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# Degradation of Ascorbic Acid during Baking

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**Abstract** Ascorbic acid is added during production of the bread as an industrial oxidizing agent in order to maintain rheological property of bread during baking. In order to determine the effect of temperature on the ascorbic acid content in the dough during fermentation at 25 ºC, 35 ºC and 38ºC and baking temperature in which dough was prepared with mixture of 50 ppm ascorbic acid and 3 kg flour. Degradation of ascorbic acid for each stage was determined by using High Performance Liquid Chromatography (HPLC). k values were determined as 0.052, 0.0445 and 0.002 $min^{-1}$ at 25 ºC, 35 ºC and 38 ºC respectively. When temperature of baking was increased to 200 ºC, 230 ºC and 210 ºC, the amount of ascorbic acid in the bread were decomposed by 76.8%, 77% and 77.8% respectively. Ascorbic acid is decomposed above 192ºC. Although the highest temperature in bread making reached 230ºC, ascorbic acid was not found to be 100% degraded. It was determined that the ascorbic acid did not completely degrade when the bread temperature was not above 100ºC. According to that kinetic calculations were estimated from the degradation of ascorbic acid which was followed a zero-order kinetic model. Activation energies during fermentation and baking stages were calculated as 47.7kJ/mol and 27.69 kJ/mol respectively.

**Keywords** Ascorbic acid, bread, baking, temperature

## 1. Introduction

Bread, which is the most basic food material for people, is a common food for all sorts of people, different age groups, consumers at different welfare levels and different cultures. Bread can be various, but the most commonly consumed line is white type of bread which is produced by hand crafted or industrial production [1]. Bread making consists of preparation of recipe, identifying and setting of process parameters, quality control of raw materials, putting raw materials in boiler conforming to food safety requirements, mixing, weighing, growth (pre-fermentation), shaping, proofing (final fermentation), knife throwing, steaming, baking, water spraying, cooling, packaging, placement and forwarding [2]. All these stages require raw materials that may be suitable for industrial or manual processing and one of the raw materials to be most used in bread production is bread wheat flour.

The parameters in the notification are formed with the principle of human health and product quality. Additionally, it is necessary to have dough in enough resistance and energy to pass on to industrial machine processes and lines the ascorbic acid added in the flour structure its shown in Fig.1. The molecular weight of the ascorbic acid ($C_6H_8O_6$) is 176.12 g/mol. The melting point is 189ºC and the breakdown point is 192ºC. Ascorbic acid soluble in ethanol and glycerol is most soluble in water [3].

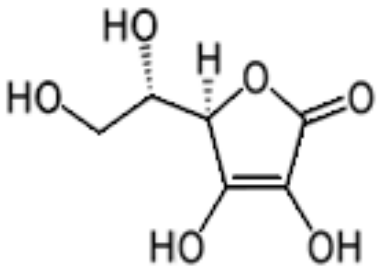


Figure 1. Chemical structure of ascorbic acid

If ascorbic acid oxidation is not maintained under appropriate conditions such as high temperature, or if it is subjected to processes that disrupt its structure, converted to dehydroascorbic acid changes [4].

The boiling was carried out in different amounts of ascorbic acid containing samples and the change by time at a research. According the applied temperature, the ascorbic acid level decreases as the time extends. It can observe ascorbic acid thorough light, stability is very low with reducing agents. Besides, stability decreases with temperature, humidity and acids (DSM) [5].

The rheological properties of the dough are reported that enhanced by the addition of ascorbic acid to the bread dough. It consists of gluten, gliadin and gluten, which are the proteins in flour. Among the gluten bonds in flour, there is better bread production due to the ascorbic acid which strengthens the sulfide bonds in the peptide chain [6].

The ascorbic acid is used at the beginning of the additives used for the improvement of the defects in the baking process by mechanical dough maturation technique. For the conversion of sulfhydryl groups to disulfide bond structures, it is preferable to use ascorbic acid in order to improve the functions of the bread. Because, when disulfide bonds are formed, the gluten in the dough is strengthened and the gas holding capacity of the dough increases. For this reason, the volume of the bread is increased and the pore structure is getting the desired network structure [7].

The ability of ascorbic acid to develop bread is measured by the increase in dough volume with fermentation. According to the result obtained in a study, the volume of fermentation was measured as 20 $cm^3$ by adding 2.5 grams of ascorbic acid to 100 kg of dough mixture. Ascorbic acid has a positive effect on the development of bread structure, bread proofing, duration of fermentation and bread volume [8].

When ascorbic acid was added to flour samples contained low and high ash values, it has been observed that bread made of ascorbic acid added in high as value dough has got better volume [9].

The aim of this study is to examine the effects of ascorbic acid, which is added as an additive in the flour, in order to exam the rheological properties of the dough. It is also aimed to determine effect of temperature on degradation values of ascorbic acid during fermentation and the baking processing stages .

## 2. Materials and Methods

### 2.1. Preparing the samples

Physical, chemical and rheological analyzes of flour were estimated before preparation dough and baking process of the used raw material were carried out. Also the effect of ascorbic acid was evaluated by the addition of 50 ppm to 3kg flour weight and property were given in Table 1.

**Table 1**: Property of flour

| Quality Parameters | Result |
|---|---|
| Wet gluten (%) | 26.5 |
| Gluten index (%) | 0.96 |
| Elasticity (Qualitative) | Average |
| Normal sedimentation (mL) | 30 |
| Delayed sedimentation (mL) | 37 |

| | |
|---|---|
| Moisture (%) | 13.6 |
| Ash (dry matter, %) | 0.800 |
| Top of the screen (212 μm) (%) | 0.8 |
| Protein (dry matter, %) | 11.07 |
| Buoyancy capacity (%) | 60.5 |
| Development time (min) | 2.3 |
| Stability (min) | 15.1 |
| Degrees of softening (FI) | 19/27 |
| Energy (IT) | 55 |
| Resistance (IT) | 429 |
| Elongation (mm | 90 |
| Maximum BU (IT) | 435 |
| Rate number | 4.7 / 4.8 |
| Taste (Qualitative) | Appropriate |
| Smell (Qualitative) | Appropriate |
| Color (Qualitative) | Yellowish |

The baking test was performed according to the Turkish method (wet gluten: Perten, ICC 106, 137/1, gluten indeks: Perten, ICC 155&158, Sedimentation: Tekpa, ICC 116, moisture: Binder, ICC 110, ash: Termoscientific, TS EN ISO 2171, top of screen: Retsch, TS 4500, protein: Foss, ICC 105, farinograph: Brabender, ICC 115/1, extensograph: Brabender, ICC 114/1) and the protocol was used and mixed as given in Table 2: flour 3000 g, 1900 ml water, 109 g of yeast, 22 g of grape vinegar, 62 g of whey powder, 26 g of salt, 11 g enzymes ( mixture of α-amylase, hemicellulose) and 50 ppm of ascorbic acid were mixed for the optimal consistency of 435 BU. Dough dividing and roll shaping were made by hand and after the standard proofing time the pieces of dough were baked at 200-230°C for 15 minutes.

**Table 2**: Process Parameters

| **Experiment type** | **Bread with ascorbic acid** |
|---|---|
| Ambient temperature (°C) | 24.7 |
| Ambient humidity (% RH) | 45 |
| Water temperature (°C) | 18 |
| pH value of dough | 4.09 |
| Dough temperature (°C) | 25 |
| Mixing time (min) | 3 min at slow / 5 min at fast |
| Dough consistency | Good |
| Boiler fermentation duration (min) | 20 |
| Pre-fermentation duration (min) | 1 |
| Final fermentation (proofing) duration (min) | 32 |
| Cabin temperature (°C) | 32 |
| Cabin humidity (% RH) | 50 |
| Dough consistency after fermentation | Good |
| Oven temperature (°C) | 200, 230 and 210 |
| Oven duration (min) | 15 |

After the raw material was mixed for about 8 minutes, temperature of the dough was increased to 27°C and the dough was held at this temperature for 20 minutes. During fermentation of the dough, temperature was increased to $32^0$C at % 50 relative humidity then it was brought in to the final fermentation stage at 38°C as shown in Figure 2 and 3. Then it was baked at 200 ºC, 230 ºC and 210 ºC, for each stage degradation of ascorbic acid was estimated by HPLC.

*(a) Boiler fermentation (b) Pre-fermentation (c) Final fermentation*

*Figure 2: Pictures of dough samples added ascorbic acid*

In figure 3, it can bee seen the transformation of the dough that was given to the oven. The dough is becoming to the bread form step-by-step in the tunnel oven. In Figure 2-a, the form of bread is actually doughy. At the next stage, at 230°C, the product was gained the bread structure. Then, at 210°C, the product was completely taken the bread form.


*Figure 3: Bread production according to the stages of dough from the time of baking*

**2.2. High Pressure Liquid Chromatography (HPLC) Analysis and Calibration Curve Obtaining**

Ascorbic acid analysis was applied at HPLC (Agilent, USA). The device column was selected as Agilent Zorbax SB-C18 brand 5µm, 4.6 × 250 mm (Agilent, 880975-902, USA), and the values was measured at a UV lamp of 245 nm wave length.

Methanol (Merck) and potassium dihydrogenphosphate (Merck) 0.05 M $KH_2PO_4$ / $H_2O$ (28:60:22) were prepared as mobile phases. Methanol, potassium dihydrogen phosphate and water were used fresh every time in the ratio of 28:60:22. After the solution was prepared, the pH was checked, the pH was requested to be 2.6 and the setting was adjusted accordingly [10].

In order to estimate calibration curve the standard solution of ascorbic acid were prepared at different concentrations as 0, 5, 20, 50, and 100 ppm (Sigma Aldrich). The standard solutions were mixed with mobile solution then filtered through a 0.45 µL filter paper (Sartorius) through via syringe (50 µL) into device. As shown in Figuıre 4 and Table 3.

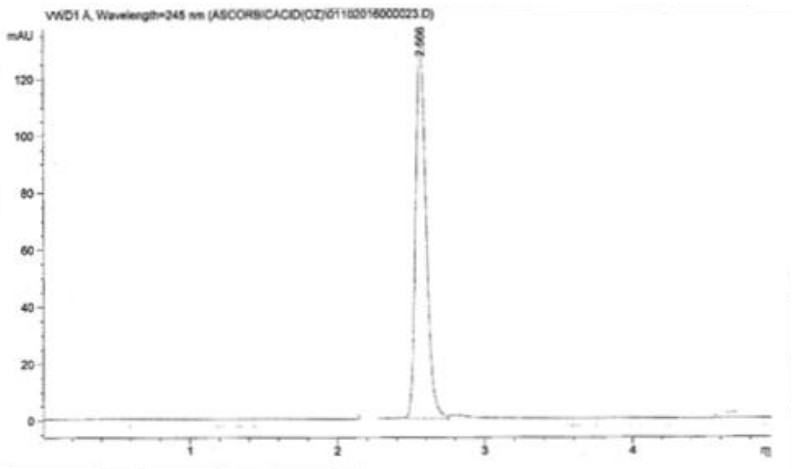


*Figure 4: Peak area obtained at 50 ppm concentration*

**Table 3**: Concentration area data

| Concentration (ppm) | Average area (Mol $min^{-1}$) |
|---|---|
| 0 | 0 |
| 5 | 40.7 |
| 20 | 252.7 |
| 50 | 638.4 |
| 100 | 2545.8 |

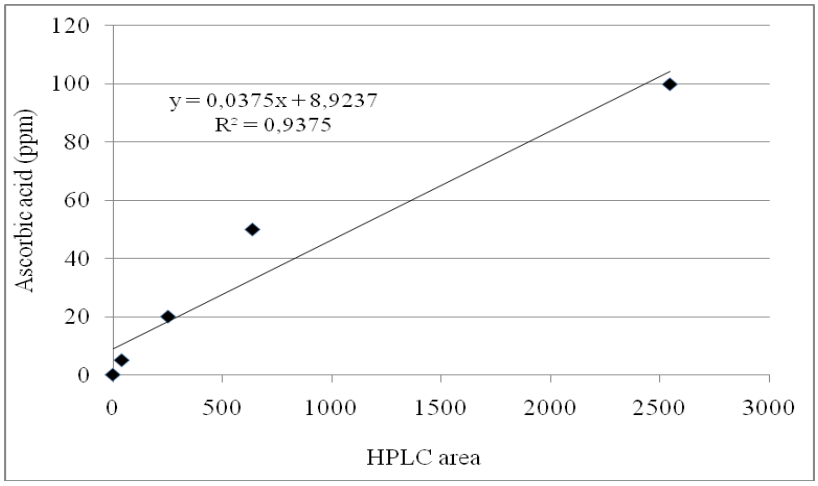


*Figure 5: Calibration Curve of Ascorbic acid*

From the calibration curve y = 0.0375x + 8.9237 formula was estimated by correlation coefficient.

| Sample Type | Area (mol $min^{-1}$) | CV% |
|---|---|---|
| 0 ppm | 0 | 0 |
| 5 ppm | 40.7 | 26.52 |
| 20 ppm | 252.7 | 14.69 |
| 50 ppm | 638.9 | 3.80 |
| 100 ppm | 2545.8 | 2.81 |

Statistical evaluations were made. The coefficient of variation (correlation coefficient) with the data obtained from the standard deviation was found and calibration curve was drown as shown in Fig.5

### 2.3. Sample Analysis

After the samples were identified, 15 gram samples were weighed and 30 ml of 4.5% metaphosphoric acid were added to the samples. The sample was stirred in the magnetic stirrer for 15 minutes and then vacuum filtered. If bread is too absorptive the liquid is filtered by applying pressure through sterile gloves or an object that will not cause contamination. The filtrate was completed with 50 ml ultrapure water.

The resulting solutions were filtered through 0.45 micron Sartorius cellulose acetate and injected into the device with 50 microliters of special syringes. Peaks were observed for 5 minutes in the analysis and the peak area obtained in approximately 2.4 minutes, 2.5 minutes as in standard preparation was subtracted.

## 3. Results and Discussion

The vitamin C values of the dough samples that not exposed to heat treatment is presented at Table 4. According to the table, vitamin C values was degraded during this bread making process.

**Table 4**: The vitamin C losses of the dough samples that were not exposed to heat treatment

| Sample Type | *Process Duration (min)* | Temp. (ºC) | Area (mol $min^{-1}$) | Vit. C (ppm) | Std. Dev. | CV% |
|---|---|---|---|---|---|---|
| Start (boiler fermentation) | 0 | 25 | 597.175 | 31.3 | 4 | 12.7 |
| Result of boiler fermentation (Pre-fermentation start) | 20 | 35 | 289.22 | 20.4 | 1.2 | 5.8 |
| Result of pre-fermentation (start of the final fermentation) | 32 | 38 | 175.27 | 15.5 | 1.6 | 10.1 |

The vitamin C losses of the samples during the baking related with the time were presented in Table 5, ıt was indicated that vitamin C values degraded during the baking process.

Normally in the tunnel oven, the path taken gradually along the band, depending on the temperature in 5 minute intervals was passed. The degradation of vitamin C during baking were estimated that 76,8% at 200 °C, 77% at 230 °C and 77.8% at $210^0$C respectively. The ascorbic acid which degrades above 192 ºC was not completely degraded at the bread due to the central temperature of bread were not exceed above 100 ºC at baking stage. While the first part of the oven when the temperature was 200 ºC, the inner temperature of doughy bread was 38 ºC. When the inner temperature of the oven was increased to 230 º C, the inner temperature of the bread was 88 ºC and when the inner temperature of the oven was 210 ºC the inner temperature of the bread was 100 ºC owing to that the ascorbic acid in the bread was not completely degraded.

**Table 5**: The vitamin C losses of the samples during baking process

| Sample Type | *Process Duration (min)* | Temp. (ºC) | Area (mol $min^{-1}$) | Vit. C (ppm) | Std. Dev. | CV % |
|---|---|---|---|---|---|---|
| Tunnel Oven Section 1 | 67. | 200 | 72.185 | 11.6 | 0.3 | 2.2 |
| Tunnel Oven Section 2 | 72. | 230 | 68.2 | 11.5 | 0,0 | 0.0 |
| Tunnel Oven Section 3 | 77. | 210 | 59.14 | 11.1 | 0.2 | 2.0 |

### 3.1. Calculation of kinetic parameters

Temperature dependence of the Maillard reaction was modelled with the Arrhenius equation:

$k = k_0 . e\text{-}Ea / RT$

where k = rate constant;

ko = pre-exponential factor;

Ea = activation energy (cal/mol or J/mol);
R = gas constant (1.987 cal/mol.K);
T = temperature in °K.

Activation energies over the temperature range 25°-38°C for dough during fermentation was calculated from the slopes of Arrhenius equation as

The degradation of ascorbic acid (k) values were calculated 0.0527 $dk^{-1}$, $k_2$: 0.0445 $dk^{-1}$ and for $k_3$: 0.0200 $dk^{-1}$ at 25ºC, 35ºC and 38ºC respectively. The activation energy was determined from slope of curve to be 10.94 kcal/mol (47.70 kJ/mol). The k values during baking were found to be 0.0070 $min^{-1}$ and 0.0445 $min^{-1}$ and the activation energy was estimated 6.62 kcal / mol ( 27.69 kJ / mol ). Lower activation energies during fermentation indicated that degradation of ascorbic acid are higher at this stage than baking.

The vitamin C losses at some bread production stages are indicated at Figure 7. As seen from this figure, the results are similar with the previous studies. Similar to other studies, it is found that the ascorbic acid has deteriorated by temperature and probably its form has changed with the increasing temperature. The k values were decreased by the temperature increase. Like other studies, first degree equation was obtained in our work. In addition, activation energy obtained from the Arrhenius equation is 47.7 kJ/mol and this value is similar with previous studies.

Penny et.al. studied on guava, mango and marula fruits. They observed the thermal kinetics of ascorbic acid in mango, guava and marula from 80°C to 150°C. According to certain temperatures and times, c vitamin (ascorbic acid) was started to deteriorate. Ascorbic acid k values, beginning to decay at 100 degrees, were found (kd: 7.2×10-3 $min^{-1}$) for Marula fruit, (kd: 1.2×10-1 $min^{-1}$) for guava fruit and (kd:1.3×10-3 $min^{-1}$) for mango fruit. Activation energies were found as (Ea: 58 kJ/mol), (Ea:39 kJ/mol) (Ea:29 kJ/mol) for guava, for mango and for marula respectively [11]. These results were in agreement with our results by means ascorbic acid sensitive to temperature.

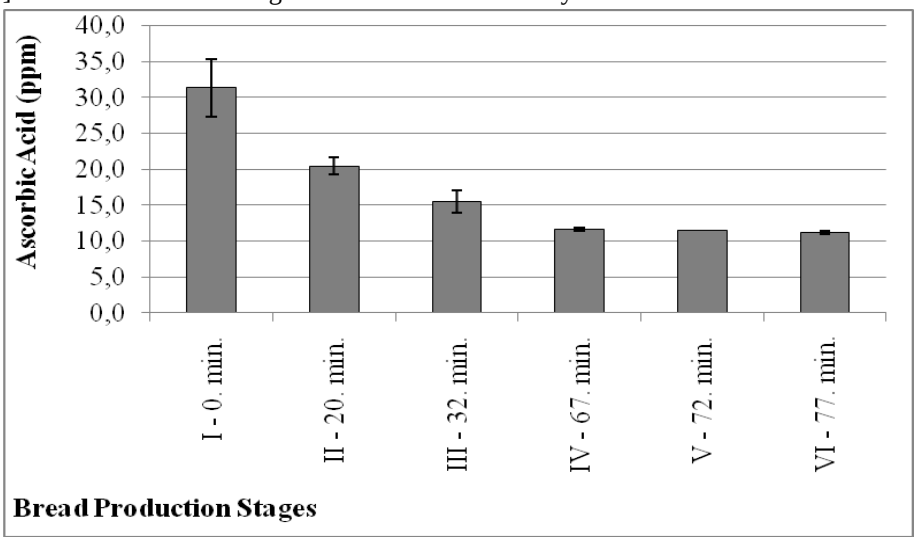


*Figure 7: The loss of ascorbic acid in bread production stages*

Other researcher was studied in asparagus veggies on the degradation of ascorbic acid at the asparagus plant at 110°C, 115°C, 120°C and 125°C was estimated the reaction rate . k was found that 0.5×10-3 $min^{-1}$ at 110°C, a $0.2\times10^{-3}$ $min^{-1}$ at 100°C [12] this values were lower than our results this may be due to structure differences of food material.

Paul and Ghosh have studied pomegranate juice [13]. They studied vitamin C and phenolic compounds in pomegranate juice. These components were investigated at 70°C and 90°C. The chemical degradation of ascorbic acid was found with the first-degree equation and Arrhenius equation was calculated. Activation energy for ascorbic acid was found 81.67 kJ/mol. This value were higher than our experimental work that meant degradation occur more slowly than baking process this may be related presence of phonelic compound in pomegranate juice.

Amla fruit or Bektashi grape, which is named Phyllanthus emblica L. in Latin, was investigated for the Bektashi grapes were heated and analyzed at 50ºC and 120ºC and a result of the degradation of ascorbic acid behave to the

first order kinetic equation was determined as 4.09 kcal/mol [14]. This value was higher than baking processing the differences owing to composition and the structure differences between fruit and dough.

Previously, thermal kinetics of ascorbic acid and thermal degradation at some baking products had been found as shown in Table 6. The relationships between the material and the processing temperatures of the samples were established and at the obtained equations, k values and activation energies were given. Table 6 indicates the data on degradation of ascorbic acid also occurred during storage..

Table 6: Ascorbic acid degradation in storage of same cereal samples [15].

| Some cereal foods | Storage conditions | Time (h) | Retention (%) | $k_0$ ($h^{-1}$) | References |
|---|---|---|---|---|---|
| Bread | 25°C, polyethylene bags | 168 | 15 | 113 | [16] |
| Bread with fiber | 25°C, moisture 45% | 144 | 52 | 208 | [16] |
| Bread without fiber | 25°C, moisture 37% | 144 | 18 | 117 | [17] |
| Bread with reduced iron and L-ascorbate | 25°C | 720 | 95 | 45 | [18] |
| Bread with reduced iron and L-ascorbic acid | 25°C | 720 | 20 | 120 | [18] |
| Ready-to-eat cereal | 23°C | 8760 | 71 | 0.39 | [19] |
| Ready-to-eat cereal | Room temperature | 8640 | 60 | 0.58 | [20] |
| Cereals | 40°C | 2160 | 93 | 0.34 | [21] |
| Cereals | 22°C | 4320 | 94 | 0.14 | [21] |

* This table is established according to Leskova et al. [15]

Leskova et al. [16] found at their experiment that when bread has been stored at 25ºC, ascorbic acid loose was 85 %. In the present study, the experiment at 25ºC, ascorbic acid loose of dough is 63 %. There are several reasons for k value to be higher at the present work. In the present work, dough was getting warmed while it had been mixed. Also, stabilization of ascorbic acid and the humidity of the products are other reasons. The main reason could be the structure of bread, while the bread is dry, dough structure's humidity is highly.

Furthermore, when compared with guava fruit which was heated from 80ºC to 150ºC and k value determined as 1.2×10-1. $min^{-1}$ when compared with fermentation dough values for degradation of ascorbic acid where as lower value for guava fruits.

## 4. Conclusion

It can be concluded that the ascorbic acid did not completely degrade when the bread center temperature was not above 100ºC. According to that kinetic calculations were estimated from the degradation of ascorbic acid which was followed a zero-order kinetic model. Activation energies during fermentation and baking stages were calculated as 47.7kJ/mol and 27.69kJ/mol respectively.

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