/blueness) at any time, respectively. Furthermore, calculated from the Hunter L-, a-, b-values, x and browning index (BI) were used to describe the colour change during drying [15, 16], defined as in Eq.(1) and Eq.(2).
\[ x = \frac{(a + 1.75L)}{(5.645L + a - 3.012b)} \]  
\[ BI = \frac{100(x - 0.3)}{0.17} \]

2.1.4. Carotenoid measurement. After the liquid nitrogen was ground, 0.5 g was weighed and placed into a 10 mL centrifuge tube, 8 ml 80% acetone was added, and the samples were extracted in darkness at 4°C for 24h. Then, the samples were centrifuged at 12000 rpm for 20 min at 4°C. The absorbance of the supernatant was determined at 663nm, 646nm and 470 nm respectively, and the carotenoid content L was calculated according to Eq.(3).

\[ L = (4.37A_{470nm} + 2.11A_{663nm} - 9.10A_{646nm}) \times V/(1000 \times FW) \]

2.1.5. The degradation model. Statistical analysis was conducted using the Sigma-Plot. BI and carotenoid changes were estimated in a non-linear regression analysis. Precision of parameters was evaluated by confidence intervals at 95%. Quality of the regression was assessed by the coefficient of determination (R²). Thus, the most effective model can be selected and finally the activation energy was estimated.

Kinetics modeling refers to a system to describe the reaction rate according to the experiment data and predict changes of the given food during processing. There have been numerous available references of literature on the colour kinetics of food materials [17-21]. The majority of these works in this study were zero-order (defined as in Eq. (4)) and first-order (defined as in Eq.(5)) kinetics models.

\[ D = D_0 \pm KT \]  
\[ D = D_0 \times \exp(kt) \]

The fitting process was conducted on test data and zero- or first-order kinetics model, calculating the k value and other parameters. Therefore, this test studied the kinetics of BI values during the hot-air (HA) drying process of the apricot in order to predict the browning changes. According to R², the appraising models fitted the condition and the higher fitting degree model was chosen to desire the browning law during the apricot HA drying.

As the browning activation energy (Ea) of drying was a determination of its changes in temperature, higher activation energy denoted higher browning degree. The method for calculating Ea used the slope of an Arrhenius plot of log k versus the reciprocal of the absolute temperature (1/T) were defined as in Eq.(6):

\[ \ln k = \frac{E_a}{R} \left( \frac{T - T_0}{T_0T} \right) + \ln k_0 \]

3. Results and Discussion

3.1. BI

3.1.1. Different air velocities. In this study, the initial BI value was 129.81 as the apricot itself contained some pigment. During the HA drying process, BI value of the apricot showed a gradually increasing tendency during the drying time. It is suggested that the browning degree was constantly rising during the whole HA drying process. When the initial moisture content of apricot reduced to 15% (w.b), firstly the BI value was 157.96 on the condition that the air velocities was 2 m/s and the drying time was 70 h;
secondly, the BI value was 156.93 on condition that the wind speed was 4 m/s, and the drying time was 68 h; at last, the BI value was 156.53 on condition that the wind speed was 3 m/s and drying time was 70 h. These results suggested that different air velocities were slightly affected by the BI value and colour quality of the apricot.

3.1.2. Different HA temperatures. In this study, during the HA drying process, BI value of the apricot showed a gradually growing tendency with the passing of the drying time (Fig.3.). It is suggested that the browning degree was constantly rising during the whole HA drying process. When the initial moisture content of apricot decreased to 15% (w.b), firstly, the BI value was 169.54 on condition that HA temperatures was 60 °C and the drying time was 52 h; followed by 60 °C, the BI value was 166.97 on condition that HA temperatures was 50 °C(10 h)→60 °C(until end) and the drying time was 58 h; the BI value was 163.51 on condition that HA temperatures was 40 °C(10 h)→60 °C(until end) and the drying time was 54 h; the BI value was 160.49 on condition that HA temperatures was 40 °C(10h)→50 °C(10 h)→60 °C(until end) and the drying time was 60 h; the BI value was 158.94 on condition that HA temperatures was 50 °C and the drying time was 64 h; at last, the BI value was 156.53 on condition that the HA temperatures was 40 °C and the drying time was 70 h; The result indicated that: the BI value form the high to low is: 60 °C>50 °C(10 h)→60 °C(until end)>40 °C(10 h)→60 °C(until end)>40 °C(10 h)→50 °C(10 h)→60 °C(until end)>50 °C>40 °C. All these results suggested that the BI value increased as the HA temperatures became higher; and the changed temperature HA drying method by stages was better than the single temperature method. From the perspective of BI values trend, early change rate of the apricot browning is less than the latter one. The apricot browning included enzymic browning and non-enzymic browning. Furthermore, one of the main conditions for enzymatic browning is temperature. The results presented in this work suggested that the changed temperature HA drying method by stages can reduce not only the drying time, but also the browning phenomenon.

3.2. Colour kinetics

Tab.3 shows that the fitting results of the apricot colour kinetics in different air velocities. The result can be revealed from two main parts. First of all, in different air velocities, zero- and first-order models can be used for R² values from 0.8794 to 0.9523. Secondly, the values of the first-order model kinetic R² (R² values are 0.8942, 0.9310 and 0.9523, respectively) were higher than those of the zero-order model in 2 m/s, 3 m/s and 4 m/s. The results showed that the hot air drying data in different air velocities can be described successfully by the first-order kinetics.

Tab.3 also indicated the R² values from 0.9199 to 0.9939 in different HA temperatures. In these models, the kinetic R² value of the zero-order model (R² values is 0.984) was higher in 40 °C (10 h)→60 °C (until end), except that, in 40 °C , 50°C,60 °C, 50 °C(10 h)→60 °C(until end),40 °C(10 h)→50 °C(10 h)→60 °C(until end), The kinetic R² values of the first-order model (R² values were 0.931, 0.9705, 0.9855, 0.9939 and 0.9844, respectively which were higher than those of the zero-order model. The results showed that the hot air drying data in different HA temperatures can be described successfully by the first-order kinetics.

These results suggested that the first-order kinetics described the fitting results of the apricot colour kinetics in different air velocities and HA temperatures successfully. The change regularity of the BI value can be seen from Fig.2.and Tab.3.
Table 3. Fitting results of colour kinetics in different air velocities and HA temperatures

| Different parameters | Factor              | Model         | \(D_0\)     | \(k\)   | \(R^2\)   |
|----------------------|---------------------|---------------|-------------|---------|-----------|
|                      | Zero-order model    | 125.46        | 0.3998      | 0.8794  |           |
|                      | First-order model   | 126.35        | 0.0028      | 0.8942  |           |
| Different air        | 2m/s                |               |             |         |           |
| velocities           |                      |               |             |         |           |
|                      | Zero-order model    | 127.16        | 0.4007      | 0.9199  |           |
|                      | First-order model   | 126.72        | 0.0028      | 0.931   |           |
|                      | 3m/s                |               |             |         |           |
|                      | Zero-order model    | 126.65        | 0.4186      | 0.9435  |           |
|                      | First-order model   | 127.16        | 0.0029      | 0.9523  |           |
|                      | 4m/s                |               |             |         |           |
|                      | Zero-order model    | 126.28        | 0.4007      | 0.9199  |           |
|                      | First-order model   | 126.72        | 0.0028      | 0.931   |           |
|                      | 40°C                |               |             |         |           |
|                      | Zero-order model    | 127.43        | 0.3676      | 0.9636  |           |
|                      | First-order model   | 129.17        | 0.0026      | 0.9705  |           |
|                      | 50°C                |               |             |         |           |
|                      | Zero-order model    | 128.63        | 0.7259      | 0.9789  |           |
|                      | First-order model   | 129.4         | 0.0049      | 0.9855  |           |
|                      | 60°C                |               |             |         |           |
|                      | Zero-order model    | 128.76        | 0.6184      | 0.984   |           |
|                      | First-order model   | 130.53        | 0.129       | 1       |           |
|                      |                      | 60°C (until end) | 129.3  | 0.0042  | 0.9829   |           |
|                      | 40°C (10h)—60°C (until end) |       |             |         |           |
|                      | Zero-order model    | 128.56        | 0.6486      | 0.9921  |           |
|                      | First-order model   | 130.53        | 0.273       | 1       |           |
|                      |                      | 60°C (until end) | 129.29 | 0.0044  | 0.9939   |           |
|                      | 50°C (10h)—60°C (until end) |   |             |         |           |
|                      | Zero-order model    | 128.82        | 0.51        | 0.9837  |           |
|                      | First-order model   | 129.81        | 0.129       | 1       |           |
|                      |                      | 50°C (10h)     | 125.43      | 0.639   | 1         |
|                      |                      | 60°C (until end) | 129.31 | 0.0035  | 0.9844   |           |
|                      | 40°C (10h)—50°C (10h)—60°C (until end) | | | | |
Figure 2. Index movement kinetic curve of apricot in wind speeds and HA temperatures

3.3. Carotenoid degradation kinetics
Tab.4 and Fig.3. shows that the fitting results of the apricot carotenoid degradation kinetics in different air velocities. The result can be revealed from that, in different air velocities, zero-order models can be used for R^2 values from 0.7945 to 0.8397. The results showed that the hot air drying data in different air velocities can be described successfully by the zero-order kinetics. Tab.4 and Fig.3. also indicated the R^2 values from 0.7675 to 0.9939 in different HA temperatures. In these models, the results showed that the hot air drying data in different HA temperatures can be described successfully by the zero-order kinetics.

These results suggested that the zero-order kinetics described the fitting results of the apricot carotenoid degradation kinetics in different air velocities and HA temperatures successfully. The change regularity of the carotenoid value can be seen from Fig.4. and Tab.3.
Table 4. Fitting results of carotenoid kinetics in different air velocities and HA temperatures

| Different parameters | Factor       | Model            | $D_0$ | $k$  | $R^2$ |
|----------------------|--------------|------------------|-------|------|-------|
| Different air velocities | 2m/s | Zero-order model  | 3.1684 | 0.0076 | 0.8356 |
| Different air velocities | 3m/s | Zero-order model  | 3.2004 | 0.0096 | 0.8397 |
| Different air velocities | 4m/s | Zero-order model  | 3.2165 | 0.0105 | 0.7945 |
| Different air velocities | 40°C | Zero-order model  | 3.2004 | 0.0096 | 0.8397 |
| Different air velocities | 50°C | Zero-order model  | 3.3519 | 0.0229 | 0.7675 |
| Different air velocities | 60°C | Zero-order model  | 3.1869 | 0.0222 | 0.9175 |
| Different HA temperatures | 40°C(10h)—60°C(until end) | Zero-order model  | 3.2329 | 0.0253 | 0.9379 |
| Different HA temperatures | 50°C(10h)—60°C(until end) | Zero-order model  | 3.2452 | 0.0346 | 0.9562 |
| Different HA temperatures | 40°C(10h)—50°C(10h)—60°C(until end) | Zero-order model  | 3.0913 | 0.0411 | 0.9939 |

Figure 3. Carotenoid movement kinetic curve of apricot in wind speeds and HA temperatures
3.4. Activation energy

The value of k was obtained from the first order reaction. The relationship \( k = 7086.67T + 28.54 \) between speed constant and drying temperatures was obtained by the linear regression with \( R^2 = 0.9447 \), \( T \in [40, 60] \) \( ^\circ\text{C} \). As shown in Eq. (4), The activation energy for the HA drying was 17.59 kJ mol\(^{-1}\).

![Graph](image)

**Figure 4** The curves between natural logarithm of BI value rate change parameter (k) of apricot in different HA temperatures

4. Conclusion

The BI and carotenoid results showed that the HA drying technique tended to produce brown product. Different HA temperatures of the hot air drying had great influences on the colour and carotenoid of the apricot. However, the air velocities was less affected. Temperature increased considerably as browning became more severe. Besides, the first-order kinetics during the drying process could describe the fitting results of the apricot colour kinetics in different air velocities and HA temperatures successfully. the zero-order kinetics during the drying process could describe the fitting results of the apricot carotenoid degradation kinetics in different air velocities and HA temperatures successfully. In this paper, the results verified the determination of apricot HA drying processing and value of product quality control.

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