Drying Kinetics and β-Carotene Degradation in Carrot Undergoing Different Drying Processes

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ABSTRACT: Superheated steam drying, which is an airless drying technology, has recently received much attention as an alternative to conventional hot air drying, which is a relatively oxygen-rich drying process and causes much product quality degradation. However, because most food products are damaged when subjected to superheated steam at atmospheric or higher pressures, lowering the dryer operating pressure is preferred. In this study, the effects of a low-pressure superheated steam drying (LPSSD), vacuum drying, and hot air drying on the drying and degradation kinetics of β-carotene in carrot were investigated experimentally. LPSSD and vacuum drying led to less degradation of β-carotene in carrot than in the case of hot air drying. The empirical models, which can describe the experimental data of β-carotene degradation in carrot undergoing different drying techniques, were also proposed. β-Carotene degradation in carrot depended more on the carrot temperature than its moisture content in all cases.

Keywords: empirical correlations, hot air drying, low-pressure superheated steam drying, vacuum drying

Introduction

In recent years, the consumption of carrot and its related products has increased steadily due to the recognition of antioxidant and anticancer activities of β-carotene in carrot, which is also a precursor of vitamin A (Speizer and others 1999; Dreosti 1993). However, in food industry, especially instant food industry, carrot must usually be dried prior to its use. Several techniques have been used to dry carrot with the goal of maintaining its natural appearance as well as its nutritional values, including β-carotene, to the maximum level possible.

Many studies (Mulet and others 1989; Ratti 1994) were performed to study hot air drying of carrot of various shapes. It was found that hot air-dried carrot was characterized by the low porosity and the high apparent density nature (Krokida and Moroulis 1997). Khraisheh and others (1997) found that the increased density and shrinkage of carrot was dependent on the operating temperature of hot air drying. Significant color changes also occurred during hot air drying of carrot (Krokida and others 1998) and the change of its red color was attributed to the changing level of β-carotene (Lin and others 1998).

Vacuum drying is an alternative technique to improve the quality of dehydrated heat-sensitive products, including carrot. Krokida and others (1997) found that vacuum drying was able to yield higher porosity and redder carrot than that dried by hot air.

During the past decade, there has been considerable interest in applying superheated steam to dry various food products with some success (Sayed-Yagoobi and others 1999; Moreira 2001; Caixeta and others 2002). Despite the many advantages of near-atmospheric pressure superheated steam drying (Devahastin and Suvarnakuta 2004), there still exist some limitations, especially when applying it to drying heat-sensitive materials, for example, foods and bio-products (Mujumdar 2000). Because most foods or other heat-sensitive products are damaged at the saturation temperature of superheated steam corresponding to the atmospheric or higher pressures, one possible way to alleviate the above-mentioned problems is to operate the dryer at reduced pressure.

Recently, the concept of low-pressure (or sub-atmospheric pressure) superheated steam drying (LPSSD) has been applied to various types of heat-sensitive materials. Elustondo and others (2001) studied sub-atmospheric pressure superheated steam drying of shrimp, banana, apple, potato, and cassava slices both experimentally and theoretically. A semi-empirical mathematical model was developed, and it was found to predict the drying kinetics reasonably well. However, no mention about the quality of dried food products was given. More recently, Devahastin and others (2004) studied experimentally drying of carrot cubes both in low-pressure superheated steam and vacuum dryers. The effects of operating pressure and temperature on the drying characteristics as well as various physical properties, i.e., volume, shrinkage, apparent density, color and rehydration behavior, of the dried carrot subjected to the 2 processes were evaluated. It was observed that steam drying provided better rehydration and redder dried carrot than that obtained in vacuum drying although the drying time in the former case was slightly longer. No mention about the chemical (nutritional) quality changes of carrot during drying was given, however.

The objective of this study was, therefore, to investigate experimentally the effects of a low-pressure superheated steam drying as well as other drying techniques, hot air and vacuum drying, on the drying kinetics and degradation of β-carotene in carrot undergoing these drying operations. Simple relationships between the amount of β-carotene and the product moisture content as well as temperature were also developed for all drying processes studied.

Material and Methods

Experimental setup

A schematic diagram of the low-pressure superheated steam dryer and its accessories is shown in Figure 1. The dryer consists of a stainless steel drying chamber, insulated with rock wool; a steam reservoir, which received steam from a boiler; and a liquid ring vac-

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uum pump (Nash, model ET32030, Nuremberg, Germany), which was used to maintain the vacuum in the drying chamber. A steam trap was installed to reduce the excess steam condensation in the reservoir. An electric heater, which was controlled by a Proportional-Integral-Derivative (PID) controller (Omron, model E5CN, Tokyo, Japan), was installed in the drying chamber to control the steam temperature and to minimize the condensation of steam in the drying chamber during the start-up period. With the use of a heater, the initial steam condensation during the start-up period was reduced considerably. An electric fan was used to disperse steam throughout the drying chamber. The change of the weight of the sample was detected continuously using a load cell (Minebea, model Ucg-3kg, Nagano, Japan). The temperatures of the sample and of the sample were measured continuously using type K thermocouples. Thermocouple signals were then multiplexed to a data acquisition card (Omega Engineering, model no. C10-DA16Jr., Stamford, Conn., U.S.A.) installed in a PC. Labtech Notebook Software (version 12.1, Laboratory Technologies Corp., Middleboro, Mass., U.S.A.) was used to read and record the temperature data. More detailed experimental setup can be found in Devahastin and others (2004). For vacuum-drying experiments, the same experimental set-up was used but without the application of steam to the drying chamber. Hot air–drying experiments were performed in a lab-scale tray dryer with an installed balance to monitor the weight change of the drying sample. The temperatures of the air and of the sample were measured continuously using the above-mentioned measuring equipment. The air velocity through the dryer was maintained at 0.8 m/s.

Sample preparation

Fresh carrot (*Daucus carota var. sativa*) was obtained from a supermarket and stored at 4 °C. Prior to the start of each drying experiment, carrot was peeled and diced (only the cortex part) into 1 cm³ cubes. The moisture content of the fresh carrot was determined by drying it at 105 °C for 12 h in a hot air oven (Memmert, model 800, Schwabach, Germany).

Drying experiments

Raw carrot cubes were dried using 3 different methods: LPSSD, vacuum drying, and hot air drying.

To perform an LPSSD experiment, approximately 35 cubes of carrot (about 40 g) were placed as singer layer on the sample holder.

Figure 1—A schematic diagram of the low-pressure superheated steam dryer and associated units: 1, boiler; 2, steam valve; 3, steam reservoir; 4, pressure gauge; 5, steam trap; 6, steam regulator; 7, drying chamber; 8, steam inlet and distributor; 9, electric fan; 10, sample holder; 11, electric heater; 12, on-line temperature sensor and logger; 13, vacuum break-up valve; 14, insulator; 15, on-line weight indicator and logger; 16, vacuum pump; and 17, PC with installed data acquisition card.

More detailed procedures of an LPSSD experiment can be found in Devahastin and others (2004). Although only 40 g of the sample was used, the results reported here should be applicable to future commercial drying applications if care is made in maintaining the same drying conditions in an industrial dryer. The experiments were performed at the steam absolute pressure of 7 kPa and the steam temperatures of 60, 70, and 80 °C. The flow rate of steam into the drying chamber was maintained at about 26 kg/h and the speed of the fan was fixed at 1100 rpm.

For vacuum-drying experiments, the same operating conditions were used but without the application of steam to the chamber. For hot air drying, the experiments were performed at the drying temperatures of 60, 70, and 80 °C at an atmospheric pressure.

To determine the relationship between the β-carotene content of carrot and its moisture content as well as temperature, the drying carrot was sampled and its β-carotene content was measured at a predetermined sampling time; that particular experiment was ended at that time. A new experiment was then performed until the next predetermined sampling time was reached. The β-carotene content of the fresh sample was also measured, so a direct comparison could be made between the fresh and dried samples. The same procedure was repeated until the complete relationship, valid over the whole range of moisture content of interest, was obtained. All experiments were performed in duplicate.

β-Carotene analysis

Drying samples were sampled at different drying times and stored in sealed aluminum foil bags to protect them from light at –18 °C prior to the β-carotene analysis. The samples were thawed at room temperature before the analysis.

The β-carotene analysis method used was a modification of that suggested by AOAC (2000), and the high-performance liquid chromatography (HPLC) method described by Howard and others (1999). To extract β-carotene, dried carrot was prepared by grinding 5 to 8 g of the sample for 2 min using a stainless steel pulverizer (Waring, model SS110, Torrington, Conn., U.S.A.). The ground sample was then placed in a flask filled with 40 mL of ethanol. Forty milliliters of 2 N potassium hydroxide was added to saponify the solution at 70 °C for 30 min. The extract was then cooled to 0 °C. β-Carotene was then extracted twice with 5 mL diisopropyl ether and the aqueous layer was discarded. The extracted solution was diluted by a mobile phase and was filtered through a 0.45 μm filter before injecting 10 μL of the sample into the liquid chromatograph column.

Symmetry® C18 5 μm (3.9 × 150 mm) HPLC column (Waters, Milford, Mass., U.S.A.) was used for β-carotene analysis. The HPLC system consists of a pump and a controller (Waters, model 600), a tunable absorbance detector (Waters, model 486), and an auto sampler (Waters, model 717 Plus). A mixture of methanol and acetonitrile (90:10) was used as the mobile phase, and its flow rate was set at 1.5 mL/min. An ultraviolet spectrophotometer detector at a wavelength of 450 nm was used for detecting β-carotene. The mobile phase was degassed using an ultrasonic generator. An HPLC β-carotene standard (Sigma, C4582, Steinheim, Germany) was run daily with the samples to accurately characterize the retention time of β-carotene. Quantification of β-carotene was carried out based on the β-carotene standard curve. The concentration of β-carotene was calculated from the relative peak area of the β-carotene standard curve. The standard curve was prepared daily by injecting solutions of HPLC β-carotene standard in diisopropyl ether at 6 concentrations (0, 2, 4, 6, 8, and 10 μg/mL) and recording their respective absorbance values. All standard curves showed good linearity ($R^2 > 0.99$). A typical chromatogram of β-carotene is shown in Figure 2.

The measured total β-carotene content is expressed in this work
in terms of the β-carotene retention ratio:

\[
\text{β-carotene retention ratio} = \frac{\beta_t}{\beta_i}
\]

where \( \beta_i \) and \( \beta_t \) are, respectively, the β-carotene contents of fresh carrot and dried carrot at the end of each drying experiment (mg/100 g dry solid). All β-carotene measurements were performed in duplicate, and the data presented are an average of the 2 measurements.

### Statistical analysis
The data were analyzed and presented as mean values with standard deviations. Differences between mean values were established using Duncan’s multiple range test. Values were considered at 95% level of significance (\( P < 0.05 \)) and a statistical program SPSS (version 10.0, Chicago, Ill., U.S.A.) was used to perform the calculation.

### Results and Discussion

#### Drying kinetics of carrot
The drying curves and temperature profiles of carrot (initial moisture contents of 9.5 to 10 kg/kg dry solid (dry basis) or 905 to 909 kg/kg sample (wet basis) undergoing different drying techniques at drying temperatures of 60 to 80 °C are shown in Figure 3. The chosen operating conditions were those of Devahastin and others (2004). The drying times needed to dry carrot to the final moisture content of about 0.1 kg/kg (d.b.) are listed in Table 1.

As illustrated in Figure 3, although vacuum drying was a faster drying process than LPSSD and hot air drying, previous studies (Devahastin and others 2004; Suvarnakuta and others 2005) have shown that the differences between the drying times of LPSSD and vacuum drying were smaller at higher drying temperatures. Raising the drying temperature further would eventually lead to equal rates of drying at the so-called inversion temperature due to the increased temperature difference between the steam and the surface temperature of carrot as well as a reduction of the initial steam condensation, which is inevitable in any superheated steam drying applications (Mujumdar 2000). Although LPSSD generally required longer drying time than vacuum drying, LPSSD provided better product physical properties, i.e., better rehydrated and redder dried carrot, than that obtained by vacuum drying over the operating temperature range of 60 to 80 °C and operating pressure of 7 kPa used in this work (Devahastin and others 2004).

In the case of hot air drying, it can be seen in Figure 3 that the drying rates during the 1st 80 min were higher than those of LPSSD. Although the hot air drying rates (slope of the drying curves) in the constant rate period were higher than those of LPSSD, hot air drying...
took as much time to dry carrot to the final desired moisture content as did LPSSD. This is because the falling rate period of hot air drying was longer than that of LPSSD. In the constant rate period, the water removal carried out by evaporation from the carrot surface in the case of LPSSD took longer time than in the case of hot air drying due to a smaller temperature difference between the drying medium (steam) and the carrot surface (if drying was carried out below the inversion temperature, as in this case). On the other hand, in the falling rate period, LPSSD was faster than hot air drying due to the more porous structure of carrot as well as the higher water diffusivity in the case of steam drying. Therefore, the 2 sets of overall drying times were not much different.

For more detailed information about the drying behavior of carrot cube undergoing LPSSD and vacuum drying the reader is referred to Devahastin and others (2004).

**Degradation kinetics of β-carotene**

The β-carotene retention in carrot during drying is presented in Table 1. The β-carotene content in fresh carrot on a dry solid basis (51.11 mg/100 g solid) was close to 54 mg/100 g solid documented by Chen and others (1993). The β-carotene content of fresh carrot varied slightly according to its maturity and initial moisture content. The ratio of the β-carotene content of fresh carrot and the dried one (β-carotene retention ratio) was then used to report the results in this study.

As seen in Table 1, all dried carrot cubes lost some β-carotene as compared with fresh ones. However, the loss of β-carotene in the case of hot air drying was significantly \((P < 0.05)\) higher (about 21% to 25%) than those observed when drying carrot by other processes to a similar level of moisture content of 0.1 kg/kg (d.b.). LPSSD and vacuum drying could, therefore, reduce the loss of β-carotene to some extent. The ability of LPSSD to conserve heat and oxygen-sensitive products (such as vitamin C) has indeed been shown earlier (Methakhup and others 2005).

It is known that carotene is degraded by free radical oxidation mechanism and that the degree of oxidation depends on the heating time, heating temperature, and oxygen content. In this case, hot air drying was the only non-airless process and, hence, caused more aerobic degradation of β-carotene compared with the other drying processes. These results were similar to those reported by Lin and others (1998) who compared β-carotene contents of carrot slices at a moisture content of 10% (d.b.) underwent vacuum microwave, air drying, and freeze drying. They reported that air drying resulted in the highest loss of β-carotene and the rapid heating and depletion of oxygen offered by vacuum microwave could reduce the loss of β-carotene.

Based on the experimental data, it was found that the total β-carotene retention in the cases of LPSSD and vacuum drying was higher than in the case of hot air drying. This is because of the oxygen-free environment of the LPSSD drying chamber. In the case of vacuum drying, however, because the level of vacuum pressure used in this study was not that low (7 kPa absolute), there still existed some oxygen that could participate in an oxidation reaction. The effect of aerobic degradation of β-carotene could not, therefore, be negligible, although its extent was still lower than in the case of hot air drying.

The relationships between the β-carotene content and the moisture content of carrot undergoing LPSSD, vacuum drying, and hot air drying are shown in Figure 4. As mentioned earlier, the level of oxidation, which is the major cause of carotene losses, depends in part on
the available oxygen content in the drying chamber. It can be seen from this figure that the level of β-carotene dropped rapidly during the start-up period of drying in all cases. This is due to the fact that moist carrot was immediately subjected to heat treatment, and there might still be some oxygen remained for oxidation initially.

It is seen from Figure 4c that the β-carotene content of carrot decreased continuously in the case of hot air drying while the levels of β-carotene in carrot undergoing LPSSD and vacuum drying remained relatively unchanged (Figures 4a and 4b) after the initial start-up period. This is due to the fact that in the case of hot air drying, lipoxygenase, and probably peroxidase, which are aerobic catalysts of an oxidation reaction, which are contained in unblanched carrot like the one used in this study, was activated significantly at temperatures in the range of 60 to 65 °C (Cui and others 2004). Therefore, it is seen that β-carotene degraded continuously in the case of hot air drying when product temperature increased to this range.

The negligible changes (until the moisture content of around 2 kg/kg [d.b.]) of β-carotene after the initial drop in the case of LPSSD might be explained by the fact that the activity of lipoxygenase and peroxidase, which are responsible for the oxidative degradation of β-carotene, was greatly reduced due to several possible effects, including the lower oxygen level in the drying chamber and the lower product temperature (see Figures 3a and 3c). After some period of time, the temperature of carrot undergoing LPSSD started to rise again. This rise induced additional degradation of β-carotene. At the drying temperature of 60°C, for example, this rise of temperature occurred after 300 min of drying or at moisture contents of less than 2 kg/kg (d.b.). The corresponding degradation of β-carotene can be seen clearly in Figure 4.

Comparison between vacuum drying and LPSSD revealed that the β-carotene retention differed slightly between the 2 processes although vacuum drying took much shorter time than LPSSD to dry the sample to the desired moisture content (Figures 3 and 4). This is because the LPSSD chamber was fully contained with superheated steam; therefore, the oxygen content remaining in the LPSSD chamber was less (none indeed) than in the case of vacuum drying chamber. In addition, the product temperature of all vacuum drying cases was higher than LPSSD cases (Figure 3), thus thermal stability of β-carotene was decreased in the case of vacuum drying. Moreover, the change of the shape of carrot undergoing LPSSD was much more uniform than in the case of vacuum drying. This result was consistent with our previous findings (Devahastin and others 2004). Thus, the LPSSD product had less surface area for heat transfer and hence had higher β-carotene retention.

**Empirical models**

Figure 5 illustrates the relationship between the β-carotene content and the product temperature during different drying processes. It is seen that β-carotene degraded continuously as the product temperature increased, especially in the case of hot air drying. Because there was no period of constant carrot temperature that corresponded to the constant rate of β-carotene degradation, the use of a kinetic model of β-carotene degradation that refers to an elementary reaction expression and the Arrhenius equation was not appropriate. Therefore, in this study, simple empirical models that enable prediction of the β-carotene degradation as a function of carrot moisture content and temperature were instead proposed. Although, as can be seen in Figure 5c, there were periods of rather constant temperature, which corre-
responded to the constant degradation rate of β-carotene toward the end of hot air drying, no attempt was made to consider only these rather short periods for a simple elementary reaction expression.

A simple empirical model that enables prediction of the β-carotene degradation as a function of carrot moisture content and temperature during LPSSD, vacuum and hot air drying was proposed in the following form:

\[
\frac{\beta_i}{\beta_f} = a + b \left( \frac{X_i}{X_f} \right) + c \left( \frac{T_i}{T_f} \right)^2 + d \left( \frac{T_i}{T_f} \right)^3 + e \left( \frac{X_i}{X_f} \right)^2 + f \left( \frac{X_i}{X_f} \right)^3 + g \left( \frac{T_i}{T_f} \right)^3
\]  

(2)

where \( \beta_i \) and \( \beta_f \) are the initial and instantaneous β-carotene contents (mg/100 g solid), respectively. \( X_i \) and \( X_f \) are the initial and instantaneous moisture contents (kg/kg, d.b.), respectively. \( T_i \) and \( T_f \) are the initial and instantaneous temperatures of carrot (°C), respectively. \( a, b, c, d, e, f, g \) are empirical constants.

The following equations were fitted to the experimental data and the fitted equations were evaluated based on their \( R^2 \) and absolute mean error of estimation. The absolute mean error values are 0.015, 0.031, and 0.012 for the case of LPSSD, hot air drying, and vacuum drying, respectively.

For LPSSD:

\[
\frac{\beta_i}{\beta_f} = 1.104 + 0.261 \left( \frac{X_i}{X_f} \right) - 0.192 \left( \frac{T_i}{T_f} \right) - 0.56 \left( \frac{X_i}{X_f} \right)^2 - 6.61 \times 10^{-3} \left( \frac{T_i}{T_f} \right)^2 + 0.39 \left( \frac{X_i}{X_f} \right)^3 + 0.01 \left( \frac{T_i}{T_f} \right)^3
\]

(3)

\( R^2 = 0.911 \)

For vacuum drying:

\[
\frac{\beta_i}{\beta_f} = 0.754 + 0.596 \left( \frac{X_i}{X_f} \right) - 0.359 \left( \frac{T_i}{T_f} \right) - 0.708 \left( \frac{X_i}{X_f} \right)^2 + 0.22 \left( \frac{T_i}{T_f} \right)^2 + 0.51 \left( \frac{X_i}{X_f} \right)^3 - 0.038 \left( \frac{T_i}{T_f} \right)^3
\]

(4)

\( R^2 = 0.90 \)

For hot air drying:

\[
\frac{\beta_i}{\beta_f} = 0.663 + 0.742 \left( \frac{X_i}{X_f} \right) + 0.165 \left( \frac{T_i}{T_f} \right) - 1.406 \left( \frac{X_i}{X_f} \right)^2 - 0.136 \left( \frac{T_i}{T_f} \right)^2 + 0.94 \left( \frac{X_i}{X_f} \right)^3 + 0.026 \left( \frac{T_i}{T_f} \right)^3
\]

(5)

\( R^2 = 0.982 \)

It can be seen from the above simple empirical relationships that the β-carotene retention depends on both the product moisture content and temperature. It should be noted that these empirical equations are based on the experimental results and conditions used in this study only. It can be seen also that the carrot temperature was the main contributor of β-carotene degradation. It is observed from the values of the main parameters of these equations (the terms of 3rd order and \( 0 < \frac{X_i}{X_f} \leq 1, 1.5 \leq \frac{T_i}{T_f} \leq 3.2 \)) that the effect of carrot temperature was larger than the effect of carrot moisture content on the β-carotene degradation of carrot during drying. This is because heat is the main reason for β-carotene degradation, especially in the low-oxygen system. Product temperature was.
therefore, the major player of the β-carotene degradation in the cases of LPSSD and vacuum. In the case of hot air drying, although the product temperature also affected more significantly the β-carotene degradation compared with the effect of moisture content, the effect of the product temperature was less obvious than in the cases of airless drying systems. This is due to the fact that for hot air drying the main cause of β-carotene degradation was the oxygen content available to an oxidative reaction of β-carotene in the drying chamber. Therefore, the effect of the product temperature was somehow overshadowed.

Conclusions

Comparison was made of the β-carotene degradation in carrot undergoing different drying techniques, such as LPSSD, vacuum drying, and conventional hot air drying. It was found that LPSSD and vacuum drying led to less degradation of β-carotene of carrot than in the case of hot air drying (up to 20% to 25% in the case of LPSSD). The empirical models, which can describe the experimental data of β-carotene degradation in carrot undergoing different drying techniques, were also proposed. The information obtained here can be used as a guideline in the design and operation of a system, which is suitable for drying heat- and/or oxygen-sensitive bio-products with the aim to minimize the quality losses of these products.

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