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The kinetics of nutritional quality changes during winter jujube slices drying process

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REVIEW ARTICLE

Abstract

The purpose of this research is to investigate the kinetics of nutrient's change (vitamin C, reducing sugar, and total acidity) of winter jujube slices that are submitted to drying at different temperatures (55, 60, 65, and 70°C) and air velocities (3, 6, and 9 m/s) during the air-impingement drying process. Results showed that the content of vitamin C and reducing sugar, and total acidity decreased with increasing drying time. Furthermore, analysis of variance indicated that the drying temperature, air velocity, and time had a significant effect on the loss of vitamin C and reducing sugar, and on total acidity ($P < 0.05$). Zero-order, first-order, and Weibull models were used to fit the experimental data, Weibull model was considered as the most suitable one for the degradation kinetics of vitamin C and reducing sugar, and change of total acidity in samples dried at different temperatures and air velocities. According to the Arrhenius formula, the activation energy of vitamin C, reducing sugar, and total acidity change kinetics were 63.78, 36.48, and 153.51 kJ/mol, respectively. This research can provide some references for enhancing dried product quality in the jujube drying industry.

Keywords: activation energy; air velocity; drying temperature; drying time; Weibull model

Introduction

Jujube is now popular among consumers because of its crispy texture and rich in nutrients. Researches have indicated that jujube is rich in a variety of nutrients (Gao *et al.*, 2011), and thus it is known as the "king of vitamins." However, fresh jujube decays easily due to its high moisture content. Hence, most farmers and factories need preservation techniques to extend the storage period and prolong the shelf-life after harvesting the fresh ones.

Drying is the most common method of food preservation, which can prolong the shelf life by reducing the moisture content (Al Juhaimi *et al.*, 2016; Mujumdar and Law, 2010). Jujube slices drying can contribute to enhance the quality of the dried product and reduce the drying time compared to whole jujubes drying, it can not only use damaged jujube effectively but also make them more convenient to store and transport than the whole jujube.

Doymaz *et al.* (2016) found that the total color change of the dried jujube fruits increased with the increasing infrared power level, and the Page model was more fitted to the experimental drying data. Chen *et al.* (2015) found that short- and medium-wave infrared radiation provided dried jujube slices that had brighter color and higher retention of vitamin C compared to hot-air drying. He *et al.* (2013) evaluated the physical properties of crispy winter jujube dried by explosion puffing drying, and they found that the dried products exhibited very close rehydration capacity with those obtained by a combination of freeze-drying and hot air drying, while the dried products had better crispness. Wojdyło *et al.* (2019) investigated different parameters of combined methods such as pre-drying by hot air drying and finishing drying by vacuum-microwave drying, and found that the content of phenolic substances and antioxidant activity of dried products decreased with the increasing air temperature and material temperature during hot air drying and vacuum-microwave drying, respectively. Gao *et al.* (2012) analyzed the change of sugar content of jujube after four drying treatments including sun drying, oven drying, microwave drying, and freeze-drying, and the results showed that freeze-dried jujubes had higher antioxidant activity than microwave-dried jujubes, but microwave-dried jujubes had higher retentions of protocatechuic acidity, catechin, and epicatechin. Although some scholars studied the change of quality indexes, these researches mainly focused on the drying methods of jujube and the changes of nutritional quality after jujube drying. There are few reports on the dynamic changes in the nutritional quality of jujube slices during drying.

The common nutritional quality indicators of jujube slices mainly cover sugar, acidity, vitamin C, and so on (Pu *et al.*, 2017). Vitamin C is one of the main vitamins for the human body, which is an important antioxidant that is linked to a reduction in the incidence of some diseases (Santos and Silva, 2008). Reducing sugar content and total acidity content are also two common nutrition quality indexes of jujube slices, which directly determine the sugar-acidity ratio which is the most direct taste response from consumers to products. Therefore, in this research, vitamin C content, reducing sugar content, and total acidity content were regarded as the representative indexes to evaluate the nutritional quality of jujube slices.

Air-impingement jet drying technology is an efficient drying method, which has been used in food baking, blanching, and drying in recent years. During the air-impingement jet drying process, a thinner boundary layer between the air and the surface of the product due to the higher air velocity and impinging directly the surface of the product, which leads to the enhancement of heat and mass transfer (Anderson and Singh, 2006; Mujumdar, 2006). The heat transfer coefficient is five-fold higher than the respective with conventional dryers. Meanwhile, the drying rate increases and the drying time decreases (Seyedein *et al.*, 1995). The kinetics of nutritional quality changes (vitamin C, reducing sugar, and total acidity) during the drying process of jujube slices were studied by air-impingement drying, which provides some theoretical support for the jujube drying industry.

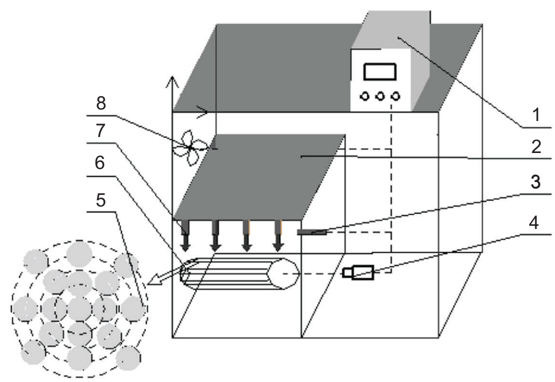
Materials and methods

Experimental materials

Fresh winter jujubes with the same maturity and similar size were purchased from Shihezi comprehensive wholesale market. All the winter jujubes were stored in a refrigerator at 4 ± 1°C and 96 ± 2% relative humidity prior to all experiments. Then the winter jujubes without mechanical damage were washed with tap water for removing the dust on the surface. Excess water on their surface was removed by blowing ambient air. Then the winter jujubes were cut into slab shape with 7.0 mm as the average thickness by a sharp blade. The moisture content of the samples was 80 ± 1.0% on a wet basis, initially (w.b.).

Sample drying

The air-impingement jet dryer (Drying Technology and Equipment Laboratory of Shihezi University) was employed to drying the samples, as shown in Figure 1. The experiments were performed and the recorded data are given in Table 1. Then the single layer of samples was placed in rows on the drying tray, each row being 40±0.2 g as a sample. A sample was collected and weighed



1. Control system; 2. Air distribution room;
3. Temperature and humidity sensor; 4. Electric motor;
5. Jujube slices; 6. Drying tray; 7. Hot air; 8. Centrifugal fan

Figure 1. Schematic diagram of pulsed air-jet impingement dryer.

Table 1. Design for the experiments with run conditions included.

Run no.	Drying temperature (°C)	Air velocity (m/s)	Pulsation ratio (r/min)
1	55	6	6
2	60	6	6
3	65	6	6
4	70	6	6
5	60	3	6
6	60	9	6

immediately by Electronic Balance every 30 min during the drying process. The moisture content of the sample was calculated and the samples sealed in the refrigerator until needed. When the moisture content of the sample was less than 20% (w.b.), the drying process was terminated.

Each sample was crushed and divided into three equal parts after the sample was taken out of the refrigerator and the content of vitamin C, reducing sugar, and total acidity was determined, respectively. All experiments were performed in triplicate to ensure the accuracy of the test data.

Moisture content

The change of moisture content was described as moisture ratio (MR). The calculation of MR was according to the method of Goyal *et al.* (2007).

$$MR = \frac{M_t - M_e}{M_0 - M_e} \quad (1)$$

where, M_t represents the moisture content of samples at drying time t, M_0 is the initial moisture content of samples, and M_e is the equilibrium moisture content. The values of M_e were relatively low compared to M_0 and M_t values, thus Equation (1) was simplified and as expressed in Equation (2).

$$MR = \frac{M_t}{M_0} \quad (2)$$

Chemical analysis

Vitamin C content of samples was determined by 2,6-dichloro-indo-phenol titrimetric method described by Caparino *et al.* (2017) with slight modification. Ten grams (10 g) sample was homogenized in a blender with 100 mL oxalic acid solution. 10 mL filtration solution was transferred to a 50 mL conical flask and titrated with 2,6-dichloro-indo-phenol (0.01 g/100 g solution) until the filtrate was pink for 15 s without fading. The titration was repeated several times for accuracy.

Reducing sugar content of samples was determined by the official LaneEynone titratable method as described in AOAC. (2005).

The total acidity content of samples was determined by a titration method following the methodology described by Jahan *et al.* (2019).

Statistical analysis

Statistical significance of the experiments was determined using a two-way analysis of variance (ANOVA) with $P < 0.05$. The Statistical Product and Service Solutions (SPSS) software is used for this analysis. The mathematical modeling of drying curves and vitamin C, reducing sugar, and total acidity was performed with Origin Pro 8 software.

The kinetic model of quality change

The quality changes of foods during processing and storage can be described by different kinetic models. The degradation kinetics of vitamin C and reducing sugar, and change of total acidity were assessed with zero-order, first-order, and Weibull distribution models [Equations (3)–(5)].

$$c_t = c_0 + k_0 t \quad (3)$$

$$c_t = c_0 \exp(k_1 t) \quad (4)$$

$$c_t = c_0 \exp[-(k_\alpha t)^\beta] \quad (5)$$

where, C_t is the nutrient quality index value at any time; C_0 is the initial value of the index; t is the time, h; k_0 is the zero-order kinetic reaction rate constant; k_1 is the first-order kinetic reaction rate constant; k_α is the Weibull distribution kinetic reaction rate constant (Corradini and Peleg, 2004); and β is the shape constant.

The effect of temperature on each indicator is in accordance with the Arrhenius equation:

$$k = A_0 \exp\left(\frac{-E_a}{RT}\right) \quad (6)$$

where, k is the reaction rate constant; A_0 is the Arrhenius constant (frequency factor); E_a is the activation energy, J /mol; R is the universal gas constant, 8.314 J /(mol· K); T is the temperature, K.

Take the logarithm of both sides of the Arrhenius equation:

$$\ln k = \frac{-E_a}{RT} + \ln A_0 \quad (7)$$

Taking ln k as the ordinate and T^{-1} as the abscissa for the curve. For the straight-line fitting of the obtained result, the slope is $E_a R^{-1}$, and the value of E_a can be calculated by taking the value of R.

Results and Discussion

Nutrient change curves

To compare the effect of different drying temperature and air velocity on the dynamics of nutritional quality changes of winter jujube slices, the curves of vitamin C versus drying time, reducing sugar versus drying time, and total acidity versus drying time under different processing parameters are shown in Figures 2–7.

Retention of vitamin C

The fitting curves of vitamin C versus drying time under different drying temperatures with a constant air velocity of 6 m s^{-1} are shown in Figure 2. It can be seen that the content of vitamin C decreased with increasing drying time ($P < 0.05$). That may be due to the higher moisture content during the initial stage of drying, and the higher activity of the enzyme, which accelerated the decrease of vitamin C retention. In all dried samples, the retention rate of vitamin C was less than 46.45%, the highest retention of vitamin C was obtained at 55°C (0.28 g 100 g^{-1}). The loss of vitamin C increased with the increasing drying temperature ($P < 0.05$). The possible reasons for this phenomenon could be the effect of oxidation and thermal degradation (Hawlader et al., 2006). The heated air inherently exposes the products to oxidation, reducing their vitamin C content (Vega-Gálvez et al., 2008). Similar results were obtained in the drying experiment of Monukka seedless grapes conducted by Xiao *et al.* (2010), in the drying experiment of red peppers conducted by Dağhan *et al.* (2018), and in the drying experiment of kiwifruit by Kaya *et al.* (2009).

The fitting curves of vitamin C versus drying time under different air velocities with a constant drying temperature of 60°C are shown in Figure 3. The vitamin C content was inversely proportional to the drying time. In all dried samples, the highest retention of vitamin C was obtained at 9 m/s (0.25 g 100 g^{-1}), the retention rate of vitamin C was less than 42.82%. Although the vitamin C content of samples in the initial drying stage was higher at the lower air velocity ($P < 0.05$), a longer drying time was needed, so the final vitamin C retention rate was the lowest.

Retention of reducing sugar

The fitting curves of reducing sugar versus drying time under different drying temperatures with a constant air velocity of 6 m/s are shown in Figure 4. In the drying process, the reducing sugar content decreased with the increase of drying time ($P < 0.05$). Reducing sugar retention rates of all dried samples were found lower than 44.32%, and the highest retention of reducing sugar was at 55°C (4.90 g 100 g^{-1}). The retention of reducing sugar was negatively correlated with the temperature ($P < 0.05$). These phenomena were probably due to reducing

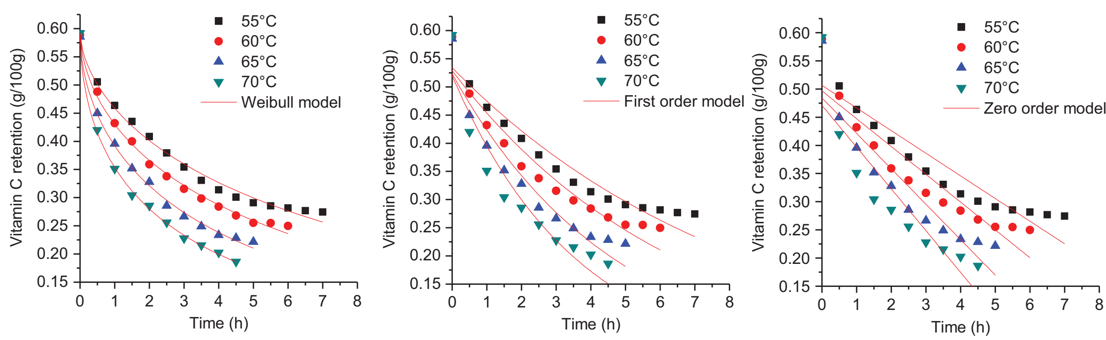


Figure 2. The fitting curves of vitamin C content variation under different drying temperatures with a constant air velocity of 6 m/s.

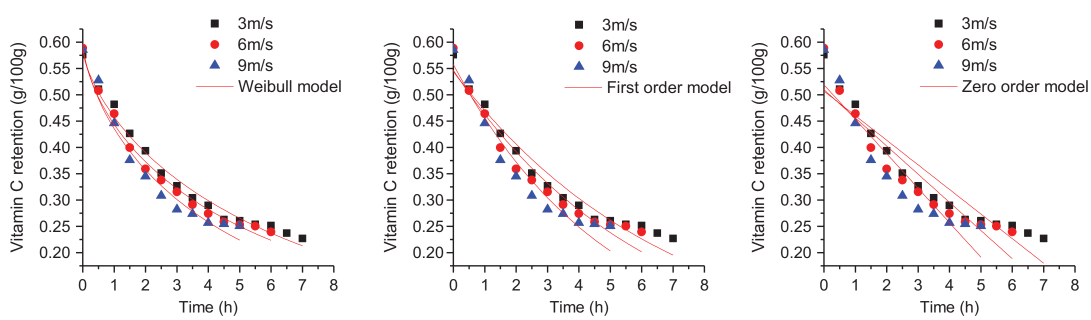


Figure 3. The fitting curves of vitamin C content variation under different air velocities with a constant drying temperature of 60°C.

sugar that occurred in the Maillard reactions under lower temperatures. Reducing sugar binding to amino acids, eventually resulted in the loss of protein content and total sugar, especially reducing sugar (Chen *et al.*, 2012). While at higher drying temperatures, one part of the reducing sugar participated in the Maillard reaction and the other part participated in the caramelization reaction (Boudhrioua *et al.*, 2002).

The fitting curves of reducing sugar versus drying time under different air velocities with a constant drying temperature of 60°C are shown in Figure 5. During the drying process, reducing sugar content of dried samples decreased gradually with time. The highest retention of reducing sugar was found at 9 m/s (4.8 g 100 g^{-1}), and reducing sugar retention rates of all dried samples were lower than 43.74% ($P < 0.05$).

Retention of total acidity

The fitting curves of total acidity versus drying time under different drying temperatures with a constant air velocity of 6 m/s are shown in Figure 6. It is shown that the total acidity retention of winter jujube slices decreased slightly with time for the same drying temperature ($P < 0.05$). The lowest total acidity retention of dried samples was obtained at 55°C (0.40 g 100 g^{-1}), and

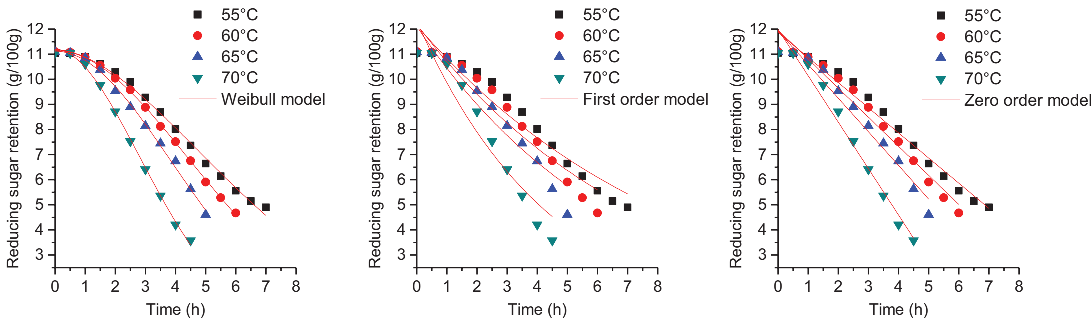


Figure 4. The fitting curves of reducing sugar content variation under different drying temperatures with a constant air velocity of 6 m/s.

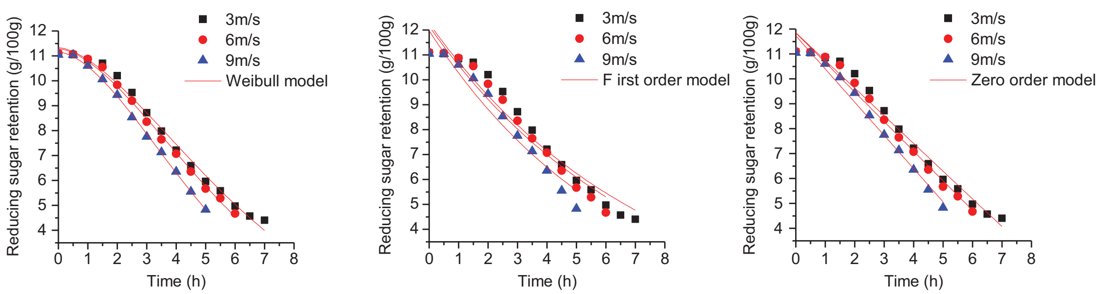


Figure 5. The fitting curves of reducing sugar content variation under different air velocities with a constant drying temperature of 60°C.

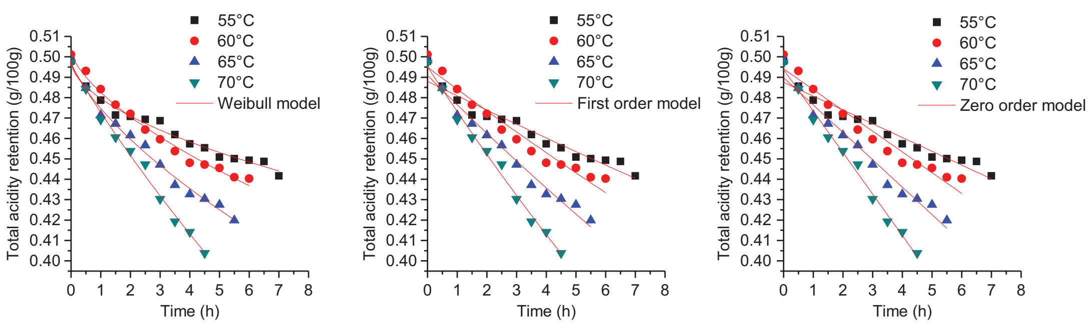


Figure 6. The fitting curves of total acidity content variation under different drying temperatures with a constant air velocity of 6 m/s.

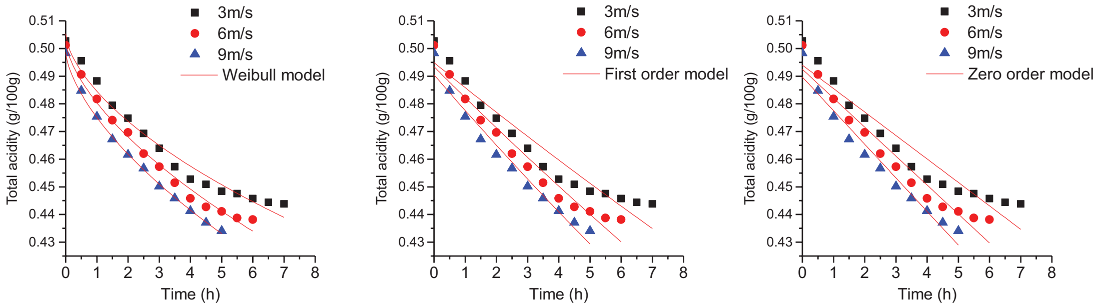


Figure 7. The fitting curves of total acidity content variation under different air velocities with a constant drying temperature of 60°C.

the retention rates were higher than 81.23% ($P < 0.05$). The decrease in acidity may be due to the conversion of the acid into sugars or some other compounds during the drying process, or the utilization of the acid in the respiration process (Prajapati *et al.*, 2011). This result is in agreement with several studies (Ashebir *et al.*, 2009; Fernandes *et al.*, 2018) that reported degradation of total acidity at high temperatures.

The fitting curves of total acidity versus drying time under different air velocities with a constant drying temperature of 60°C are shown in Figure 7. The reducing sugar content of dried samples decreased gradually with time. It was shown that the lowest total acidity retention of dried samples was obtained at 9 m/s (0.43 g 100 g^{-1}), and the retention rates were higher than 87.11% ($P<0.05$). Total acidity retention of dried samples decreased gradually with time.

Table 2. The fitting parameters of vitamin C.

Model	T (°C)	V (m/s)	k	β	R^2
$C = C_0\exp[-k_\alpha t]^\beta$ Weibull model	55	6	0.1066	0.6106	0.9892
	60		0.1443	0.5905	0.9949
	65		0.2090	0.5799	0.9960
	70		0.2928	0.5383	0.9986
$C = C_0\exp(k_1 t)$ First-order model	55	6	−0.1177		0.9324
	60		−0.1534		0.9260
	65		−0.2119		0.9205
	70		−0.2755		0.8992
$C = C_0 + k_0 t$ Zero-order model	55	6	−0.0402		0.8667
	60		−0.0493		0.8506
	65		−0.0629		0.8307
	70		−0.0741		0.7905
$C = C_0\exp[-k_\alpha t]^\beta$ Weibull model	60	3	0.1447	0.7289	0.9847
		6	0.1619	0.6723	0.9870
		9	0.1950	0.7064	0.9671
$C = C_0\exp(k_1 t)$ First-order model	60	3	−0.1463		0.9608
		6	−0.1661		0.9467
		9	−0.2017		0.9352
$C = C_0 + k_0 t$ Zero-order model	60	3	−0.0467		0.8901
		6	−0.0535		0.8693
		9	−0.0655		0.8490

Significance analysis

The drying temperatures, time, and air velocities had a significant effect on the vitamin C, reducing sugar, and total acidity content of samples during their drying process as obtained by the two-way ANOVA ($P<0.05$).

Degradation kinetics

Vitamin C degradation kinetics

The vitamin C degradation kinetic results are displayed in Table 2. Based on the criteria of the highest determination coefficients ($R^2 = 0.9892–0.9986$), the Weibull model was selected as the most suitable model for vitamin C degradation kinetics in samples dried at different temperatures. The values of kinetic constants (k_α) and shape constants (β) of the Weibull model were obtained by fitting the experimental data. The k_α values for vitamin C obtained through the Weibull model were 0.1066, 0.1443, 0.2090, and 0.2928 at 55, 60, 65, and 70°C, respectively. Lower k_α values indicate lower degradation rates or, put differently, a long time before nutrient collapse (Marfil *et al.*, 2008). The parameter k_α was directly affected by drying temperatures in this study. The degradation rate of vitamin C increased with the drying temperature. The shape constant β represents a behavior index, and if $\beta < 1$ the reaction rate decreases with time (Cunha *et al.*, 1998; Dağhan *et al.*, 2018). The β values were 0.6106, 0.5905, 0.5799, and 0.5383, respectively. The vitamin C had a higher degradation rate at the beginning of the process. The variation of vitamin C content showed similar changes under different air velocities with a constant drying temperature of 60°C. The degradation rate of vitamin C decreased with time during the drying process,

Table 3. The fitting parameters of reducing sugar.

Model	T (°C)	V (m/s)	k	β	R^2
$C = C_0\exp[-k_\alpha t]^\beta$ Weibull model	55	6	0.1342	1.7943	0.9956
	60		0.1566	1.9588	0.9994
	65		0.1836	1.9982	0.9958
	70		0.2435	1.9169	0.9982
$C = C_0\exp(k_1 t)$ First-order model	55	6	–0.1149		0.9324
	60		–0.1298		0.9260
	65		–0.1483		0.9205
	70		–0.2224		0.8992
$C = C_0 + k_0 t$ Zero-order model	55	6	–1.0015		0.8667
	60		–1.1574		0.8506
	65		–1.3387		0.8307
	70		–1.8484		0.7905
$C = C_0\exp[-k_\alpha t]^\beta$ Weibull model	60	3	0.1465	1.6270	0.9914
		6	0.1573	1.6685	0.9963
		9	0.1780	1.7108	0.9987
$C = C_0\exp(k_1 t)$ First-order model	60	3	–0.1349		0.9441
		6	–0.1382		0.9441
		9	–0.1529		0.9418
$C = C_0 + k_0 t$ Zero-order model	60	3	–1.1113		0.9767
		6	–1.1872		0.9800
		9	–1.3328		0.9807

and vitamin C had a faster degradation rate at higher air velocities.

Reducing sugar degradation kinetics

The reducing sugar degradation kinetic results are given in Table 3. Based on the criteria of the highest determination coefficients (R^2 = 0.9956 – 0.9994), the Weibull model was selected as the most suitable model for reducing sugar degradation kinetics in dried samples at different temperatures. The shape constant $\beta > 1$, the degradation rate of reducing sugar increased with time. The k_α values for reducing sugar obtained through the Weibull model were 0.1342, 0.1566, 0.1836, and 0.2432 at 55, 60, 65, and 70°C, respectively. Reducing sugars had a higher degradation rate at higher air velocities. The variation of reducing sugar content showed similar changes under different air velocities with a constant drying temperature of 60°C. The degradation rate of reducing sugar increased gradually during the drying process and reducing sugar had a faster degradation rate at higher air velocities.

Total acidity change kinetics

The total acidity change kinetic results are as shown in Table 4. Based on the criteria of the highest determination coefficients (R^2 = 0.9806–0.9903), the Weibull model was selected as the most suitable model to total acidity change kinetics in samples dried at different temperatures. The values of kinetic constants (k_α) and shape constants (β) of the Weibull model were obtained by fitting the experimental data. The k_α values for total acidity obtained through the Weibull model were 0.1066, 0.1443, 0.2090, and 0.2928 at 55, 60, 65, and 70°C, respectively. The change rate of total acidity increased with the drying temperature. The β values were found 0.6106, 0.5905, 0.5799, and 0.5383, and the total acidity had a higher change rate at the beginning of the process. The variation of total acidity content showed similar change under different air velocities with a constant drying temperature of 60°C. The change rate of total acidity slowed down during the drying process, and total acidity had a faster change rate at higher air velocities.

The Weibull model has an interesting potential for describing microbial, enzymatic, and chemical degradation kinetics (Cunha *et al*., 1998). In recent years, it has been widely used to describe the changes in quality during drying, such as the drying kinetics (Aghbashlo *et al*., 2010; Uribe *et al*., 2011), the rehydration kinetics (Akar and Barutçu, 2019; Goula and Adamopoulos,

Table 4. The fitting parameters of total acidity.

Model	T (°C)	V (m/s)	k	β	R^2
$C = C_0\exp[-k_\alpha t]^\beta$ Weibull model	55	6	0.0034	0.5819	0.9806
	60		0.0095	0.6845	0.9864
	65		0.0166	0.7396	0.9892
	70		0.0427	0.9603	0.9903
$C = C_0\exp(k_1 t)$ First-order model	55	6	–0.0146		0.9352
	60		–0.0221		0.9575
	65		–0.0298		0.9735
	70		–0.0454		0.9812
$C = C_0 + k_0 t$ Zero-order model	55	6	–0.0402		0.9302
	60		–0.0493		0.9497
	65		–0.0629		0.9673
	70		–0.0741		0.9899
$C = C_0\exp[-k_\alpha t]^\beta$ Weibull model	60	3	0.0061	0.6198	0.9737
		6	0.0090	0.6587	0.9882
		9	0.0104	0.6626	0.9987
$C = C_0\exp(k_1 t)$ First-order model	60	3	–0.0184		0.9269
		6	–0.0228		0.9532
		9	–0.0266		0.9646
$C = C_0 + k_0 t$ Zero-order model	60	3	–0.0085		0.9172
		6	–0.0105		0.9446
		9	–0.0122		0.9575

2009), the changing kinetics of color (Ong *et al.*, 2012; Yang *et al.*, 2018), and the degradation of vitamin C (Santos and Silva, 2009; Wang *et al.*, 2018), of total carotenoids and total polyphenols (Eim *et al.*, 2013). Desirable fitting results were obtained in this research with the application of the Weibull model in the degradation of vitamin C and reducing sugar, and change of total acidity.

Activation energy for Weibull model parameters

Arrhenius plots of the natural logarithm of the rate constant (k) versus the inverse of T (K) for vitamin C, reducing sugar, and total acidity are shown in Figure 8. The activation energy is related to the slope of this graph and seems that the temperature dependence of the drying rate constant (k) was fitted to a linear model. The E_a values of vitamin C, reducing sugar, and total acidity were found to be 63.78, 36.48, and 153.51 kJ/mol, respectively. Activation energy usually indicates the energy required for a reaction to reach the activation state (Qiu *et al.*, 2018), the higher activation energy suggests the harder degradation of the nutrient caused by drying, and a higher temperature can accelerate the process mentioned above (Zhou *et al.*, 2017).

Discussions

This study described the changes of vitamin C, reducing sugar, and total acidity of jujube slices during the drying process and appropriate models were fitted with experimental data. However, the detection process of nutrients is complicated and easy to be affected by unexpected conditions. The indices such as moisture content and color which are easily monitored can serve to predict the variation of the nutritional components during drying if the correlation between them can be established.

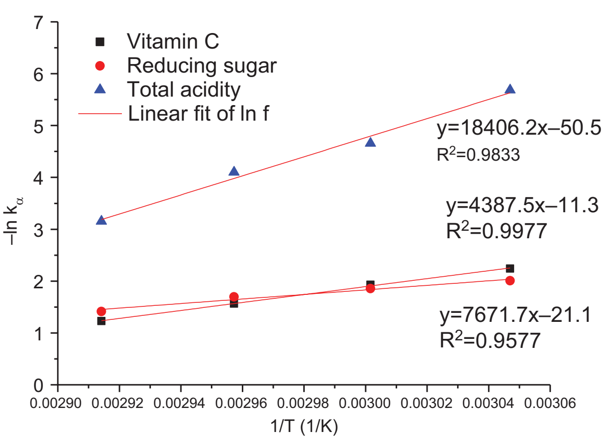


Figure 8. The fitting diagram of vitamin C, reducing sugar, and total acidity.

Conclusions

In this paper, the kinetics of nutritional quality changes of winter jujube slices during drying at different temperatures and air velocities were studied. Within the range of experimental conditions, the results were showed that: the retention of vitamin C, reducing sugar, and total acidity of winter jujube slices decreased during the drying process. Thereby, drying temperatures, time, and air velocity had a significant effect on the preserving rate of vitamin C, reducing sugar, and total acidity.

Weibull model was selected as the most suitable model for vitamin C, reducing sugar, and total acidity degradation kinetics in samples dried at different temperatures and air velocities. According to the Arrhenius formula, the activation energy of thermal degradation of vitamin C, reducing sugar, and total acidity were 63.78, 36.48, and 153.51 kJ/mol, respectively.

Acknowledgments

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