



Kinetics of Reshteh Khoshkar Color Changes During Atmospheric and Vacuum Deep-fat Frying

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ABSTRACT

The effect of frying pressure on the kinetics of color changes during atmospheric and vacuum deep fat frying of Reshteh Khoshkar has been studied. The Hunter color parameters redness, yellowness, lightness and total color difference were used to estimate color changes during frying as a function of process. Lightness (L^*) decreased from 85.37 to 75.01 with vacuum frying time, while redness (a^*), yellowness (b^*) and total color difference increased from -2.09, 4.92 and 0 to 1.22, 37.01 and 31.56, respectively. It was observed that the severity of colour change was higher in atmospheric frying process than the vacuum frying process. The changes in color parameters were modeled by zero-order, first-order and a combined kinetics model. The two first-order and combined kinetics models fitted properly the values of color changes during frying, with good coefficient of determination. The combined model used can describe the experimental colour parameters better than the other studied kinetics models.

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1. INTRODUCTION

Reshteh Khoshkar is one of the favorite local sweets in north of Iran-Gilan province. Reshteh Khoshkar is made from rice flour which is fried by deep-fat frying. Due to its flexibility and versatility and the sensory properties of the fried products, frying is widely accepted as a food preparation method [1]. Remarkable oil absorption is observed during frying. However, numerous studies have confirmed that an excessive eating of fried food has a significant adverse effect on health, leading to an increased incidence of coronary heart disease, hypertension, diabetes or cancer [2]. For this reason, numerous studies have been published on frying technology in recent years with the aim of providing nutritional and safe products to satisfy the expectations of consumers [3]. Vacuum-frying is defined as frying carried out at pressures below atmospheric levels [4, 5]. Several advantages has been attributed to this

technology such as: (1) reduced oil and fat content in the fried product; (2) the preservation of natural organoleptic properties especially flavors and color due to the deficiency of oxygen and the low temperature during the frying process; (3) fewer harmful effects on oil quality for longer times [6]; (4) a decreased acrylamide content [7], and (5) the preservation of nutritional compounds [8-10].

Among the different properties of fried Reshteh Khoshkar, color is considered as the most significant visual quality in the perception of the Reshteh Khoshkar quality, which directly affects the consumer acceptance. In other words, the color of the fried product is almost the first physical parameter evaluated by consumers. When Reshteh Khoshkar is fried, physicochemical changes of components affect its color. The color formation is the result of the Maillard reaction, nonenzymatic browning reactions between amino acids or proteins, reducing sugars at the surface, caramelization, involving the removal of water and thermal break down of sugars without amine participation [11].

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In recent years, color kinetics studies have been oriented to thermal processing of different food materials [12-15]. Karim et al. [16] studied the effects of coagulants and carrageenan on tofu color, concluded that the coagulants affect the tofu color more than the carrageenan. Cai et al. analysed tofu color to compare its qualities from bench and production scale processes [17]. Krokida et al. applied a first order kinetics model to explain color changes of French fries during deep fat frying process [2]. The effect of process variables, such as oil temperature, cross-sectional thickness of the sample and concentration of hydrogenated cotton seed oil in total oil, on color parameters during deep-fat frying were returned into reaction rate constant (k) using empirical approaches. Ateba and Mittal modeled crust color kinetics of meatballs during frying using first-order reaction kinetics [18].

The objective of present work was to investigate; (1) production of Reshteh Khoshkar by atmospheric and vacuum frying, (2) the kinetics of visual color using Hunter tristimulus color scale during deep-fat frying of Reshteh Khoshkar to predict the color change during frying.

2. MATERIALS METHOD

2. 1. Sample Preparation The rice flour (Hashemi variety) procured from local market was sieved using BS 200 mesh to get very fine flour (<75 μ m). Rice flour and distilled water equally were mixed at ambient temperature for 25 minutes at the lowest speed of a mixer (Mashhad Baking Industries Co, Iran). The resulting paste was mixed with distilled water to produce suspension. The suspension was poured in specific mould. A cupric tray was placed over moderate heat to warm it up and slurry mix was poured on hot tray. After cooking and preparing of Reshteh Khoshkar they were folded and then sizes sized (10 \times 4 \times 0.65cm³) using a sharp knife.

2. 2. Frying Equipment Both vacuum frying and atmospheric frying were carried out using an electrically heated, 8L stainless steel vessel covered with a stainless steel (316L) lid, which was thermostatically controlled to maintain the set frying temperature (\pm 1 $^{\circ}$ C) using a temperature control system (Micro-controller X, model PXR4, Fuji Electric Instruments, Japan). In vacuum frying experiments, the frying vessel was connected to a two-stage high vacuum pump (model DV-48 N 250, Platinum, USA) with the capacity to generate a vacuum up to 6.5kPa (which corresponds to a water boiling point of approximately 38 $^{\circ}$ C). For the atmospheric frying experiments, the same procedure and equipment were used but the vacuum pump was switched off [9].

2. 3. Frying Conditions In both sets of experiments, the fryer vessel was filled with 8 L of sunflower oil (NINA, Iran), which was preheated to frying temperature for 1 h prior to frying and discarded after 3 h of frying. Frying carried out in tow different pressures (47.4 and 101.325kPa). Equivalent thermal driving forces were used in both processes. The thermal driving force was defined by Mariscal and Bouchon as the difference between the oil temperature and the boiling point of water at the working pressure [9, 19]. To compare the atmospheric frying to the vacuum frying, an oil temperature of 160 $^{\circ}$ C was considered for vacuum frying. For the atmospheric frying experiments, while maintaining the same thermal driving force (80 $^{\circ}$ C) as used for vacuum frying, samples were fried using 180 $^{\circ}$ C oil temperature. Also, one frying time (190s) was used.

2. 4. Color Measurement Samples were removed from the fryer at different intervals: 0, 10, 40, 70, 100, 130, 160 and 190s. After removal, surface oil was wiped out immediately using a soft paper. The surface color of the Reshteh Khoshkar was measured using a computer vision system. A Color digital camera (model IXY 30S, Canon, Japan) connected to a computer via USB interface was mounted on a stand inside a large opaque box with black interior surfaces. The iris was operated using the Automatic mode, with lens aperture at f=8 and speed 1/3(1/6) (no flash, no zoom) in order to achieve high uniformity and repeatability. The angle between the camera lens axis and the sample was set at around 90 $^{\circ}$ in an effort to reduce gloss. Images were stored in high resolution (180dpi) and superfine quality JPEG (Joint Photographic Experts Group) format in RGB color coordinates. The images were acquired into a computer and analysed with a software package Image J1.40g (National Institutes of Health, USA). To remove the noise of the images and to enhance their contrast by the Image J software, median filter was used. The preprocessed images were segmented and separated from the black background using the Photoshop software (Adobe Photoshop, V8, New York, NY). The RGB images were converted into $L^*a^*b^*$ units using the Image J software, and data were obtained through the software in terms of L^* (lightness, ranging from zero [black] to 100 [white]), a^* (ranging from +60 [red] to -60 [green]) and b^* (ranging from +60 [yellow] to -60 [blue]). The total color change (TCD) was calculated by the following equation:

$$TCD = \sqrt{(L_2^* - L_1^*)^2 + (a_2^* - a_1^*)^2 + (b_2^* - b_1^*)^2} \quad (1)$$

where, subscripts 1 and 2 are before and after frying parameters, respectively. As for each specified condition, three samples were used to apply image analysis, so the mean values of the measured $L^*a^*b^*$ were reported.

2. 5. Kinetics of Color Changes The complexity of Reshte Khoshkar implies a wide range of non-enzymatic browning reactions caused by thermal treatments. Consequently it is difficult to establish a reaction mechanism and to obtain a kinetics model describing the global process adequately [20]. There are multiple studies on the kinetics of color of different food materials in the literature. The majority of these references report zero-order (Equation (2)) or first-order (Equation (3)) reaction kinetics.

$$C = C_0 \pm k_0 \times t \quad (2)$$

$$C = C_0 \times \exp(\pm k_1 \times t) \quad (3)$$

where, (-) and (+) indicate degradation and formation of any quality parameter, respectively. On the other hand, sometimes, relatively simple models described (Equations (2) and (3)) do not adequately represent the color change phenomena. Therefore, a combined kinetics has been developed in which color change reactions are considered to consist of two stages. A first stage of colored compound formation following a zero order kinetics, the second stage consider decomposition of the colored polymers into non-colored compounds following a first-order kinetics. According to this combined kinetics, the color degradation and formation process can be expressed by Equation (4) [21].

$$C = \frac{k_0}{k_1} - \left[\frac{k_0}{k_1} - C_0 \right] \exp(\pm k_1 \times t) \quad (4)$$

The terms C and C_0 are the concentrations of color parameters at any time t and initial concentration, respectively; k_0 is the zero-order kinetics constant and k_1 is the first-order kinetics constant in Equations (2)–(4).

3. RESULTS AND DISCUSSION

3. 1. Change in Color Parameters During Processes

One of the most important quality attributes of fried products is color. A photo gallery shows the changes in color as a result of the frying processes applied in this study (Figure 1). It was observed that both frying processes decreased the Lightness parameter of Reshte Khoshkar and the samples turned much darker. For instance, when frying at equivalent thermal driving force of 80°C, L^* diminished from an initial value of 91.61 (un-fried sample) to a final value, after frying for 190s, of 79.35. On the other hand, L^* remained nearly constant in vacuum fried samples, and diminished from an initial value of 85.43 (un-fried sample) to a final value, after frying for 190 s, of 75.54 (Figure 2).

L^* is a critical parameter in the frying industry, and is usually used as a quality control factor, therefore its adequate control is of great importance. The decrease in L^* with time was most probably as a result of Maillard browning and caramelization. The rate of the Maillard reaction depends on its chemical environment such as water activity, pH and chemical composition of the food; however, the most predominant factor on the rate of the reaction is temperature [22]. In addition, lipid oxidation at Reshte Khoshkar surface and oil absorption could have made minor contribution to the L^* change. Similar results were obtained by various researchers and it has been reported that decreases in L value correlated well with increases in the browning of food materials and pigment destruction [23-29].

Figure 3 shows change in Hunter a value of Reshteh Khoshkar produced by various processes. The a value increased during processing by either method with time.

The a^* values increased from negative (toward green) to positive (increasing redness), and atmospheric fried Reshteh Khoshkar with dark red color were produced.

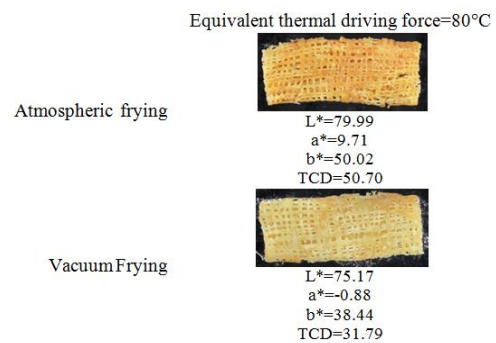


Figure 1. Digital photographs of fried Reshte Khoshkar under atmospheric and vacuum frying conditions with values for the color parameters and color change

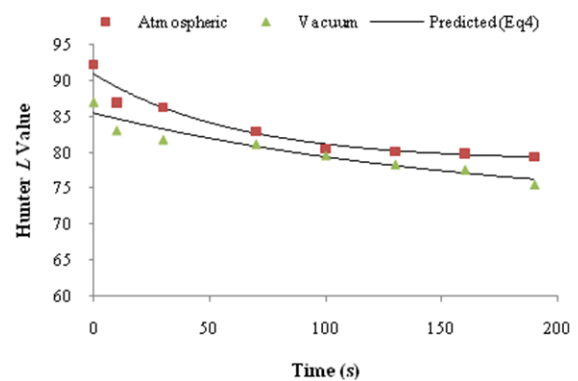


Figure 2. Variation of Hunter color L value of Reshte Khoshkar produced by various processes

In fact, values obtained for vacuum fried samples (-4.77) was close to that of the unfried sample (-0.07) showing a little effect of vacuum frying on the color of the fried product. In general, the increase in parameter a^* was associated with a decrease in parameter L^* . Visually, the increase in parameter a^* and the decrease in parameter L^* translated into a slightly more intense golden color which was perfectly acceptable in all fried samples [30]. A similar behaviour for this parameter was found by other authors [2, 9, 23-26, 28, 31, 32].

The golden surface color of the Reshteh Khoshkar developed during frying was primarily related to yellowness. The yellowness increased with frying time resulting in maximum golden color at 190s frying at 180C (atmospheric frying) (Figure 4). In general, higher b parameter values give more yellow products which is desirable for fried products. Similar results for the decrease in b value were found by many authors [28, 32, 33].

Also, Hunter L , a and b values were used to calculate total color differences during frying processes, which indicated the magnitude of overall color difference between raw and fried food. TCD values increased with time during processes as shown in Figure 5. For atmospherically fried samples, TCD increases progressively. On the other hand, the changes in TCD is not as intense in vacuum fried samples. Higher values obtained for atmospherically fried Reshteh Khoshkar can be attributed to the higher oil temperature which forcefully encourages nonenzymatic browning reactions. It indicates more color change occurred due to atmospheric frying. Visual observation confirmed the results obtained with the colorimeter, i.e., the atmospheric-fried Reshteh Khoshkars were darker and redder than the vacuum-fried Reshteh Khoshkars. Vacuum frying intelligibly reduces color changes because of the rate of Maillard reactions is lower than the rate of reaction under atmospheric frying condition.

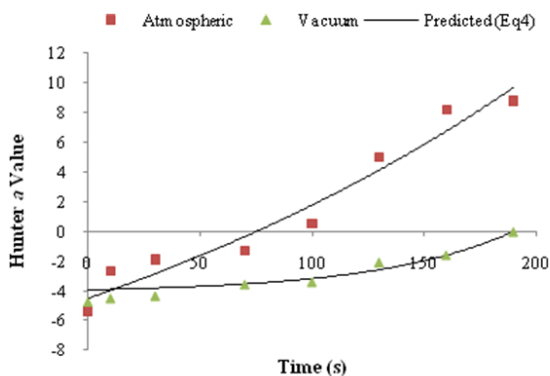


Figure 3. Variation of Hunter color a value of Reshteh Khoshkar produced by various processes

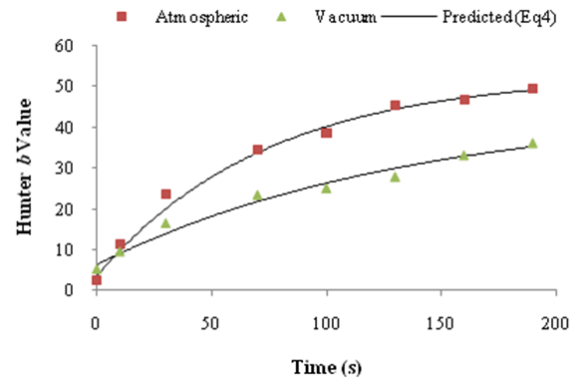


Figure 4. Variation of Hunter color b value of Reshteh Khoshkar produced by various processes

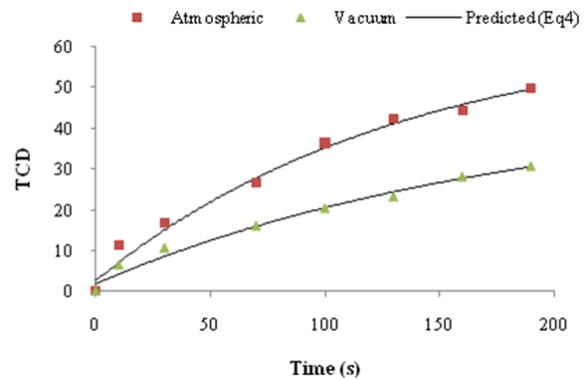


Figure 5. Change in total color difference value of Reshteh Khoshkar produced by various processes.

3. 2. Kinetics Consideration of Color Parameters

In the present research, change of color parameters L , a , b and TCD with the treatment time was fitted to a zero-, first-order and combined kinetics model by non-linear regression. Since Hunter a value showed fluctuation during all concentration processes without a constant trend, it gave very poor correlation. Correlation coefficients and initial value of parameters estimated were used as the basis to select the model which best described the experimental data. The values of parameters estimated from the fittings were given in Tables 2-4.

The zero-order model kinetics constant values (k_0) were higher in all cases than those of first-order model (k_1). It can be calculated from Tables 2 and 3 that when atmospheric frying was applied, regardless of zero or first-order models, the kinetics constant for L value was about 2 times greater than that of vacuum frying process. A similar pattern was also found for the other parameters. The regression analysis revealed that combined model described the experimental data of

parameters L, a, b and TCD better than the zero- and first-order models due to high correlation coefficients and reasonable C_0 values obtained (Table 4). An excellent correlation existed between the color

parameters and frying times at all frying processes. On the other hand, there was no difference between the R^2 values of zero order and combined model for TCD value analysis.

TABLE 1. Kinetics parameters of zero-order model (Equation (2)) for L, a, b and TCD values

| Color Parameter | Frying Process | $C_0 \pm SE$ | $k_0 \pm SE$ | R^2 |
|-----------------|----------------|--------------|--------------|-------|
| L | Atmospheric | 88.703±0.846 | -0.059±0.008 | 0.728 |
| | Vacuum | 84.834±0.981 | -0.049±0.009 | 0.575 |
| a | Atmospheric | -5.025±0.661 | 0.073±0.006 | 0.870 |
| | Vacuum | -4.379±0.555 | 0.018±0.005 | 0.359 |
| b | Atmospheric | 10.777±1.958 | 0.237±0.018 | 0.888 |
| | Vacuum | 8.831±1.174 | 0.153±0.011 | 0.902 |
| TCD | Atmospheric | 6.755±1.701 | 0.248±0.016 | 0.920 |
| | Vacuum | 3.681±1.128 | 0.152±0.010 | 0.908 |

SE: Standard error of estimation, R^2 : Coefficient of determination

TABLE 2. Kinetics parameters of first-order model (Equation (3)) for L, a, b and TCD values

| Color Parameter | Frying Process | $C_0 \pm SE$ | $k_f \pm SE$ | R^2 |
|-----------------|----------------|--------------|-----------------------|-------|
| L | Atmospheric | 88.866±0.848 | 7.242E-004±9.181E-005 | 0.738 |
| | Vacuum | 84.912±0.996 | 6.134E-004±1.121E-004 | 0.578 |
| a | Atmospheric | 0.184±0.237 | 0.021±0.007 | 0.617 |
| | Vacuum | -4.287±0.663 | -0.005±0.002 | 0.296 |
| b | Atmospheric | 16.885±2.169 | 0.006±8.702E-004 | 0.770 |
| | Vacuum | 12.005±1.197 | 0.006±6.786E-004 | 0.832 |
| TCD | Atmospheric | 13.444±1.879 | 0.007±9.167E-004 | 0.816 |
| | Vacuum | 7.669±1.117 | 0.008±9.462E-004 | 0.821 |

SE: Standard error of estimation, R^2 : Coefficient of determination

TABLE 3. Kinetics parameters of combined model (Equation (4)) for L, a, b and TCD values

| Color Parameter | Frying Process | $C_0 \pm SE$ | $k_0 \pm SE$ | $k_f \pm SE$ | R^2 |
|-----------------|----------------|--------------|--------------|--------------|-------|
| L | Atmospheric | 90.922±0.934 | -1.295±0.437 | -0.016±0.005 | 0.838 |
| | Vacuum | 85.464±1.288 | -0.429±0.602 | -0.006±0.008 | 0.586 |
| a | Atmospheric | -4.509±0.778 | -0.068±0.007 | 0.004±0.003 | 0.878 |
| | Vacuum | -3.935±0.541 | -0.068±0.036 | 0.016±0.012 | 0.444 |
| b | Atmospheric | 3.533±1.089 | -0.717±0.054 | -0.014±0.001 | 0.982 |
| | Vacuum | 6.389±1.338 | -0.328±0.062 | -0.007±0.003 | 0.930 |
| TCD | Atmospheric | 2.672±1.751 | -0.481±0.066 | -0.007±0.002 | 0.953 |
| | Vacuum | 1.898±1.353 | -0.251±0.048 | -0.005±0.003 | 0.924 |

SE: Standard error of estimation, R^2 : Coefficient of determination

Both models can describe the TCD data adequately. Therefore, only the plots of combined model were given (Figures 1–4). Comparing both constants of combined model (Table 4), it was observed that k_0 value is notably higher than k_1 for parameters L, a and b which implies that the two stages (color formation and color destruction) supposed by the model occur. This indicates that the rate of color formation is higher than the color destruction for all processes.

A combination of high temperature and low moisture content cause to begin browning reactions such as the caramelization of sugars and Maillard reaction (nonenzymatic browning reactions nonenzymatic browning reactions). Maillard reactions include those involving reducing sugars, aldehydes, and ketones with amines, amino acids, peptides, and protein [26, 34]. In Reshteh Khoshkar, the reactants could have been reducing sugars and amino acids. Caramels, melanoidan pigments, were probably generated by the heat treatment of carbohydrates such as sucrose, glucose, or inverted sugar in the Reshteh Khoshkar.

4. CONCLUSIONS

According to the results obtained, vacuum frying could be used in production of Reshteh Khoshkar successfully. Kinetics of color development or degradation was successfully modeled using zero- and first-order kinetics and combined model. The combined model used can describe the experimental color parameters better than the zero- and first-order kinetics models. This model implied that the color formation and color destruction occurred during frying processes of Reshteh Khoshkar.

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Color

Kinetics

در این پژوهش اثر فشار سرخ کردن بر تغییرات رنگ رشته خوشکار طی سرخ کردن عمیق بررسی شد. پارامترهای رنگی هانتر شامل زردی، قرمزی، روشنایی و تغییرات کلی رنگ برای تخمین تغییرات رنگ طی سرخ کردن به عنوان تابعی از فرایند مورد استفاده قرار گرفتند. پارامتر روشنایی با گذشت زمان سرخ کردن طی خلأ از ۸۵/۳۷ به ۷۵/۰۱ کاهش یافت درحالی که پارامترهای زردی، قرمزی و تغییرات کلی رنگ به ترتیب از ۲/۰۹، ۴/۹۲ و ۰ به ۱/۲۲، ۳۷/۰۱ و ۳۱/۵۶ افزایش یافتند. مشاهده شد که شدت تغییرات رنگ در فرایند سرخ کردن تحت شرایط اتمسفری بیشتر از شرایط تحت خلأ بود. مدل‌های درجه صفر، درجه اول و مدل مرکب برای بررسی تغییرات رنگ به کار رفتند. نتایج نشان دادند که تغییرات زردی، قرمزی، روشنایی و تغییرات کلی رنگ با هر دو مدل درجه اول و مدل مرکب قابل بیان هستند. مدل مرکب فراسنجه های رنگ مورد آزمون را بهتر از سایر مدل‌های سینتیکی مورد بررسی تشریح کرد.

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