

Kinetic Modeling of Quality Aspects of Fermented Sausage (Sucuk) During Storage

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Abstract

Quality characteristics of traditional fermented sausage (sucuk) including pH, free fatty acid (FFA), thiobarbituric acid reactive substances (TBARS), residual nitrite contents, colour values (L^* , a^* , b^* , hue angle (Hue), browning index (BI), chroma and total colour difference (ΔE^*)), total mesophilic aerobic bacteria (TMAB), lactic acid bacteria (LAB), total *Enterobacteriaceae* (TE) and *Staphylococcus* and *Micrococcus* (SM) counts were investigated during storage period, and kinetic model estimation for the changes in these quality parameters were performed. After 9 days of fermentation period, the sucuk samples were stored for 90 days under controlled conditions. Analyses were done at the beginning, 30th, 60th and 90th days of the storage period. Zero, first and second order kinetic model equations represented successfully the changes in chemical and colour properties. A linear (first order) kinetic model equation demonstrated the kinetics of microbial changes well in the sucuk samples during storage period.

Keywords: Traditional fermented sausage, Sucuk, Storage, Kinetic model, Quality

Fermente Sucuğun Depolama Sırasında Kalite Özelliklerindeki Değişimin Kinetik Modellemesi

Özet

Geleneksel fermente sucuğun pH, serbest yağ asidi değeri (FFA), tiyobarbitirik asit reaktif maddeler (TBARS), kalıntı nitrit içeriği, renk değerleri (Hunter L^* , a^* , b^* , hue açısı (Hue), esmerleşme indeksi (BI), kroma ve toplam renk farkı (ΔE^*)), toplam mesofilik aerobik bakterisi (TMAB), laktik asit bakterisi (LAB), toplam *Enterobacteriaceae* (TE) ile *Staphylococcus* ve *Micrococcus* (SM) sayısı değerlerindeki değişimler depolama süresince incelenmiş ve bu özelliklerdeki değişimlerin kinetik modellemesi gerçekleştirilmiştir. Sucuklar 9 günlük fermentasyonun ardından kontrollü koşullarda 90 gün boyunca depolanmıştır. Analizler depolamanın 0, 30, 60 ve 90. günlerinde yapılmıştır. Sucukların depolama sırasındaki kimyasal özellikleri ve renk değerlerindeki değişimleri 0, 1 ve 2. dereceden kinetik modeller başarılı bir şekilde ifade ederken mikrobiyal özelliklerindeki değişimleri doğrusal (birinci dereceden) kinetik modelin iyi bir şekilde temsil ettiği saptanmıştır.

Anahtar sözcükler: Geleneksel fermente sucuk, Depolama, Kinetik model, Kalite

INTRODUCTION

Fermented sausage production is a method to preserve meat since ancient times. Contrary, today the production of fermented sausages is carried out for their desired sensory attributes by the consumers. Sucuk, is a widely consumed traditional fermented sausage in Turkey and culturally neighboring countries in Asia, Europe and North Africa. There are numerous documents showing that ancient Turks made and consumed sausages thousands of years ago. It has been documented that sucuk was an easy to

carry, easy to prepare and a palatable meat product in Manas saga, a thirteen hundred years old Kyrgyz legend ^[1].

Literally, sucuk is produced from a mixture of meat and fat. This mixture may include cattle, sheep and/or water buffalo meat, beef fat and sheep tail fat, salt, sugar, garlic and some spices and seasonings. After mixing it is filled into a casing and then subjected to fermentation at certain conditions resulting in a semi dry or dried meat product ^[2,3].

Fermentation is the main stage of the curing process of sausages, since at this phase the main physical, chemical



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and microbiological changes start to occur. These transformations also continue in storage and are influenced by attributes of the raw material and the process conditions, which determine the sensory properties, shelf life and safety of the final product. These changes are mainly; changes in initial microflora, acidification, pH decrease, reduction of nitrates into nitrites than the nitric oxide, production of nitrosomyoglobin, solubilisation and jellification of myofibrillar and sarcoplasmic proteins, proteolytic, lipolytic and oxidative phenomena and dehydration [4-7]. Due to these continuous changes, the quality parameters of the last product show wide variations.

Kinetic modeling can be used to predict changes in physical, chemical or microbiological quality parameters of food products during processing and storage [8]. Numerous studies exist about kinetic modeling of quality changes in foods. Kinetic modeling of quality parameters of sucuk during fermentation was reported previously [9]. However, changes in quality parameters in sucuk like other food products continue during storage period after production processes. Due to these changes the product may become unconsumable. Kinetic modelling is a good way of demonstrating these changes in quality parameters during production (like fermentation) and storage for food products (like sucuk). Therefore, the aim of this study was to make a kinetic modeling of the changes in physical, chemical or microbiological quality parameters of the traditional fermented sausage "sucuk" during 90 days of storage period.

MATERIAL and METHODS

Three batches of the sucuk were produced under industrial conditions in a meat processing plant situated in İzmir, Turkey. Sucuk production was done according to method reported previously [9]. After fermentation the sucuk samples were vacuum packed in polyethylene bags and stored at 4°C during the storage period.

The study was carried out in three replicates. Percent moisture, salt, ash, fat, protein, contents of the samples were analyzed at the beginning of the storage. pH, free fatty acid, thiobarbituric acid reactive substances, residual nitrite content, instrumental colour and total mesophilic aerobic bacterial (TMAB), total *Enterobacteriaceae* (TE), *Staphylococcus* and *Micrococcus* (SM) and lactic acid bacteria (LAB) counts were analyzed at the beginning, 30th, 60th and 90th days of storage. Determination of the chemical, color and microbial parameters were carried out according to the methods reported previously [9].

Kinetic Modeling

Zero-order (Eqn. 1), first order (Eqn. 2) and second order (Eqn. 3) kinetic models were used to describe the chemical and physical changes during the storage of the sucuk samples [8];

$$c = c_0 - kt \quad (1)$$

$$c = c_0 \exp(-kt) \quad (2)$$

$$\frac{1}{c} = \frac{1}{c_0} + kt \quad (3)$$

where, c is the quality parameter; c_0 is the value of this quality parameter at the beginning of the storage period, t is the storage time (day) and k is the rate constant (day⁻¹).

The linear (first order) kinetic model was used to demonstrate the changes in microbial quality parameters of the samples during the storage;

$$\frac{dN}{dt} = -k'N \quad (4)$$

after integration, it is,

$$\ln\left(\frac{N}{N_0}\right) = -k't \quad (5)$$

Base-10 logarithms of population sizes are used generally to present microbial changes [10,11];

$$\log\left(\frac{N}{N_0}\right) = -kt \quad (6)$$

where, N_0 and N are the initial number and number of survivors after a time t (day) of microorganisms and spores (cfu/g), respectively, k' is the rate constant (day⁻¹) and $k = k'/\ln 10$ (day⁻¹).

RESULTS

Percent moisture, salt, ash, fat and protein contents of the samples at the beginning of the storage were found as 35.29, 3.33, 4.57, 31.65 and 17.38%, respectively.

Estimated kinetic parameters of pH, FFA, TBARS and residual nitrite during storage are presented in *Table 1*. The positive (+) sign of the k shows a decrease while the negative (-) sign shows an increase in quality parameter during the storage. Comparison of the experimental values with the modeling results is given in *Fig. 1*. Only the models having highest R² values are presented in the graphs. During the 90 days of storage in refrigerator conditions the pH value of sucuk decreased from 5.05 to 4.76 (*Fig. 1-A*).

The FFA amount of the sucuk samples showed a significant increment during the storage. The FFA amount increased from 3.40 mg KOH/g fat to 5.15 mg KOH/g fat

Table 1. Estimated model constants for pH, FFA, TBARS and residual nitrite

| Quality Parameter | Zero Order Model | | | First Order Model | | | Second Order Model | | |
|-----------------------------|------------------|------------------------|----------------|-------------------|------------------------|----------------|--------------------|------------------------|----------------|
| | c ₀ | k (day ⁻¹) | R ² | c ₀ | k (day ⁻¹) | R ² | c ₀ | k (day ⁻¹) | R ² |
| pH | 4.9960 | 0.0030 | 0.8005 | 4.9953 | 0.0006 | 0.8049 | 4.9950 | 0.0001 | 0.8093 |
| FFA (mg KOH/g fat) | 3.3390 | -0.0196 | 0.9929 | 3.3814 | -0.0047 | 0.9985 | 3.4106 | -0.0011 | 0.9974 |
| TBARS (mg malonaldehyde/kg) | 0.3985 | -0.0016 | 0.9711 | 0.3995 | -0.0034 | 0.9567 | 0.4001 | -0.0075 | 0.9395 |
| Residual Nitrite (ppm) | 5.2430 | 0.0084 | 0.5228 | 5.1049 | 0.0014 | 0.4765 | 4.9579 | 0.0002 | 0.4408 |

FFA: Free Fatty Acid, TBARS: Thiobarbituric Acid Reactive Substances

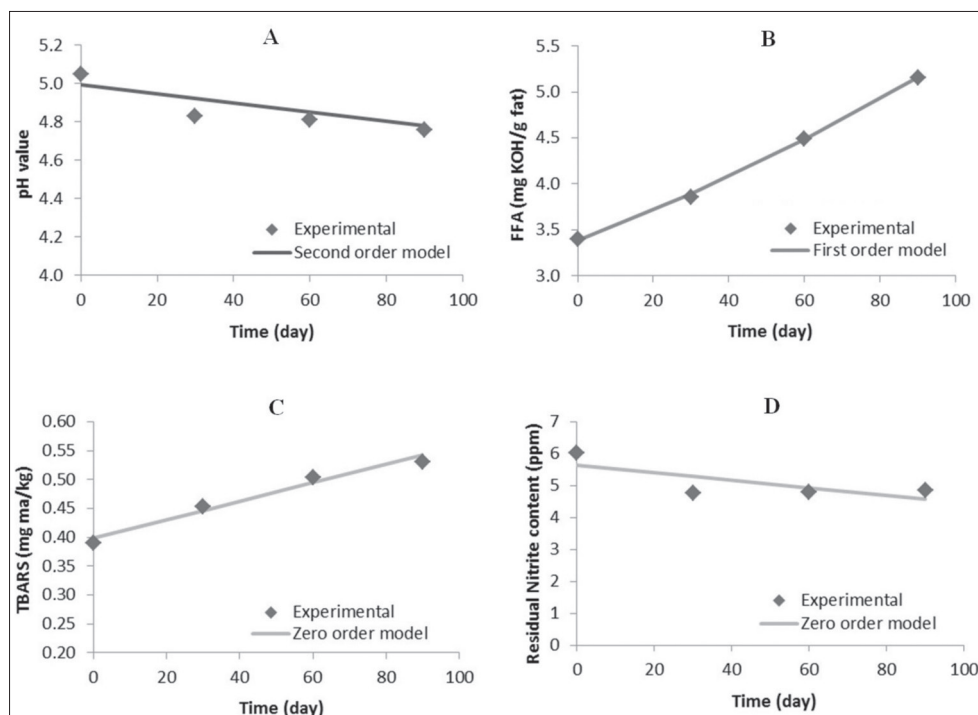


Fig 1. Changes in pH (A), FFA (B), TBARS (C) and residual nitrite (D) values during storage

FFA: Free Fatty Acid, TBARS: Thiobarbituric Acid Reactive Substances

Table 2. Estimated model constants for L*, a*, b*, Hue, BI, chroma and ΔE*

| Quality Parameter | Zero Order Model | | | First Order Model | | | Second Order Model | | |
|-------------------|------------------|------------------------|----------------|-------------------|------------------------|----------------|--------------------|------------------------|----------------|
| | c ₀ | k (day ⁻¹) | R ² | c ₀ | k (day ⁻¹) | R ² | c ₀ | k (day ⁻¹) | R ² |
| L* | 45.447 | 0.0428 | 0.8829 | 45.4449 | 0.0010 | 0.8883 | 45.4545 | 0.00002 | 0.8935 |
| a* | 15.386 | 0.0231 | 0.9872 | 15.3990 | 0.0016 | 0.9900 | 15.4083 | 0.0001 | 0.9923 |
| b* | 12.008 | 0.0167 | 0.9583 | 12.0131 | 0.0015 | 0.9630 | 12.0192 | 0.0001 | 0.9672 |
| Hue | 0.6625 | -6.0E-05 | 0.4607 | 0.6625 | -0.0001 | 0.4600 | 0.6625 | -0.0001 | 0.4592 |
| BI | 54.494 | 0.0319 | 0.9146 | 54.5054 | 0.0006 | 0.9140 | 54.6448 | 0.00001 | 0.9135 |
| Chroma | 19.517 | 0.0285 | 0.9787 | 19.5309 | 0.0016 | 0.9824 | 19.5313 | 0.00009 | 0.9856 |
| ΔE* | 7.1663 | -0.0417 | 0.9409 | 7.1807 | -0.0048 | 0.9183 | 7.1839 | -0.0006 | 0.8916 |

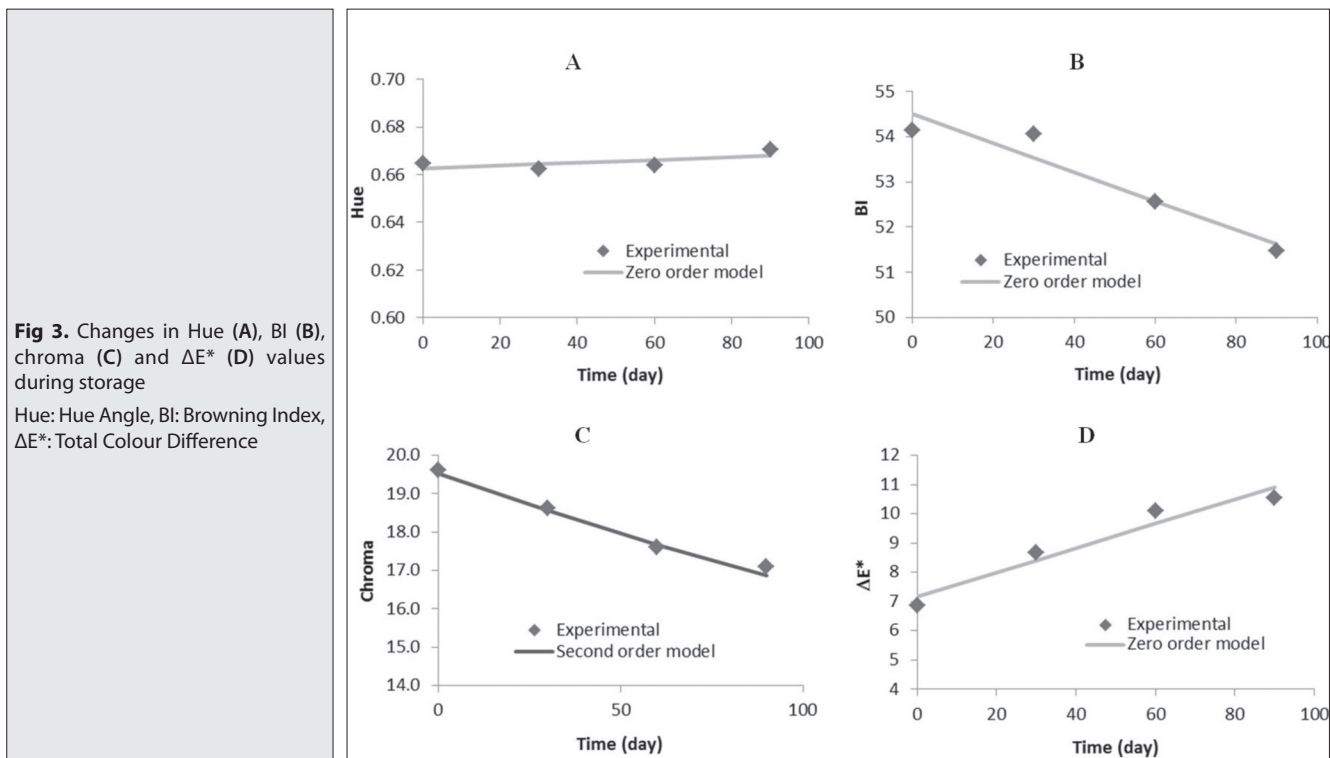
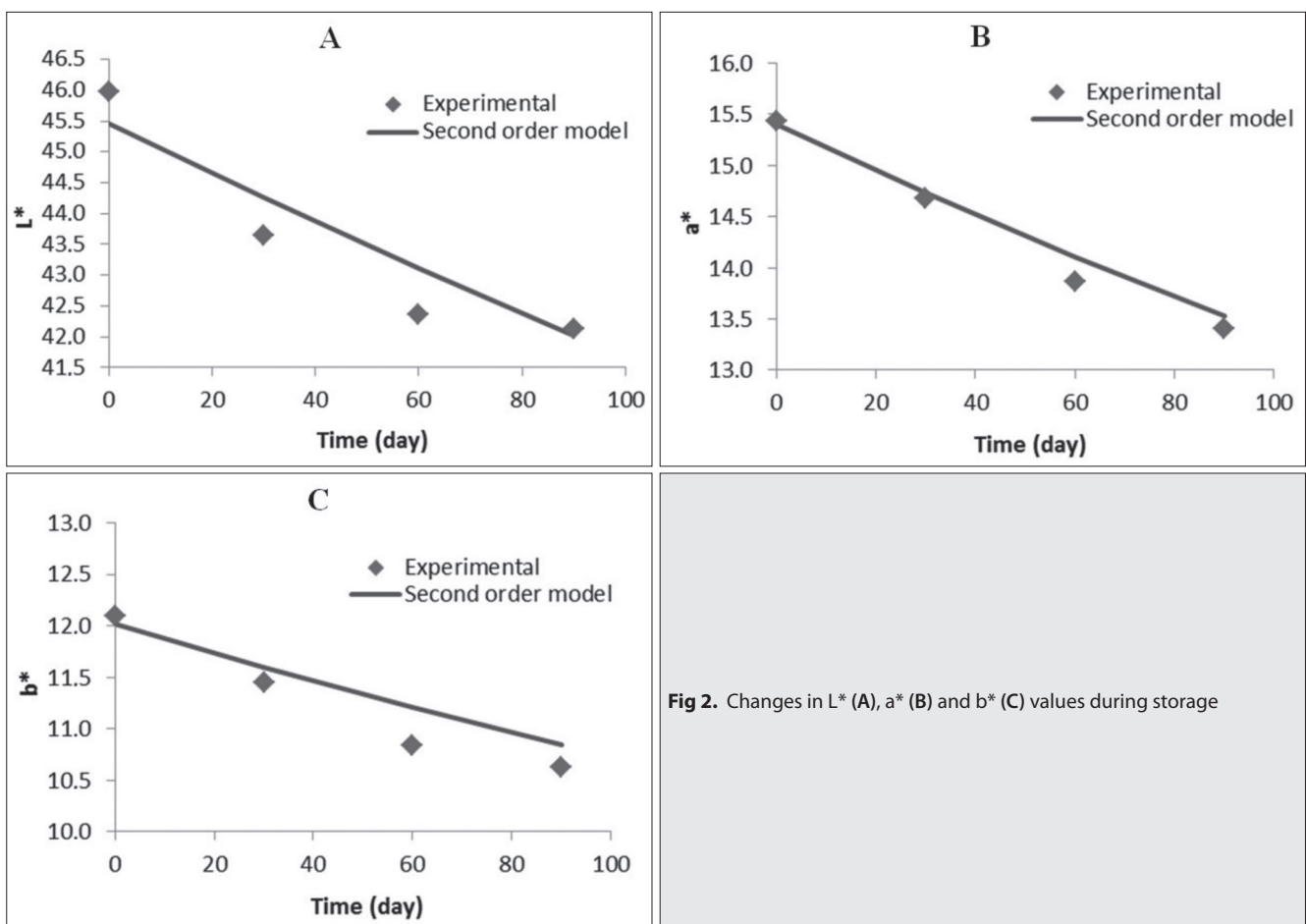
Hue: Hue Angle, BI: Browning Index, ΔE*: Total Colour Difference

during 90 days of storage (Fig. 1-B). The increase in FFA amount during storage was well represented by all of the three kinetic models with negative k values (Table 1).

The TBARS value rose from 0.390 to 0.530 mg malonaldehyde/kg during the storage (Fig. 1-C). The increase in TBARS amount during storage was best demonstrated

by zero order kinetic model with negative k value (Table 1).

The residual nitrite content showed a decrement in storage and its amount in sucuk was lower than the added nitrite amount during the preparation of sucuk dough (Fig. 1-D). The models tested were demonstrated the experimental data of the residual nitrite content with low



correlation. Amongst them the zero order model had the highest R^2 value of 0.5228 (Table 1).

The estimated kinetic parameters of L^* , a^* , b^* , hue angle (Hue), browning index (BI), chroma and total

| Microbial Counts | Log N_0 (cfu/g) | k (day ⁻¹) | R ² |
|------------------|-------------------|--------------------------|----------------|
| TMAB | 8.503 | 0.0022 | 0.5509 |
| LAB | 7.894 | 0.0047 | 0.7630 |
| SM | 6.303 | 0.0145 | 0.8208 |
| TE | - | - | - |

TMAB: Total Mesophilic Aerobic Bacteria, LAB: Lactic Acid Bacteria, SM: Staphylococcus and Micrococcus, TE: Total Enterobacteriaceae

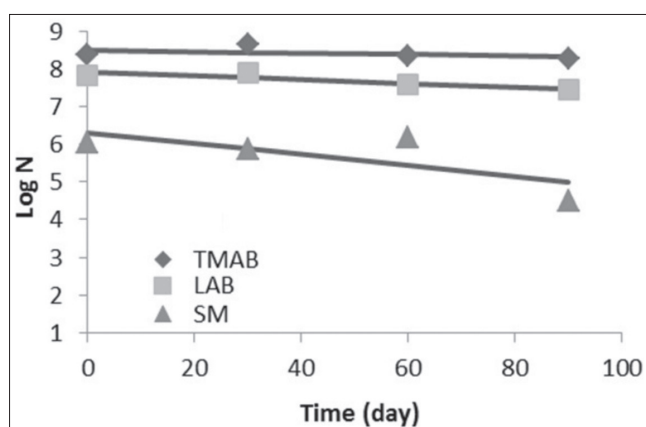


Fig 4. Changes in TMAB, LAB and SM values during storage
TMAB: Total Mesophilic Aerobic Bacteria, LAB: Lactic Acid Bacteria, SM: Staphylococcus and Micrococcus

colour difference (ΔE^*) during the storage are given in Table 2. The L^* , a^* and b^* values of the sucuk decreased during the storage (Fig. 2). These changes in L^* , a^* and b^* values during storage were best represented by a second order model (Table 2, Fig. 2). The hue angle of the sucuk increased very slightly, the BI and Chroma values decreased significantly and the ΔE^* values increased significantly during storage (Fig. 3). The decrease in chroma value was represented by a second order model and changes in others were best demonstrated by zero order models (Table 2, Fig. 3).

The estimated parameters of the first order kinetic model for microbial counts of the sucuk are given in Table 3. Statistically the model had moderate level R^2 for LAB and SM and low level R^2 for TMAB. However, graphical analysis of the experimental and the model values show that the errors between them are very low and the model equation demonstrated the kinetics of microbial changes in the sucuks well (Fig. 4). The TMAB, LAB and SM counts decreased until the end of storage, however, this decrease in the TMAB and LAB is very slight which was caused the R^2 values to be lower.

DISCUSSION

Turkish Food Codex states that the fermented sucuks

have a maximum moisture content of 40%, minimum protein content of 16% and a maximum fat content of 2.5 times of protein content [12]. At the beginning of the storage (or at the end of fermentation) properties of the sucuk samples were in these ranges.

According to Turkish Food Codex high quality ripened sucuk should have a pH at most 5.4 [12]. The sucuks were still in this range during the storage (Fig. 1-A).

An increase in FFA content of sucuk during fermentation was also reported in a previous study [9]. This increase is faster than the increase in FFA content during storage, because the rate constants reported for fermentation period are greater than the rate constants obtained for storage period. The fast increase in the FFA amount during fermentation indicates that the lipolysis is carried out by auto-hydrolysis and enzymatic hydrolysis reactions; however the slow increase in the FFA content during storage could be attributed to the limitations of the enzymatic hydrolysis due to the lower water activity. Similar changes in the FFA amount of fermented sausages have been observed by several authors [13,14].

The TBARS value increases with a higher rate during fermentation of sucuk due to the more intense lipid oxidation during processing [9]. The increment in TBARS value continued with a slower rate during storage due to the decomposition of the formed TBARS to volatile compounds. Balance between the rate of formation and the rate of decomposition determines the amount of TBARS in a product [15,16].

The residual nitrite is the amount analytically detectable in the product and its value is considerably lower than the amount added, since it interacts with various constituents of the meat during manufacturing process [17]. The residual nitrite levels decreased significantly in both fermentation and storage periods; however the rate of decrease was higher in fermentation than that of storage [9]. Alteration of the redox potential to a reduced state in vacuum may increase the transformation of the nitrite ion to nitric oxide; due to this a reduction of residual nitrite in the sucuk was observed during the storage. The residual nitrite levels may decrease during storage and distribution, also during preparation and consumption [18]. The residual nitrite levels in traditional sucuks have been reported in the range of 4.00 - 11.25 mg/kg [19].

The L^* value decreases in sucuk samples during fermentation stage, due to the moisture loss or drying [20,21] results shows that this decrease continued during storage. The a^* value indicating the redness of the sucuk decreased during storage (Fig. 2-B). The denaturation of myoglobin may cause this decrease in the redness value. These changes in the colour parameters during storage continued at slower rates than the changes in fermentation stage [9].

The TMAB and LAB counts decreased slightly until

the end of storage (Fig. 4). This is a result of lactic acid production by LAB and decrease in pH^[22,23].

The TE was uncounted during storage, therefore parameters of the models were unable to estimate (Table 3). However, a decrease in TE count during fermentation was reported previously^[9], as a result of the decrease in pH, dehydration^[23], and suppression of *Enterobacteriaceae* by fermentation microflora^[24]. This shows that this decrease continued during storage and the TE became uncountable. Due to the lack of data, the model equation for storage period was not given for the TE counts.

Sucuk is a fermented sausage and its quality characteristics changes during storage period. The changes in pH, FFA, TBARS, residual nitrite contents, L*, a*, b*, Hue angle, BI, chroma and ΔE^* values, TMAB, LAB, TE and SM of the sucuk were determined during 90 days of storage after 9 days of fermentation period. Increases or decreases in these parameters were observed during fermentation. Kinetic modelling of these changes was performed. Zero, first and second order kinetic model equations demonstrated successfully the changes in chemical and colour parameters, and linear kinetic model equation demonstrated well the changes in microbial parameters.

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