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ПЕРАПРАЦОЎКА І ЗАХАВАННЕ СЕЛЬСКАГАСПАДАРЧАЙ ПРАДУКЦЫІ**PROCESSING AND STORAGE OF AGRICULTURAL PRODUCTS**

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Evgeny D. Rozhnov, Marina N. Shkolnikova, Olga N. Musina*Polzunov Altai State Technical University, Barnaul, Russian Federation***KINETICS AND MECHANISM OF CAROTENOID DEGRADATION
IN PUMPKIN POWDER: EFFECT OF STORAGE TEMPERATURE
AND PACKAGING ATMOSPHERE**

Abstract. Carotenoids are highly susceptible to oxidative and thermal degradation, which compromises the nutritional and functional quality of plant-based food powders. This study aimed to establish the kinetic parameters governing carotenoid degradation in enzyme-hydrolyzed pumpkin powder under varying storage temperatures (4, 20, and 30 °C) and gas atmospheres (vacuum, nitrogen, carbon dioxide, and ambient air). Carotenoid content was monitored spectrophotometrically over 12 months, and degradation kinetics were modeled using first-order reaction kinetics and the Arrhenius equation. The degradation process followed first-order kinetics in all conditions ($R^2 > 0.998$). Oxygen presence dramatically accelerated carotenoid loss: degradation rate constants in air were 2.4–5.1 times higher than in inert or vacuum environments. Activation energies (E_a) were significantly higher in oxygen-free systems (48.8–59.4 kJ/mol) compared to air (41.4 kJ/mol), indicating a shift from oxidation-driven to thermally driven degradation mechanisms. Based on the kinetic models, shelf life (defined as 20 % carotenoid loss) was predicted across temperature – atmosphere combinations. For cold-chain storage (0...4 °C), nitrogen or CO₂ packaging provided the longest shelf life (~20 months), whereas vacuum packaging proved superior under temperature abuse (e.g., 30 °C), extending shelf life to ~13 months versus 2.5–7.5 months in air. The practical significance of this work lies in providing a scientific basis for packaging selection: vacuum packaging is recommended for long-term storage, especially with the risk of temperature fluctuations, while packaging under a nitrogen or carbon dioxide atmosphere is optimal for guaranteed cold chain storage.

Keywords: carotenoids, degradation kinetics, Arrhenius equation, modified atmosphere packaging, pumpkin powder, shelf life

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Барнаул, Российская Федерация***КИНЕТИКА И МЕХАНИЗМ ДЕГРАДАЦИИ КАРОТИНОИДОВ В ТЫКВЕННОМ ПОРОШКЕ:
РОЛЬ ТЕМПЕРАТУРЫ И СОСТАВА УПАКОВОЧНОЙ АТМОСФЕРЫ**

Аннотация. Каротиноиды обладают высокой чувствительностью к окислению и термическому разложению, что ограничивает их стабильность в пищевых порошках растительного происхождения. Целью настоящего исследования являлось установление кинетических закономерностей и параметров деградации каротиноидов в порошке ферментализованного тыквенного пюре при различных температурах хранения (+4, +20 и +30 °C) и газовых средах (вакуум, азот, диоксид углерода и воздух). Содержание каротиноидов отслеживали спектрофотометрически в течение 12 мес. Установлено, что во всех условиях деградация подчиняется кинетике первого порядка ($R^2 > 0,998$). Показано, что наличие кислорода является ключевым фактором окисления: константы скорости деградации в воздухе в 2,4–5,1 раза превышали аналогичные показатели в инертных средах. Энергия активации в инертных атмосферах (48,8–59,4 кДж/моль) оказалась выше, чем в воздухе (41,4 кДж/моль), что указывает на смену механизма деградации

с окислительного на термический при удалении кислорода. На основе полученных моделей рассчитаны сроки годности тыквенного порошка (потеря $\leq 20\%$ каротиноидов): при холодовом хранении ($0...+4\text{ }^{\circ}\text{C}$) предпочтительна упаковка в атмосфере азота или CO_2 (срок ~ 20 мес.), тогда как при возможных температурных отклонениях (до $+30\text{ }^{\circ}\text{C}$) наиболее эффективна вакуумная упаковка (~ 13 мес. против $9,5\text{--}11,0$ мес. в инертных средах). Упаковка в воздушной среде не рекомендована: при холодовом хранении срок годности $\leq 7,5$ мес., а при комнатной температуре $\sim 2,5$ мес. Практическая значимость работы заключается в научном обосновании выбора упаковки: для длительного хранения с риском температурных колебаний рекомендована вакуумная упаковка, а для гарантированного холодового хранения – упаковка в атмосфере азота или диоксида углерода.

Ключевые слова: каротиноиды, кинетика деградации, уравнение Аррениуса, модифицированная газовая среда, тыквенный порошок, срок годности

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Introduction. Carotenoids constitute a large group of natural pigments responsible for the yellow, orange, and red coloration of many fruits and vegetables. Beyond their contribution to organoleptic appeal, they exhibit significant biological activity, serving as provitamin A compounds (e.g., β -carotene, α -carotene) and as potent antioxidants (e.g., lycopene, lutein, zeaxanthin) capable of neutralizing free radicals and reducing the risk of oxidative stress-related diseases. However, their chemical structure – characterized by a long chain of conjugated double bonds – renders them highly susceptible to various degradation factors.

Temperature is one of the most significant and universal influences on carotenoid stability. Elevated temperatures accelerate the kinetics of all chemical reactions leading to degradation, including oxidation, isomerization, and thermal decomposition. The impact of thermal processing and pasteurization on carotenoid retention is complex. On the one hand, heat treatment (e.g., blanching, pasteurization) inactivates enzymes such as lipoxygenase and peroxidase, which catalyze the oxidation of both carotenoids and lipids [1, 2]. This protective effect is corroborated by Guerra-Vargas et al. [3], who reported enhanced carotenoid retention in canned pickled peppers and carrots following pasteurization. On the other hand, high temperatures can induce isomerization of the biologically active *trans*-isomers into less active *cis*-forms and promote direct thermal degradation. The kinetics of such thermal degradation, which follows the Arrhenius model, have been thoroughly described in studies by Lin and Chen [4] and Jirasatid et al. [5]. Low-temperature storage (e.g., freezing or refrigeration) is the most effective strategy for slowing carotenoid degradation. D'yakov and Belinska [6] demonstrated high carotenoid retention in quick-frozen pulpy juices; however, even freezing cannot completely halt degradation processes [7]. In contrast, elevated storage temperatures (e.g., room temperature) dramatically intensify all degradation pathways [8–10].

Oxygen is the primary catalyst of oxidative carotenoid degradation – an autocatalytic process initiated by free radical formation. Two main oxidation pathways have been identified:

(i) direct attack of molecular oxygen on the conjugated double bonds of carotenoids, leading to bond cleavage and the formation of epoxides, apocarotenals, and other low-molecular-weight compounds, resulting in loss of color and biological activity [7, 11];

(ii) lipid-mediated oxidation: Since carotenoids often coexist with lipids in plant matrices, lipid oxidation – catalyzed by light, heat, or metal ions – generates hydroperoxides and free radicals that subsequently attack carotenoid molecules, significantly accelerating their degradation [1, 12]. Nikolaeva [1] explicitly linked lipid oxidation in mechanically damaged carrots to carotenoid loss.

Light, particularly its ultraviolet and blue spectral components, acts as a powerful pro-oxidant. Photons provide the energy required to initiate photooxidation and photoisomerization reactions. Atencio et al. [13] highlighted the extreme photosensitivity of carotenoids in beverages. Consequently, protection from light (opaque packaging or dark storage) is essential to minimize losses [4, 13].

Product moisture content and, more critically, water activity (A_w) also profoundly influence carotenoid stability by determining the physical state of the system and the mobility of reactants. High A_w values, typical of liquid and semi-liquid systems, such as juices and purées, facilitate the diffusion of oxygen

and pro-oxidants, thereby accelerating oxidative reactions. Significant carotenoid losses in tomato and pumpkin purées during storage have been reported [14, 15]. In contrast, low A_w values characteristic of dried powders generally enhance stability. However, in such systems, other factors become dominant: high surface area, direct oxygen exposure, and oxidation risk. Macura et al. [16] and Regier et al. [17] compared drying methods for carrots and concluded that freeze-drying (lyophilization) is less detrimental to carotenoids than hot-air drying, due to reduced thermal stress and oxidation. Tang and Chen [7] emphasized the critical importance of hermetic packaging to shield carotenoids from oxygen.

Acidic conditions promote acid-catalyzed hydrolysis and isomerization of carotenoids. Guerra-Vargas et al. [3] investigated the effect of acetic acid in brine on carotenoid stability, demonstrating that this factor must be considered in conjunction with others. Conversely, the presence of protective compounds – such as ascorbic acid, tocopherols, and phenolic substances – can shield carotenoids by scavenging free radicals. Samoylov et al. [18] demonstrated the stabilizing effect of antioxidants in paprika extract syrups, while Nguyen et al. [19] confirmed the protective role of ascorbic acid in pumpkin purée.

Ensuring carotenoid retention during food processing and *storage* remains a critical challenge for the food industry and food science. The physical factors described above underpin key technological operations used in the processing of carotenoid-rich plant materials (Table 1).

Table 1. Effect of processing technology on carotenoid retention in plant materials

Processing technology	Primary impact	Effect on carotenoids	References
Pasteurization / Sterilization	Heating; inactivation of enzymes and pathogenic/undesirable microorganisms	Dual effect: enzyme inactivation vs. thermal degradation and isomerization	[3, 4]
Hot-air drying	Water removal, heating, oxygen exposure	Significant degradation: oxidation, isomerization, high losses	[11, 17, 20]
Freeze-drying (lyophilization)	Water removal under vacuum at low temperatures	High retention: minimal thermal and oxidative damage	[7, 16]
Freezing	Rapid cooling; suppression of chemical and enzymatic reactions	Very high retention, provided rapid freezing is applied	[6]
HPP (High-pressure processing)	Inactivation of microorganisms and enzymes without heating	Optimal retention / enhanced extractability	[14, 21]

Generally, these factors do not act in isolation but form a complex network of interactions, wherein a change in one parameter inevitably affects the intensity of others. Below, we examine the most significant interrelationships among these factors.

Temperature ↔ Oxygen: Elevated temperature not only directly accelerates oxidation, but also reduces oxygen solubility in liquid matrices while simultaneously increasing the diffusional mobility of oxygen molecules. Overall, this markedly intensifies oxidative degradation. In particular, in dry powders, high temperature accelerates the reaction with atmospheric oxygen [7].

Temperature ↔ Moisture: During high-temperature drying (e.g., hot-air drying), the product is simultaneously exposed to two stressors (heat and oxygen) across a large surface area. This leads to substantial losses: As water is removed, the product matrix undergoes structural changes, and carotenoids become more susceptible to oxidation by atmospheric oxygen due to the disappearance of the protective aqueous phase [11, 20]. In contrast, freeze-drying – avoiding high-temperature exposure – better preserves carotenoids, though the final product still requires protection from oxygen [16, 17].

Light ↔ Oxygen: This is a classic synergistic pair. Light provides the energy required for initiation, while oxygen serves as the substrate for photooxidation reactions. Beverages or purées packaged in transparent containers and exposed to light degrade many times faster than identical products stored in darkness [13].

Product matrix ↔ All factors: The native biochemical matrix of the raw material determines the intensity of all carotenoid degradation processes. In intact plant cells, carotenoids are stabilized within chromoplasts and are often associated with proteins or lipids, which provides natural protection. However, mechanical damage during cutting, grinding, or peeling disrupts cellular compartments, facilitates oxygen access, and activates enzymes (e.g., lipoxygenases, peroxidases) that trigger oxidation. Study [1] clearly

demonstrates how mechanical injury to carrots accelerates lipid oxidation, which directly correlates with carotenoid loss. Carotenoid stability also varies by cultivar, as shown in works [22, 23].

Homogenized systems (purées, pulpy juices, pastes) are characterized by complete disruption of cellular structure, leading to carotenoid release and exposure to oxygen and enzymes. Carotenoid stability in such matrices strongly depends on the presence of lipids, which can act either as pro-oxidants (when oxidized) or as a protective medium that enhances carotenoid solubilization. Additionally, pH is a key factor: for example, carotenoid degradation in tomato purée (pH $\approx$ 4.2) may proceed differently than in pumpkin purée, which has a near-neutral pH [2]. Furthermore, studies on pumpkin purée [19, 24] indicate that carotenoid stability is directly linked to the product's rheological properties and composition.

Aqueous dispersions and emulsions (juices, beverages) represent one of the least favorable environments for hydrophobic carotenoids. In the aqueous phase, they are prone to oxidation and isomerization. Stabilization typically requires the formation of colloidal systems (e.g., emulsions using emulsifiers) or the application of microencapsulation techniques. Study [13] focuses on the stability of pumpkin carotenoids in a light-sensitive beverage, where photooxidation becomes the primary degradation pathway.

Carotenoids are highly soluble in lipids, and in the absence of oxygen, a lipid medium can effectively protect them. However, in the presence of oxygen, lipids readily undergo oxidation, generating free radicals that attack carotenoid molecules. Thus, stability in oil-based systems depends on the degree of unsaturation of the oil and the presence of antioxidants.

Dried products, such as powders from carrots or pumpkins, are generally considered more stable because water removal slows many chemical reactions. Nevertheless, specific surface area and porosity play a crucial role in determining oxidation rates. Studies [7, 16, 25, 26] thoroughly examine the degradation kinetics of carotenoids in powders during storage.

The addition of other ingredients can either stabilize or destabilize carotenoids. For instance, incorporating Japanese quince and strawberry into pumpkin purée [27] may introduce additional acids and phenolic compounds that influence stability. Ascorbic acid added to pumpkin purée has demonstrated effective stabilizing properties [19].

The aim of this study was to establish the kinetic patterns and parameters of thermal and oxidative degradation of carotenoids in enzyme-hydrolyzed pumpkin powder as influenced by storage temperature and packaging atmosphere composition, thereby providing a scientific basis for selecting optimal storage conditions and packaging types.

The following specific *objectives* were addressed:

- to evaluate the effect of packaging atmosphere on carotenoid retention in pumpkin powder in the absence of light;
- to assess the impact of temperature on carotenoid stability in enzyme-hydrolyzed pumpkin powder;
- to analyze experimental kinetic data and develop mathematical models accurately describing carotenoid degradation under the studied conditions.

Materials and Methods. The experimental *material* was enzyme-hydrolyzed pumpkin powder, prepared according to the method previously described by the authors [28]. Native pumpkin purée was obtained by homogenizing the pulp of *Cucurbita pepo* “Rossiyanka” cultivar. Enzymolysis was carried out under the following conditions: the native purée was heated to (70 ± 2) °C, after which an aqueous solution (water-to-enzyme ratio 10 : 1) of a multi-enzyme preparation containing Amylorizin and Protozyme was added under constant stirring. The mixture was then incubated at 70 °C with continuous agitation for 60 minutes. The enzyme-hydrolyzed purée was dried in a 5–7 mm layer in a vacuum drying oven (Labtex LT-VO/50, Russia) at 60–80 °C until the final moisture content did not exceed 5 %. The dried product was standardized by particle size using a ball mill and a universal laboratory sieve shaker (RL-1 MT, Russia). The maximum allowable particle size was 0.25 mm. The milled fractions were thoroughly homogenized to ensure compositional uniformity across all experimental samples. The final moisture content of the powder prior to packaging was (4.4 ± 0.2) %. The visual appearance of pumpkin purée at different stages of the technological process is shown in Figure 1.

Design of the experiment. The study examined the effect of 4 packaging atmospheres on carotenoid retention: vacuum (residual pressure $\leq$ 5 mbar), nitrogen (N₂), carbon dioxide (CO₂), air atmosphere (control, $\sim$ 21 % O₂).

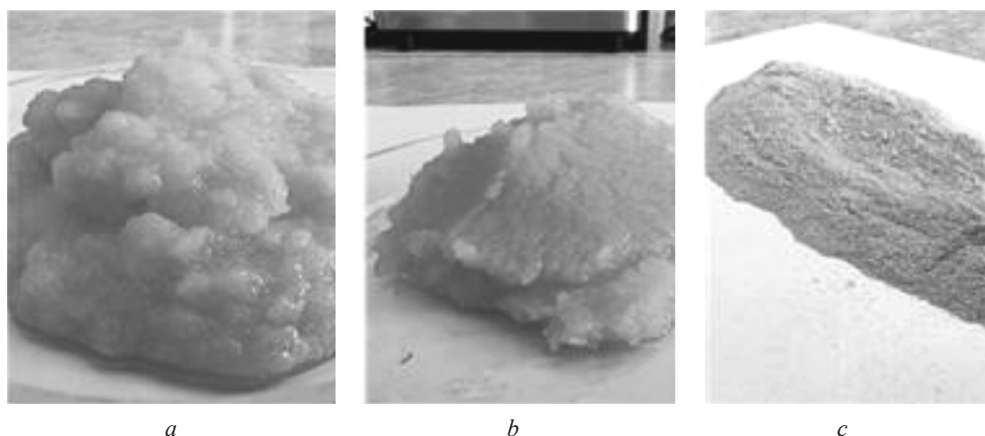


Figure 1. Visual appearance of pumpkin purée samples: *a* – purée after homogenization; *b* – purée after enzymolysis; *c* – purée after drying

Three storage temperature regimes were the following:

- refrigerated storage at 4 °C,
- standard room-temperature storage at 20 °C (climatic chamber KS-200 SPU, Smolensk SPU Scientific & Production Association, Russia),
- elevated-temperature (stress) storage at 30 °C (thermostatic chamber TS-1/80 SPU, Smolensk SPU Scientific & Production Association, Russia).

The total storage duration was 12 months. Samples were withdrawn for analysis at 1, 2, 3, 6, 9, and 12 months. Each combination of experimental factors was performed in triplicate.

A precisely weighed portion (20.0 ± 0.1 g) of enzyme-hydrolyzed pumpkin powder was placed into individual barrier-type heat-sealable aluminum-laminated pouches. Vacuum packaging was performed using a CASO FastVAC 1200 vacuum sealer (China). Modified atmosphere packaging (MAP) was achieved by evacuating the pouch, then flushing with the respective gas (N_2 or CO_2) through a gas inlet tube, followed by re-evacuation. This gas-flush cycle was repeated 10 times to ensure complete atmosphere replacement. After the final gas flush, pouches were heat-sealed without vacuum. Control samples (air atmosphere) were sealed without evacuation or gas flushing.

The moisture content prior to packaging was determined according to GOST 28561-90 “Fruit and vegetable products. Methods for determination of dry matter or moisture”. The carotenoids content was measured in accordance with GOST ISO 6558-2-2019 “Fruit, vegetables and derived products. Determination of carotene content by spectrophotometric method”, using a Shimadzu UV-1800 single-beam scanning spectrophotometer (Japan).

Data analysis. Statistical analysis was performed using three-way ANOVA to assess the significance of the effects of packaging atmosphere, storage temperature, and time on carotenoid retention. Differences between mean values were considered statistically significant at $p < 0.05$. Linear regression equations and graphical data visualization were generated using Microsoft Office Excel (Microsoft, USA). Statistical processing was carried out with Statistica 10.0 software (StatSoft, USA).

Results and Discussion. The initial carotenoid content in the dried enzyme-hydrolyzed pumpkin powder was 185.6 mg/100 g. For food systems, the most probable degradation pathway for such components is a first-order reaction. This hypothesis is fully supported by the linear dependence of the experimental data in the coordinates $[\ln(C) - t]$, which are conventionally used to describe first-order reaction kinetics (Figure 2).

Analysis of the resulting linear dependencies allowed determination of the reaction rate constants (k), obtained as the slopes of the regression lines (Table 2). It was established that, across all studied packaging atmospheres, carotenoid degradation kinetics followed a first-order model (coefficient of determination $R^2 > 0.998$ for all linear fits).

Analysis of the rate constants reveals that inert atmospheres significantly retard carotenoid degradation compared to air. At 4 °C, the degradation rate constant under vacuum was 2.4 times lower than in air;

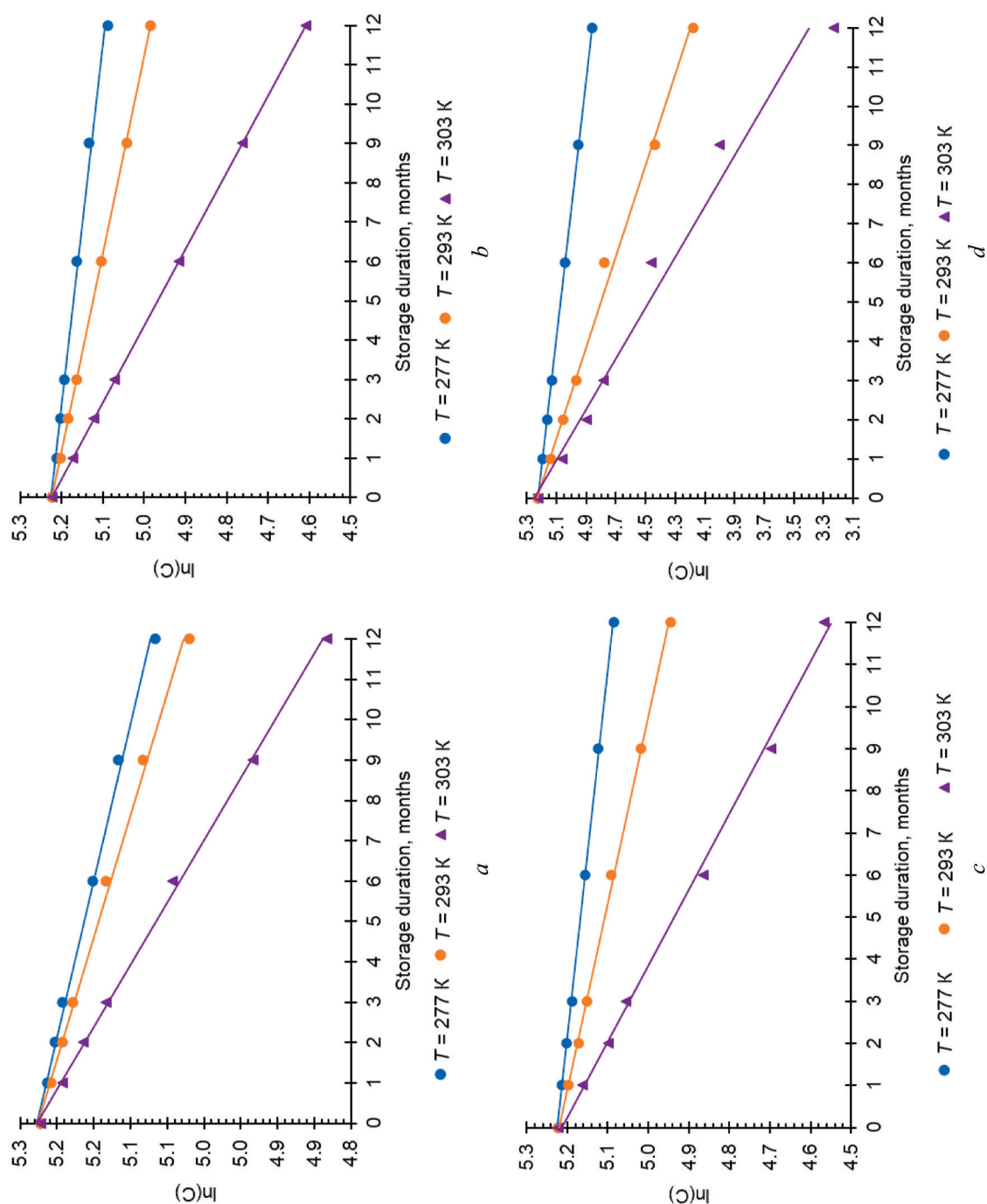


Figure 2. Kinetic experimental data: *a* – storage under vacuum; *b* – storage in N_2 atmosphere; *c* – storage in CO_2 atmosphere; *d* – storage in ambient air

Table 2. Results of experimental data processing

Packaging atmosphere	Temperature, K	Linear regression equation	R ²	k, month ⁻¹
Vacuum	277	$y = -0.0128x + 5.2227$	0.9987	0.0128
	293	$y = -0.0171x + 5.2216$	0.9995	0.0171
	303	$y = -0.0332x + 5.2218$	0.9989	0.0332
N ₂	277	$y = -0.0114x + 5.2223$	0.9986	0.0114
	293	$y = -0.0201x + 5.2216$	0.9993	0.0201
	303	$y = -0.0519x + 5.2219$	0.9984	0.0519
CO ₂	277	$y = -0.0118x + 5.2217$	0.9989	0.0118
	293	$y = -0.0234x + 5.2219$	0.9995	0.0234
	303	$y = -0.0554x + 5.2239$	0.9982	0.0554
Air	277	$y = -0.0305x + 5.2229$	0.9995	0.0305
	293	$y = -0.0888x + 5.2239$	0.9992	0.0888
	303	$y = -0.1679x + 5.2239$	0.9989	0.1679

Table 3. Calculated values of activation energy (E_a) and pre-exponential factor (A) for Arrhenius equations

Packaging atmosphere	E_a , kJ/mol	A, month ⁻¹
Vacuum	48.83	2.00×10^7
N ₂	59.36	1.71×10^9
CO ₂	58.49	1.13×10^9
Air	41.41	1.18×10^6

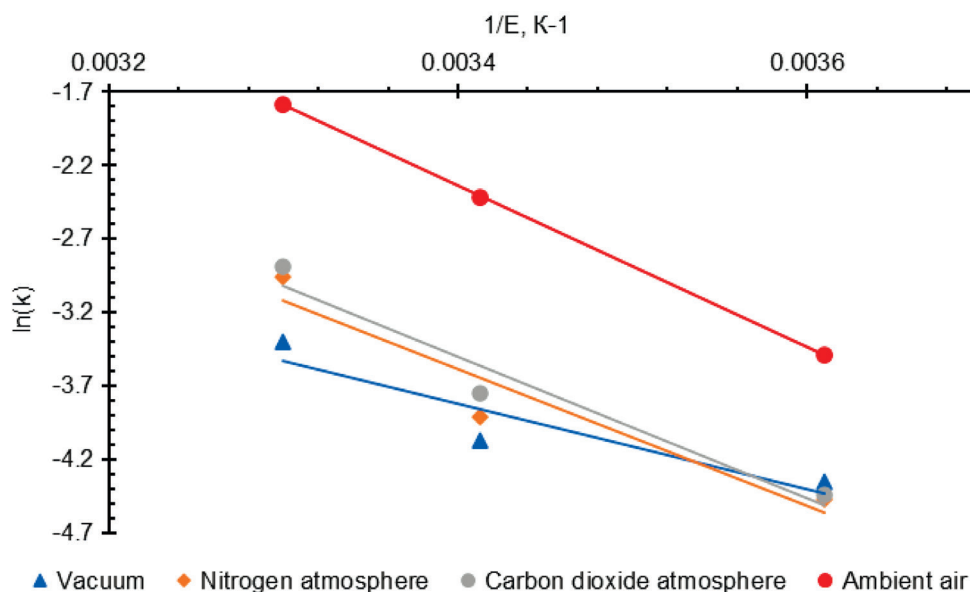


Figure 3. Arrhenius plots

in nitrogen and carbon dioxide, it was 2.7 and 2.6 times lower, respectively. At the highest tested temperature (30 °C), the rate constants in vacuum, nitrogen, and CO₂ were 5.1, 3.2, and 3.0 times lower than in air, respectively.

Table 3 presents the calculated values of activation energy (E_a) and the pre-exponential factor (A) for the Arrhenius equation.

Arrhenius plots were subsequently constructed based on the experimental data (Figure 3).

Analysis of the E_a values in Table 3 allows several key conclusions. The relatively high activation energies for samples stored under vacuum or in inert gas atmospheres indicate that the reaction rate in these conditions is strongly temperature-dependent. In the absence of oxygen, carotenoid degradation

proceeds primarily via thermal decomposition. In contrast, the lower E_a value for the air atmosphere (41.41 kJ/mol) suggests that degradation is less sensitive to temperature and is instead limited by oxygen availability – since oxygen concentration remains constant and in excess in sealed packages, the process is characteristic of oxidation-limited kinetics.

A comparison of nitrogen and carbon dioxide atmospheres shows very similar rate constants and activation energies. The minor differences fall within experimental error, indicating that both gases are equally effective as protective inert atmospheres for enzyme-hydrolyzed pumpkin powder.

Using the derived Arrhenius parameters and the classical first-order kinetic equation, the shelf life of the pumpkin powder was calculated under the criterion of no more than 20 % carotenoid loss:

$$t = \frac{\ln \frac{C_0}{C_t}}{k_i},$$

where C_0 – initial carotenoid content, mg/100 g; C_t – carotenoid content at the critical storage time (corresponding to 80 % retention), mg/100 g; k_i – rate constant under specific conditions (packaging atmosphere, temperature), month⁻¹.

The calculated data are presented graphically in Figure 4. The vertical distance between curves reflects the relative effectiveness of one atmosphere versus another at a given temperature. For instance, the gap between the vacuum and air curves illustrates the shelf-life extension achieved through vacuum packaging.

The slope of each curve indicates the sensitivity of shelf life to temperature changes. The steep slope for air storage demonstrates that shelf life declines sharply with increasing temperature, confirming strong temperature dependence. Conversely, the gentler slope for vacuum packaging indicates superior resilience to temperature fluctuations.

Figure 4 shows that at temperatures below 10 °C, modified atmospheres of N₂ and CO₂ provide slightly longer shelf life than vacuum. However, as temperature increases further, vacuum packaging becomes significantly more effective.

These findings provide a robust scientific basis for selecting optimal storage conditions and packaging strategies for this product.

The present study quantitatively evaluated the impact of two critical storage factors (temperature and packaging atmosphere) on carotenoid stability in enzyme-hydrolyzed pumpkin powder. The results are consistent with established literature on the degradation kinetics of labile lipophilic pigments and offer new insights into the synergistic effects of these factors.

Kinetic order of the reaction and degradation mechanism. The high coefficients of determination ($R^2 > 0.998$) obtained when fitting the experimental data to the first-order kinetic model unequivocally indicate that the degradation rate of carotenoids is directly proportional to their current concentration. This conclusion holds true across all tested packaging atmospheres. Our findings align with earlier studies [7, 10] and confirm that both oxidative degradation in the presence of oxygen and thermal decomposition under inert atmospheres follow the same formal kinetic order. This consistency validates the use of the Arrhenius equation to describe the temperature dependence of the degradation process.

Critical role of oxygen and effectiveness of barrier packaging. A direct comparison of rate constants (k) clearly demonstrates the detrimental impact of molecular oxygen. At 4 °C, the degradation rate in air ($k = 0.0305$ month⁻¹) was 2.4–2.7 times higher than in inert atmospheres. At 30 °C, this difference widened to 3.0–5.1 times. This provides compelling evidence that oxidative pathways dominate carotenoid degradation in aerated systems. These results strongly justify the use of modified atmosphere packaging (MAP) for preserving the functional properties of enzyme-hydrolyzed pumpkin powder. All tested inert environments (vacuum, nitrogen, and carbon dioxide) proved highly effective compared to air.

Activation energy as an indicator of reaction mechanism. The most insightful aspect of our analysis lies in the activation energy (E_a) values. For samples stored in air, E_a was relatively low (41.41 kJ/mol),

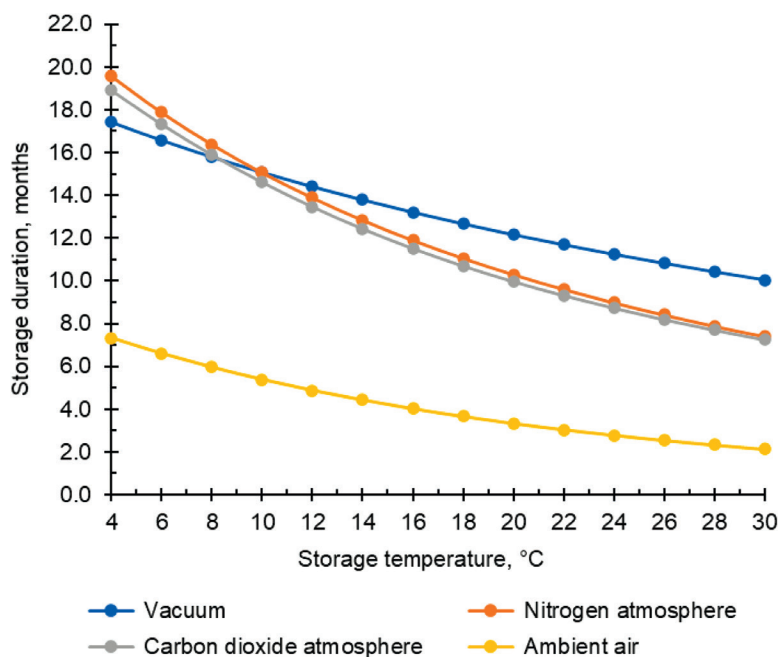


Figure 4. Dynamics of shelf life of enzyme-hydrolyzed pumpkin powder based on Arrhenius model predictions

which is typical for reactions limited not by temperature but by the concentration of a key reactant – in this case, oxygen. Since oxygen was present in excess and constant within sealed pouches, the reaction rate showed only moderate temperature dependence, as oxygen availability was the primary driver. In contrast, samples stored under vacuum or in inert gases exhibited significantly higher E_a values (48.83–59.36 kJ/mol). This shift indicates a fundamental change in the rate-limiting step: In the absence of oxygen, degradation proceeds primarily via thermal decomposition, isomerization, or reaction with trace residual oxygen – processes that involve a high energetic barrier. Consequently, under oxygen-free conditions, the degradation rate becomes strongly temperature-dependent.

Comparative analysis of inert gas atmospheres. The statistically insignificant difference between nitrogen ($E_a = 59.36$ kJ/mol) and carbon dioxide ($E_a = 58.49$ kJ/mol) confirms their nearly identical effectiveness as protective atmospheres for enzyme-hydrolyzed pumpkin powder. This practical observation allows flexibility in gas selection based on cost, availability, or technological considerations (e.g., CO_2 may offer additional bacteriostatic benefits). Of particular scientific and practical interest is the superior performance of vacuum packaging at elevated temperatures. Although at 4 °C the degradation rate under vacuum ($k = 0.0128$ month⁻¹) was slightly higher than under N_2 ($k = 0.0114$) or CO_2 ($k = 0.0118$), at 30 °C vacuum proved significantly more effective ($k = 0.0332$ vs. 0.0519 and 0.0554, respectively). This may be attributed to either (i) gradual micro-ingress of oxygen through the pouch material over time in gas-filled packages, or (ii) more efficient removal of oxygen adsorbed on the powder particle surfaces under vacuum conditions.

Shelf-life prediction and practical recommendations. The Arrhenius-based shelf-life curves (see Figure 4) provide a robust decision-making tool for industrial applications. For supply chains with guaranteed refrigerated storage (0–4 °C), nitrogen or CO_2 packaging is optimal, yielding a predicted shelf life of 19–20 months (i.e., time until 20 % carotenoid loss). For room-temperature storage and distribution, vacuum packaging is superior, offering a shelf life of ~13 months, compared to 9.5–11.0 months under N_2 or CO_2 . Air packaging is unacceptable: even under refrigeration, shelf life does not exceed 7.5 months, and at room temperature, 20 % carotenoid loss occurs within just 2.5 months.

Conclusion. The present study confirmed that the degradation of carotenoids in enzyme-hydrolyzed pumpkin powder follows first-order kinetics. The effects of storage temperature and packaging atmosphere composition on the degradation rate were quantitatively assessed. It was established

that the use of modified atmosphere packaging increases the product's shelf life by 3 to 8 times compared to storage in air. Moreover, the observed shift in activation energy depending on the packaging atmosphere indicates a fundamental change in the degradation mechanism: from oxidation-driven under aerobic conditions to thermally driven in oxygen-depleted environments. For the first time, it was demonstrated that vacuum packaging outperforms inert gas atmospheres (N_2 and CO_2) for enzyme-hydrolyzed pumpkin powder stored at elevated temperatures (e.g., room temperature). This finding has significant practical implications for real-world supply chains, where strict temperature control cannot always be guaranteed.

The practical relevance of this work lies in providing scientifically grounded recommendations for packaging selection: vacuum packaging is recommended for long-term storage under conditions prone to temperature fluctuations or abuse; nitrogen or carbon dioxide atmospheres are preferable when refrigerated storage (0–4 °C) is reliably maintained.

Future research directions may include: (i) investigating the influence of product moisture content on the protective efficacy of various gas atmospheres; (ii) identifying and quantifying specific oxidation by-products; (iii) exploring the application of enzyme-hydrolyzed pumpkin powder in functional food systems, building on existing experience with pumpkin-based ingredients in dairy formulations [29, 30].

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