Degradation kinetics of functional components of honeysuckle flowers during controlled-atmosphere heat pump drying

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Abstract: To investigate the change law of functional components and exterior color of honeysuckle flowers (HF) during controlled-atmosphere heat pump drying, nitrogen was used as drying medium in this study to reduce the oxygen concentration. The influences of drying temperature, HF's loading amount and oxygen concentration on chlorogenic acid content, cynaroside content and *L* value (on behalf of browning degree) were explored, and the degradation kinetics models of chlorogenic acid and cynaroside were constructed. The results showed that chlorogenic acid content, cynaroside content and *L* value decreased with the rise of temperature, HF's loading amount and oxygen concentration. The degradation kinetics models of chlorogenic acid and cynaroside during the drying process were established through introducing an exponent *r* related to time *t* in the first order reaction kinetics equation. The models had good fitting precision and can be used to predict the degradation law of chlorogenic acid and cynaroside.

Keywords: honeysuckle flowers, controlled-atmosphere heat pump drying, chlorogenic acid, cynaroside, degradation kinetics

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1 Introduction

Honeysuckle flowers (HFs) are the dry buds or early opening flowers of *Lonicera japonica* Thunb. in the *Caprifoliaceae* family[1]. These flowers show pharmacological effects including anti-bacterial and anti-viral properties, protection of the liver and gallbladder, and lowering of blood pressure and blood lipid levels[2-5]. Freshly picked HFs have a moisture content of approximately 80%, and must be promptly dried[6]. As a typical moisture-containing porous colloidal material, HFs are extremely thermosensitive and moisture-sensitive[7,8], and would brown easily when dried. The browning is caused mainly by polyphenol oxidase catalyzing oxidation of polyphenols compounds[9]. *Chinese Pharmacopoeia* specifies that chlorogenic acid (CGA) and cynaroside are the major functional components of HFs[10], of which the content should be no less than 1.5% and 0.05%, respectively[1]. Drying causes oxygenolysis of CGA and cynaroside and this is the main reason of browning, which means the reduction of HFs medicinal value.

Heat pump drying is a form of drying that using a drying medium for closed circulation, achieving dehumidification through the heat pump condenser. Because the relatively low drying temperature and the closed circulation that makes it possible to change the

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drying medium, controlled-atmosphere low-oxygen drying can be realized. Thus, heat pump drying is suitable for drying thermosensitive and oxygen-sensitive materials[11-14]. Hawlader et al.[15,16] examined the influence of drying methods on material properties, and found that compared with hot air drying, controlled-atmosphere heat pump drying could significantly improve the color of the material, whose effect was similar to that of vacuum or freeze-drying. Siew and Chuang[17] suggested that compared with furnace drying or vacuum drying, heat pump drying could significantly improve the chromaticity of *Ganoderma tsugae*, reduce its ΔE value and improve the product quality. Liu et al.[18] reported that controlled-atmosphere drying of enoki mushrooms could significantly reduce browning and lower the loss rate of active ingredients in the product. Therefore, controlled-atmosphere heat pump drying is an effective method for high-quality drying of HFs.

Currently, reports on heat pump drying of HFs are focusing mainly on the drying process, whereas there was no systematic investigation on the loss of the medicinal ingredients. Wang et al.[19] studied the changes in lotus seedpod proanthocyanidin content (LSPC) at different drying temperatures, and established a first-order reaction kinetics model that could accurately predict the thermal degradation of LSPC. A study conducted by Lau et al.[20] showed that after heat treatment, changes in the texture and color of green asparagus fit a first-order kinetics model. The present study examined the changes of CGA content, cynaroside content and color appearance in HFs during controlled-atmosphere heat pump drying, and established a model for the degradation kinetics of CGA and cynaroside with a good fitting result and prediction. The research results could provide a theoretical basis for improving product quality and reducing efficacy losses during production process.

2 Materials and methods

2.1 Test materials and reagents

HF samples were purchased from the Mengjin Honeysuckle Flower Plantation in Luoyang, Henan Province, China; the variety was Yifeng No. 1. During harvesting, the leaves and fully opened flowers were removed, and only those flower buds with moderate maturity, no mechanical damage, no insect bites, and of light green color were collected as the raw material, and they were stored at 4°C before use. The operators wore clean latex gloves to avoid directly touching the HFs during harvesting and drying process. In addition, special attention was paid to minimize the flipping of the flower buds. The moisture content on dry basis of fresh HFs was 4.13-4.15 g/g.

The methanol, ethanol, and phosphate were of analytical grade; the methanol used for high performance liquid chromatography (HPLC) was HPLC grade. A CGA reference standard (National Institutes of Food and Drug Control of China, lot 110753-201314) and a cynaroside reference standard (Shanghai Qiming Biotechnology Co., Ltd., lot MUST- 13,060,908) were used.

2.2 Experimental instruments and equipment

The following equipment was used: a GHRH-20 heat pump dryer, produced by the drying equipment factory of Guangdong Provincial Institute of Agricultural Machinery (Guangdong, China); Agilent 1260 HPLC system (Column: Agilent ZORBAX SB-C18 reverse phase column, 4.6 mm × 250 mm, 5μm, UV detector (Agilent Technologies, Santa Clara, CA, U.S.); 101 electric blast drying oven (Beijing Kewei Yongxing Instrument Co., Ltd., Beijing, China); X-rite Color I5 colorimeter (Agilent Technologies, Santa Clara, CA, U.S.); TGL-18C high-speed desktop centrifuge (Shanghai Anting Scientific Instrument, Shanghai, China); KQ3200DE CNC ultrasonic cleaner (Kunshan Ultrasonic Instrument Co., Ltd., Jiangsu, China); HH-S6 digital thermostat water bath (Jintan Medical Instrument Factory, Jiangsu, China); Sartorius 200S electronic analytical balance (Sartorius AG, Göttingen, Germany).

2.3 Drying method

First, the parameters of the heat pump drying instrument were set. Before each experiment, the dryer was preheated for 30 min. The HF samples were evenly placed on the material plate, and each sample was numbered. After the material plate was placed into the drying chamber, drying started. Taken out interval between two samples was 1 h, and the dryer door was

quickly shut to continue drying. The above steps were repeated until the moisture content of the material was reduced to less than 12%, after which drying was terminated.

The oxygen concentration in the drying chamber was fixed at 21%, the HF's loading amount was fixed at 1 kg/m^2; the drying temperatures were set as 40°C, 50°C and 60°C respectively, and the various indicators of the materials were measured over time to examine the effects of different temperatures on the product quality. Next, the temperature of the drying chamber was fixed at 50°C, the HF's loading amount was fixed at 1 kg/m^2; the oxygen concentrations were set to 5%, 10% and 15% respectively, and the various indicators of the materials were measured to examine the effects of different oxygen concentrations on the drying process. Finally, the temperature of the drying chamber was fixed at 50°C, the oxygen concentration was fixed at 21%; the HF's loading amount was set to 0.8 kg/m^2, 1.2 kg/m^2 and 1.6 kg/m^2 respectively, to examine the effects of different HF's loading amounts on the drying process.

2.4 Measurement methods

2.4.1 Color measurement

After drying, a colorimeter was used to measure the Lab color representations of each sample, and the *L* (luminance) value was used to indicate the degree of browning of the sample. The higher the *L* value, the lower the degree of browning[19].

2.4.2 Measurement of CGA content and cynaroside content

HPLC conditions were set as[22-23]: flow rate: 1 mL/min; detection wavelength: 327 nm, 350 nm; column temperature: 25°C; injection volume: 10 μL; mobile phase: A: 1% phosphoric acid solution; B: 1% phosphoric acid-methanol solution (V:V=10:90); gradient elution: 0-25 min-30 min, 30% B-59% B-100% B.

Preparation of reference standard solutions: 48.3 mg CGA reference standard and 1.5 mg cynaroside reference standard were weighed with high precision. Each was dissolved in methanol and made up to a final volume of 50 mL, so mass concentrations were 966 μg/mL for the CGA and 30 μg/mL for thecynaroside reference standard solutions, respectively.

Preparation of the test solutions: Each dried sample was added 70% ethanol to 50 mL for extraction in a 70°C water bath for 2 h, and then was subjected to filtration. This was repeated once. The filtrates were combined and the total volume was set to 100 mL. Then we measured 5 mL extract, centrifuged it at 8000 r/min for 10 min, and filtered it through a 0.45 μm microfiltration membrane. Then, HPLC was used to determine the CGA and cynaroside content.

2.5 Test indicators

C was defined as the mass fraction of the main functional components in a unit mass dry HFs. To establish the degradation kinetics model for the main functional components of HFs during controlled-atmosphere heat pump drying, a dimensionless parameter, i.e., the content ratio, was introduced. It is a ratio between the content of the main functional components in a dry HFs sample *C* and the content of the main functional components in a fresh HFs sample C_0, denoted by C_R, i.e.,

$$C_R = \frac{C}{C_0} \tag{1}$$

3 Results and discussion

3.1 Linear relationship

After precise measurement, 2 μL, 4 μL, 6 μL, 8 μL and 10 μL CGA reference standards were loaded. A linear fitting between the sample volume *X* (μg) and the peak area *Y* was performed, and the CGA standard curve was obtained:

$Y = 3970.32X - 12.75$, $R = 0.99996$, linear interval 1.932-9.66 μg.

Then, 2 μL, 4 μL, 6 μL, 8 μL and 10 μL cynaroside were precisely measured and loaded. A linear fitting between the sample volume *X* (μg) and the peak area *Y* showed that the cynaroside standard curve was: $Y = 4162.93X - 2.28$, $R = 0.99999$, linear interval 0.06-0.3 μg.

3.2 Changes of CGA content, cynaroside content and *L* value under different drying parameters

3.2.1 Impacts of drying temperature on CGA content, cynaroside content and *L* value

Figure 1 shows the CGA content, cynaroside content and *L* value at different temperatures.

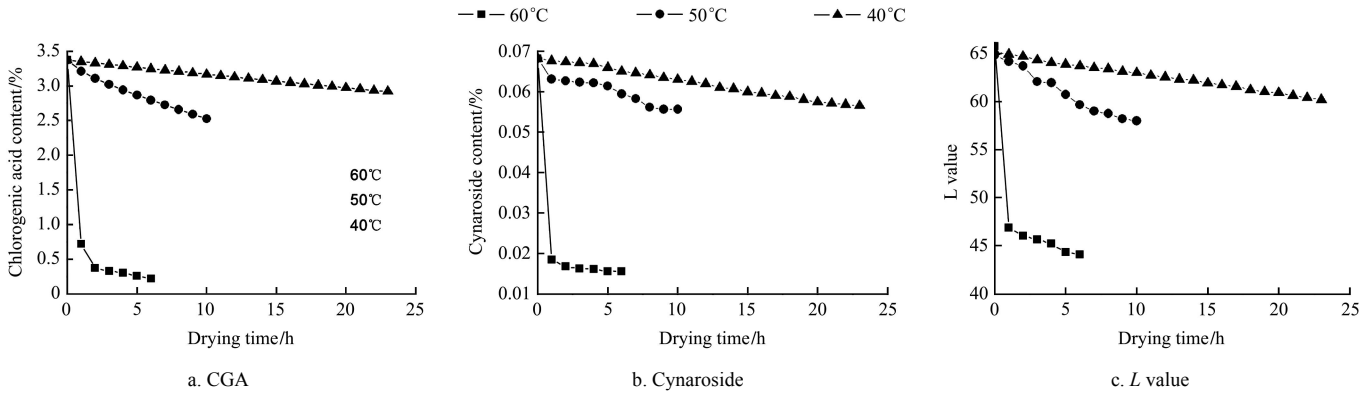


Figure 1 CGA content, cynaroside content and L values at different temperatures

All three indicators exhibited a decreasing trend with the increase of drying time. In addition, the higher the temperature was, the higher the rate of descent. At drying temperatures of 40°C and 50°C, the browning of HFs was relatively mild; at the end of the drying, CGA losses were 13.43% and 25.12%, respectively, and the cynaroside losses were 18.41% and 17.07%, respectively. At a drying temperature of 60°C for 1 h, HFs showed severe browning, and the color turned from light green to dark brown; the *L* value reduced to 46.89, CGA and cynaroside losses were 78.72% and 72.89%, respectively. This may be because the polyphenol oxidase in HFs has the highest activity in the temperature range of 50°C-60°C. In the subsequent drying process, the decline of CGA content, cynaroside content and the *L* value slowed. This might been caused by reduced enzyme activity due to the decreased moisture content of the material, changes of reaction environment due to decreased water activity, large amount of CGA and cynaroside loss, and the accumulation of reaction products.

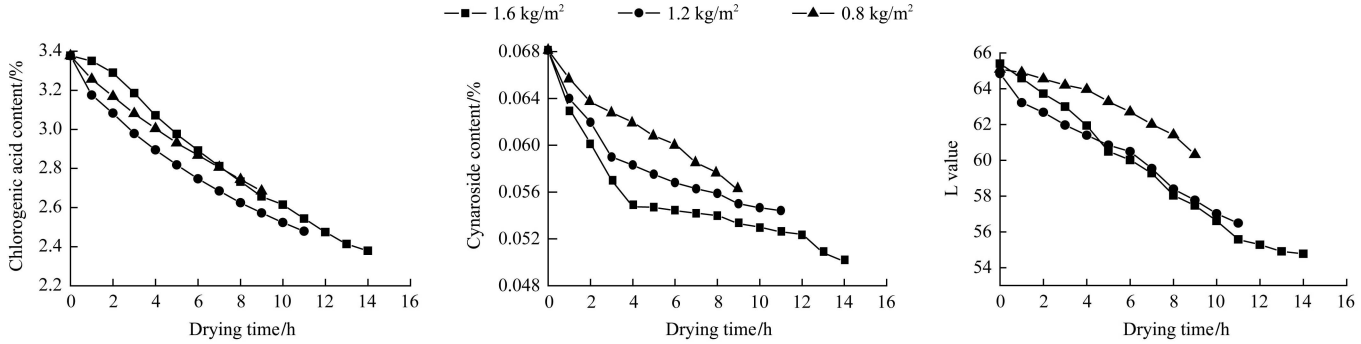
Comparisons between Figures 1a and 1c, and Figures 1b and 1c reveal that CGA content and cynaroside content associated with the *L* value. Regression analysis showed that at 40°C, 50°C and 60°C, the correlation coefficients between the CGA content and *L* value during the drying process were 0.9986, 0.9858 and 0.9977, respectively; the correlation coefficients between the cynaroside content and *L* value were 0.9969, 0.9425 and 0.9942, respectively. All correlations were positive and significant (p<0.05). Therefore, enzyme-induced browning was the main cause of the loss of HFs functional components.

3.2.2 Impact of HFs loading amount on CGA content, cynaroside content and *L* value

As illustrated in Figure 2, under different HFs loading amounts, the CGA content, cynaroside content and *L* value decreased with the increase of drying time. The larger the HFs loading amount was, the greater the loss of the functional components and the poorer the quality of the dried products at the end of the drying period. With the increase of HFs loading amount, the CGA content showed a tendency of decline first, followed by an increase. CGA is the primary substrate of the oxidation reaction catalyzed by polyphenol oxidase, and its degradation rate is largely affected by the activity of this enzyme. With the increase of HFs loading amount, water evaporation from the material slowed, and the drying process was prolonged, which extended the duration of the enzyme action. Hence, there was a greater loss of CGA content[24-25]. With the further increase of HFs loading amount, the heating rate of the material reduced, and a relatively low temperature might reduce the activity of the enzyme, thereby reduce the loss of CGA content. Unlike CGA, the cynaroside content decreased with the increase of HFs loading amount. It has been reported that flavonoids cannot be directly oxidized by polyphenol oxidase; instead, quinones catalyzed by CGA enzymes and flavonoids go through oxidative coupling[26,27]. This may explain why changes of cynaroside content in response to the HFs loading amount differ from those observed for CGA. Changes of *L* value in response to the HFs loading amount were similar to the CGA content in the early stage of drying,

indicating that enzymatic oxidation may be the main reason of HFs color deterioration.

Linear regression analysis showed that with a HFs loading amount of 0.8 kg/m^2, 1.2 kg/m^2 and 1.6 kg/m^2, the correlation coefficients between the CGA content and *L* value during the drying process were 0.9516, 0.9813 and 0.997, respectively; the correlation coefficients between the cynaroside content and *L* value were 0.9535, 0.9233 and 0.8861, respectively. All correlations were significantly positive.



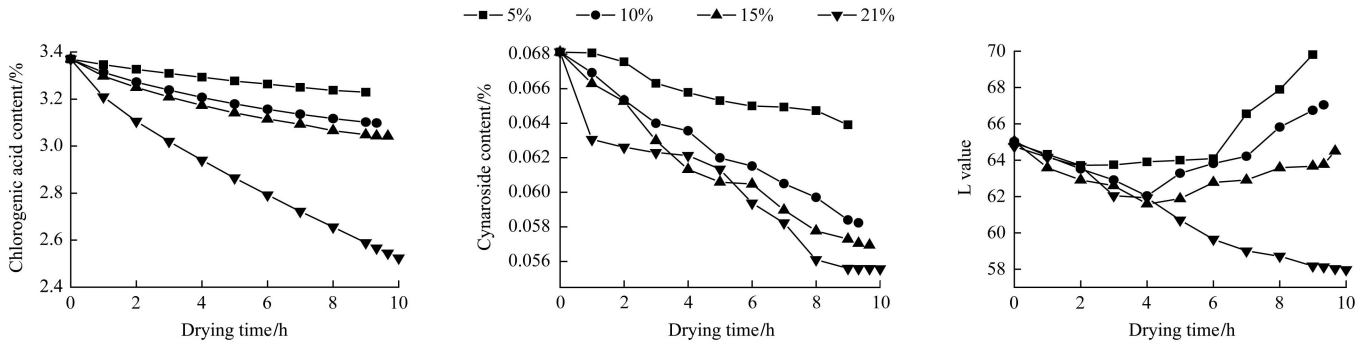
a. CGA b. Cynaroside c. *L* value

Figure 2 CGA content, cynaroside content and *L* values at different HFs loading amounts

3.2.3 Impact of oxygen concentration on CGA content, cynaroside content and *L* value

Figure 3 shows CGA content, cynaroside contents and *L* values at different oxygen concentrations.

It can be found that with extending of the drying time, the CGA content and cynaroside content showed a decreasing trend, and the lower the oxygen concentration was, the slower the decline. When regular atmospheric air was chosen as the drying medium, the CGA and cynaroside losses were 25.12% and 18.41%, respectively, at the end of the drying period. When the oxygen concentration was reduced to 5.0%, the CGA and cynaroside losses were 4.19% and 6.18%, respectively. This suggests that reducing the oxygen concentration in the drying chamber can significantly improve the retention rates of both CGA and cynaroside, and is an effective means of inhibiting browning. In an air space (drying medium) of 1 m^3 with regular atmospheric pressure (0.1 MPa), there are approximately 5.64×10^{24} oxygen molecules. After filling with nitrogen, reduce the oxygen concentration was reduced to 5%, 1 m^3 of drying medium contained approximately 1.35×10^{24} oxygen molecules[28]. Thus, lowering the oxygen concentration reduces the contact probability of CGA and cynaroside in HFs with oxygen molecules, and suppresses browning in a fundamental way.



a. CGA b. Cynaroside c. *L* value

Figure 3 CGA content, cynaroside content and *L* values at different oxygen concentrations

When regular atmospheric air was used as the drying medium, browning was the main factor that determined the color appearance of HFs. Hence, with extending of the drying time, HFs darkened, and the *L* value showed a decreasing tendency. However, when the oxygen concentration was reduced, the *L* value first declined and then increased, and the color of the HFs turned lighter. This may because browning was progressively

suppressed, and its impact on the color appearance of HFs was weakened. Subsequently, when HFs were exposed in the air for a long period of time, their original pigments (mainly chlorophyll) started to degrade, resulting in an increase in the L value after the initial decrease, and the HFs changed from bright green to light yellowish green.

Correlation analysis revealed that when regular atmospheric air was used as the drying medium for HFs, the CGA content and cynaroside content was significantly and positively correlated with the L value. However, when the oxygen concentration of the drying medium was reduced, these correlations decreased notably. This suggests that under this condition, browning is no longer the main factor that determining the color appearance of HFs.

3.3 The CGA and cynaroside degradation kinetics models

In this study, the dimensionless content ratio C_R was used to establish the CGA and cynaroside degradation kinetics models. The kinetics of the changes in the main components or functional components of the material are typically zero-order or first-order[29-30].

The zero-order kinetics equation is:

$$C_R=-kt \quad (2)$$

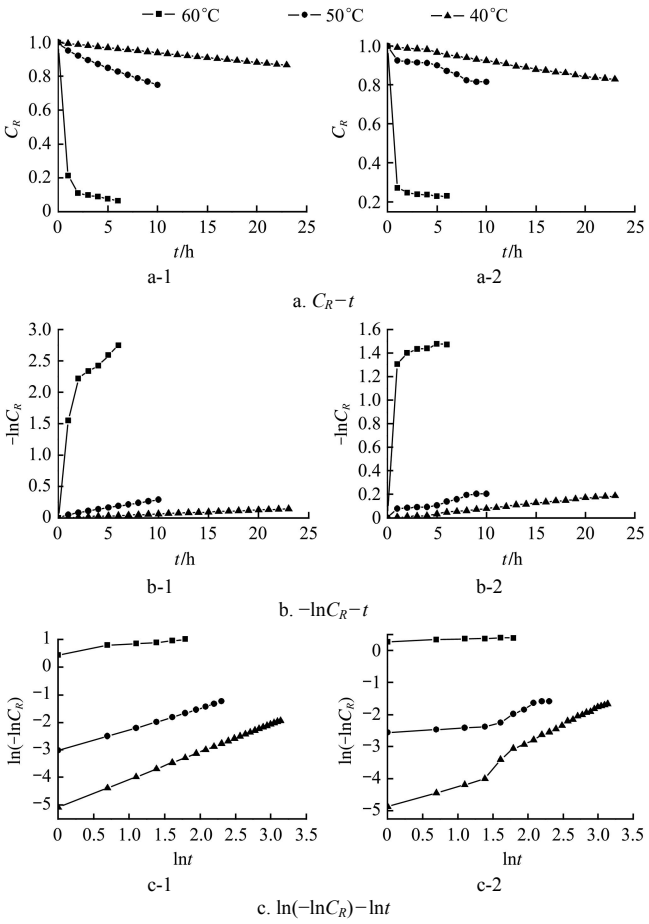
The first-order kinetics equation is:

$$\ln C_R=-kt \quad (3)$$

where, t is reaction time, h; k is reaction rate constant, h^{-1}.

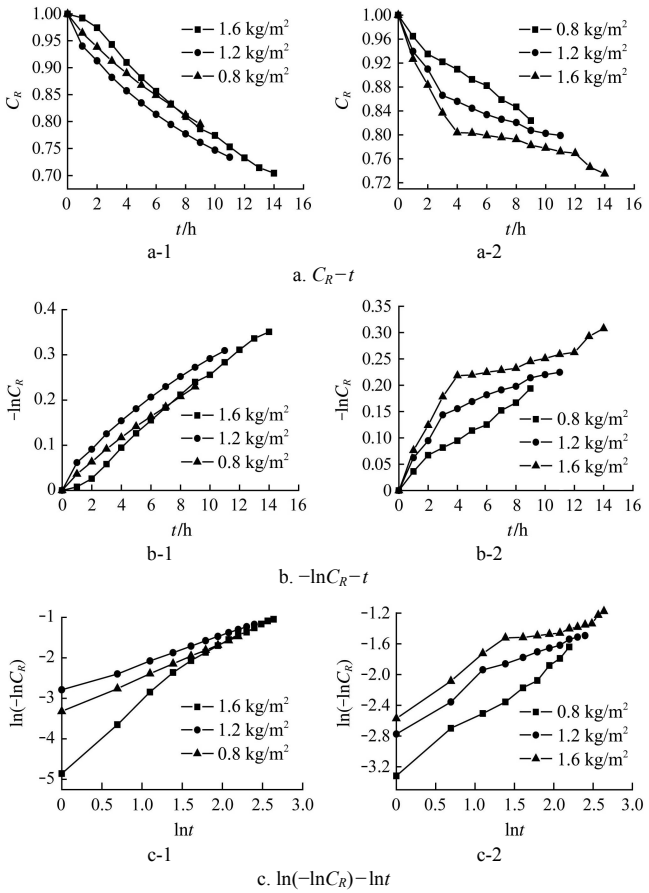
From Equations (2) and (3), it can be seen that C_R should show a linear relationship with time t (zero-order kinetics), and $\ln C_R$ should show a linear relationship with time t (first-order kinetics). The curves of the changes in the CGA content and cynaroside content with drying time t were fitted using Equations (2) and (3). The results are shown in Figures 4a, 4b-6a, 6b.

Figures 4-6 indicate that C_R and $\ln C_R$ exhibit a non-linear relationship with t[31]. The reason for this may be that the temperature went up when drying proceeded, which leads to an unstable state of the material, and this results in the non-linear or non-logarithm relationship between drying time and the degradation rate of CGA and cynaroside. To accurately represent the impact of temperature, HFs loading amount



Note: a-1, b-1, c-1: CGA, a-2, b-2, c-2: cynaroside.

Figure 4 Fitted curve at different temperatures



Note: a-1, b-1, c-1: CGA, a-2, b-2, c-2: cynaroside.

Figure 5 Fitted curve at different HFs loading amounts

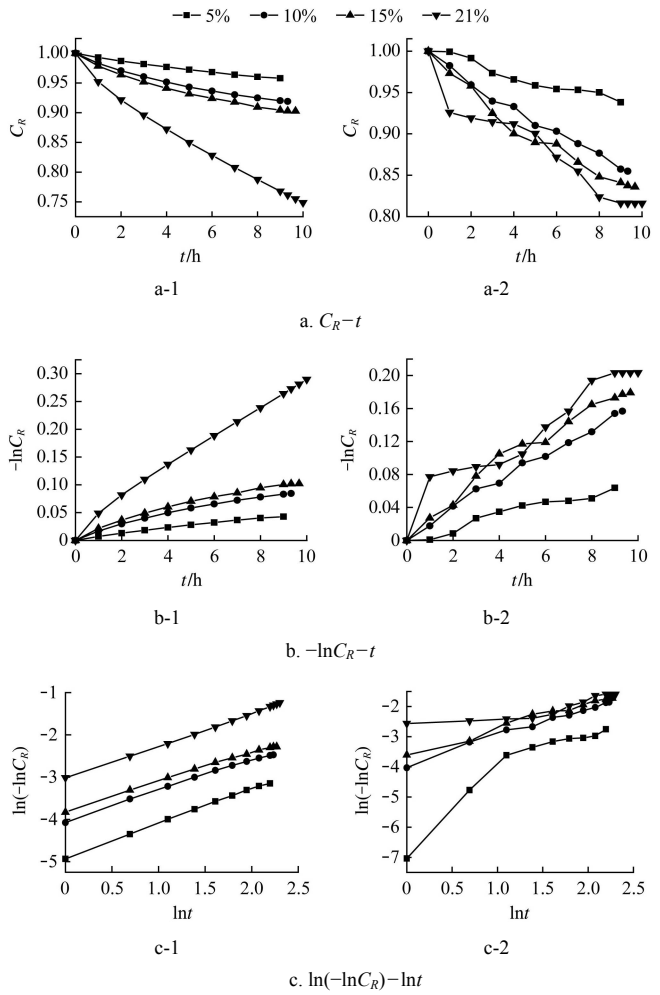
and oxygen concentration on the degradation of CGA and cynaroside during drying, the first-order kinetics equation was modified by adding an exponent r to the time parameter. In this way, the equation becomes:

$$\ln C_R = -kt^r \quad (4)$$

Taking the logarithm of both sides:

$$\ln(-\ln C_R) = \ln k + r\ln t \quad (5)$$

The curves of the changes in the CGA content and cynaroside content were fitted using Equation (5) and the results are shown in Figures 4c-6c. Compared with the previous model fitted, there is a stronger linear correlation in the $\ln(-\ln C_R)-\ln t$ coordinate system. In addition, the linear correlation for CGA is stronger than that for cynaroside. Therefore, Equation (5) can more accurately describe the degradation kinetics of CGA and cynaroside compared with Equations (2) and (3).



Note: a-1, b-1, c-1: CGA, a-2, b-2, c-2: cynaroside.

Figure 6 Fitted curve at different oxygen concentrations

3.4 Determination of model parameters

An analysis of how $\ln(-\ln C_R)$ changed with $\ln t$ under different conditions was performed. The results are shown in Tables 1 and 2. The intercept of the line is $\ln k$, with slope r.

Table 1 Fitted values of parameters in CGA degradation model

No.	Temperature /°C	Loading amount/kg·m^{-2}	Oxygen Concentration/%	r	lnk	R^2
1	60	1.0	21	0.294	0.499	0.931
2	50	1.0	21	0.770	−3.038	0.999
3	40	1.0	21	1.004	−5.082	0.999
4	50	0.8	21	0.845	−3.325	0.999
5	50	1.2	21	0.692	−2.826	0.998
6	50	1.6	21	1.405	−4.546	0.977
7	50	1.0	5	0.822	−4.915	0.999
8	50	1.0	10	0.715	−4.027	0.997
9	50	1.0	15	0.684	−3.787	0.997

Table 2 Fitted values of parameters in the cynaroside degradation model

No.	Temperature /°C	Loading amount/kg·m^{-2}	Oxygen concentration/%	r	lnk	R^2
1	60	1.0	21	0.068	0.277	0.947
2	50	1.0	21	0.477	−2.796	0.813
3	40	1.0	21	1.137	−5.189	0.982
4	50	0.8	21	0.720	−3.297	0.988
5	50	1.2	21	0.522	−2.671	0.969
6	50	1.6	21	0.454	−2.369	0.914
7	50	1.0	5	1.784	−6.290	0.881
8	50	1.0	10	0.930	−3.917	0.989
9	50	1.0	15	0.847	−3.584	0.981

As shown in Tables 1 and 2, under different drying conditions, the drying parameters r and lnk differed. For the CGA degradation model, the R^2 values were greater than 0.93; for the cynaroside degradation model, the R^2 values exceeded 0.81. Thus, it can be seen that after transformation of all experimental data, the models well descripted the changes in CGA and cynaroside during the controlled-atmosphere heat pump drying of HFs. Parameters r and lnk are functions of temperature T, HFs loading amount D and oxygen concentration V. The following quadratic equations were used to quantify the relationship between r, lnk and T, D, and V:

$$r = a_0 + a_1T + a_2T^2 + a_3D + a_4D^2 + a_5V + a_6V^2 \quad (6)$$

$$\ln k = b_0 + b_1T + b_2T^2 + b_3D + b_4D^2 + b_5V + b_6V^2 \quad (7)$$

DPS3.01 software was used for stepwise regression of multiple factors and square terms to obtain the regression equations and the corresponding variance analysis tables for the CGA and cynaroside degradation models. The results are shown as follows:

Parameters for the CGA degradation model:

$r=3.99263+0.023225T-5.09003D-0.03769V-0.00059T^2+2.38294D^2+0.00118V^2$,

$\ln k=-10.86828-0.35256T+13.29866D+0.13477V+0.00632T^2-6.10199D^2-0.00055V^2$;

Parameters for the cynaroside degradation model:

$r=6.34892-0.05346T-1.5633D-0.20634V+0.52036D^2+0.00518V^2$,

$\ln k=-10.6044-0.24527T+1.11014D+0.6053V+0.00519T^2-0.01563V^2$.

All the parameters of the regression equations were statistically significant (Table 3). The models fit the actual degradation of CGA and cynaroside during the controlled-atmosphere heat pump drying process of HFs, and are thus of practical significance.

Table 3 Analysis of variance

		R^2	Residual standard deviation	F value	Significant level α
chlorogenic acid	r	0.990	0.0058	34.284	0.05
	$\ln k$	0.995	0.227	72.727	0.05
cynaroside	r	0.969	0.1426	18.480	0.05
	$\ln k$	0.987	0.339	46.903	0.01

Two consecutive exponentiations of Equation (5) yields:

$$C_R=\exp(-kt^r) \quad (9)$$

Where, when $k=\exp(-10.86828-0.35256T+13.29866D+0.13477V+0.00632T^2-6.10199D^2-0.00055V^2)$, and $r=3.99263+0.023225T-5.09003D-0.03769V-0.00059T^2+2.38294D^2+0.00118V^2$, the equation is for CGA degradation kinetics during controlled-atmosphere heat pump drying of HFs; when $k=\exp(-10.6044-0.24527T+1.11014D+0.6053V+0.00519T^2-0.01563V^2)$, and $r=6.34892-0.05346T-1.5633D-0.20634V+0.52036D^2+0.00518V^2$, equation is for cynaroside degradation kinetics during controlled-atmosphere heat pump drying of HFs.

3.5 Model validation

To determine the fitting results between the CGA and cynaroside degradation regression equations and the experimental values, the theoretical values predicted by the models were compared with the experimental data obtained at 40°C, 1 kg/m^2, 21%, 50°C, 1 kg/m^2, 21% and 60°C, 1 kg/m^2, 21% conditions. As shown in Figure 7, the model values fit the experimental values well; for CGA and cynaroside, R^2 values were 0.99884 and 0.99858, respectively. At any time point, the relative deviations (relative deviations = |experimental value − model value|/experimental value) were smaller than 5.44% and 2.99% for CGA and cynaroside, respectively. This suggests that the established model can well characterize the degradation kinetics of CGA and cynaroside during controlled-atmosphere heat pump drying of HFs.

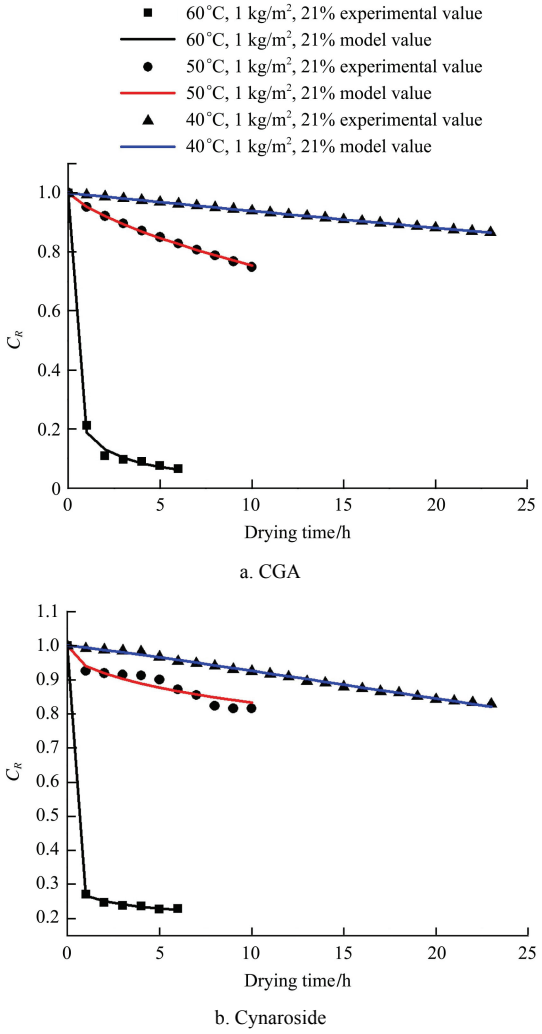


Figure 7 Comparison between the experimental values and model values

4 Conclusions

1) Drying temperature, HFs loading amount and oxygen concentration in the drying chamber significantly affected the CGA content, cynaroside content and L value during controlled-atmosphere heat pump drying of HFs. Under higher temperatures, greater HFs loading amounts, or higher oxygen concentration, the CGA and cynaroside

losses became greater, and the *L* value reduced at end point. Reducing the oxygen concentration in the drying chamber could significantly increase the retention rate of CGA and cynaroside, and is an effective means of suppressing browning.

2) Significant positive correlations were obtained when regular atmospheric air served as the drying medium during heat pump drying of HFs; the correlation coefficient between the *L* value and CGA content exceeded 0.95, and the correlation coefficient between the *L* value and cynaroside content was greater than 0.88. When reducing the oxygen concentration in the drying chamber to 5%, the correlations between the *L* value and contents of CGA and cynaroside were no longer significant.

3) In the controlled-atmosphere heat pump drying of HFs, the degradation kinetics of CGA and cynaroside did not follow zero-order and first-order reaction kinetics. By taking the logarithms and linearizing the experimental data and introducing an exponent *r* to the time *t* in the first-order reaction kinetics, a model equation for the degradation kinetics of CGA and cynaroside during the drying process was obtained.

4) Results of validation test showed that the model values well fit the experimental values. Hence, the established model can be used to predict and characterize the degradation of CGA and cynaroside during the controlled-atmosphere heat pump drying of HFs.

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