Research Article GU J Sci, Part A, 11(3): 589-597 (2024) 10.54287/gujsa.1529814

Gazi University
Journal of Science
PART A: ENGINEERING AND INNOVATION
http://dergipark.org.tr/gujsa

Kinetics of Colour, Clarity Changes and HMF Formation in Pear Juice Concentrate During Storage

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Keywords

Pear Juice Concentrate
Kinetics
Colour
HMF
Storage
Clarity

Abstract

In terms of providing delicious taste and excellent source of nutritional content, pears are highly consumed fruit all around the world. Pear juice concentrate (PJC) is one of the most frequently used products in the manufacturing processes of beverages, syrup base for canning fruits, vinegar, and wine. Colour, clarity, and the formation of hydroxy methyl furfural (HMF), a mark of Maillard browning reactions, were appraised as quality indices changes of PJC throughout storage. The samples were kept at 47°, 37°, and 27°C for 32 weeks and kinetic criteria were calculated for changes in color, clarity, and the generation of HMF. According to the model of zero-order reaction, the results demonstrated that the quantity of HMF rose linearly with temperature and storage period. The values of clarity and colour were both linearly reduced to align with the zero-order reaction kinetic. The dependence on temperature of the rate constant of the reactions examined and the activation energy values were calculated as 153.14, 93.81 and 61.48 kJ mol^{-1} for the generation of HMF, clarity, and colour changes with the help of Arrhenius equation.

Cite

Karadeniz, F., Işık, B., Kaya, S., Aslanali, O., & Midilli, F. (2024). Kinetics of Colour, Clarity Changes and HMF Formation in Pear Juice Concentrate During Storage. *GU J Sci, Part A*, *11*(3), 589-597. doi:10.54287/gujsa.1529814

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Article Process

Submission Date	07.08.2024
Revision Date	14.08.2024
Accepted Date	28.08.2024
Published Date	30.09.2024

1. INTRODUCTION

Pear, one of the eldest cultivated species, is among the widely consumed fruits in the world thanks to its high nutritious content and satisfying taste (Nikicevic, 2005). Between the years of 1994 and 2022 top 10 pear producers were ranked as China, USA, Italy, Argentina, Spain, Türkiye, South Africa, Japan, Republic of Korea, and Belgium. In the year of 2022 Türkiye's pear harvested area was 23.706 ha while pear production was 551.086 tons (FAOSTAT, 2024).

Pear not only provides a great source of carbohydrates, phenolic compounds, vitamins, and minerals but also high amount of dietary fiber, which popularizes them in the production of food purees for babies and mix nectars (Saeeduddin et al., 2015). Additionally, vinegar, wine, beverages, and syrup base for fruit canning are also among the uses of pear juice concentrate (Cornwell & Wrolstad, 1981). As a chemo-preventive agent, chlorogenic acid, one of the main phenolic compounds in pears, helps patients avoid chronic illnesses like cardiovascular disease and cancer. It also strengthens the immune system and lessens the side effects of chemotherapy medications. It is known that pears have been utilized as herbal derived medicine to mitigate cough, constipation, and alcoholism for more than 2000 years in China. While pears have low levels of fat and protein, they are abundant in vitamins C, E, and B complex as well as potassium, copper, and fiber (Öztürk et al., 2015).

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Pears should be conserved or processed in time following the harvest period so as not to encounter quality changes through handling. For instance, pear juice, is prone to browning easily during processing and storage. Once brown color has occurred, the color of pear juice becomes an unacceptable dark color from attractive golden yellow. Thus, the commodity characteristics of pear juice, such as its nutritional value, organoleptic features, and marketability decreases, and manufacturers are mostly subjected to large losses and customer rejections (Cornwell & Wrolstad, 1981). Browning observed in fruits and vegetables stems from enzymatic and non-enzymatic browning reactions. For concentrated fruit juices browning is mainly occurring due to the reactions related to non-enzymatic browning produced by the Maillard reaction (MR) leading to black and brown pigments formation as well as differences in odor and taste (Ibarz et al., 2008). The nonenzymatic browning reactions that result from MR, degradations of pigments, caramelization, and ascorbic acid are the primary reasons of browning in processed foods (Cornwell & Wrolstad, 1981). It is widely known that the Maillard reaction causes to HMF formation, which serves as measure for the degree of heat treatment performed (Lee & Nagy, 1988; Zhu et al., 2023). MR is also observed through the storage and the processing of fruit juice concentrates. Chen et al. (2024) reported that the Maillard reaction is the main reason for browning in orange juice concentrate during storage. Maillard reaction is what causes the browning and unpleasant attributes in apple and pear juice (Kathuria et al., 2023).

Since foods' organoleptic characteristics are of high importance for consumers, the investigation of the process and storage conditions of the products is considered critical. The kinetic process of chemical browning reactions has been examined by numerous researchers (Beveridge & Harrison, 1984; Karadeniz et al., 2024a). The modeling of kinetic mechanism enables to assess the impact of process conditions on crucial quality indices. Degradation kinetics, naming reaction order, activation energy, and rate constant, is vital to have knowledge about the food quality loss through storage besides thermal process treatments.

The purpose of this study is to present the association between the data obtained from the afore mentioned variables evaluated and to characterize the kinetic mechanism of nonenzymatic browning in PJC by examining the HMF quantity, color, and clarity variations along the storage at 47°, 37°, and 27°C.

2. PRODUCTION OF PJC SAMPLES

Göknur (Göknur Gıda A.Ş., Niğde) fruit and vegetable juice concentrate factory produced pear juice concentrate according to flow chart given in Figure 1. This process is repeated to prepare duplicate samples. The prepared samples were put as duplicate sets in storage rooms adjusted at 47°, 37°, and 27°C. Samples that were randomly chosen were taken on weekly basis from a 47°C storage room on two weeks intervals from a 37°C storage room, and every three weeks from a 27°C storage room. The samples were then analyzed with respect to the parameters of HMF amount, colour, and clarity. The samples' pH, total soluble solids (TSS), and titratable acidity (%, citric acid) were also assessed to define the characteristics of PJC.

3. CHEMICAL SUBSTANCES

For this research, Merck is the firm that all chemicals were provided from.

4. DETERMINATION OF PHYSICOCHEMICAL AND CHEMICAL ATTRIBUTES OF PJC

4.1. pH, TSS (°Bx), and Titratable Acidity

TSS was measured with an ATAGO refractometer with the model of RX-5000α (Atago Co., Ltd., Japan). Following the dilution process to reach the single strength °Bx level (11.9 °Bx), an automatic pH meter (Mettler-Toledo GmbH, Switzerland) was used to examine the pH value of the PJC. Using the same pH meter, the potentiometric method was used to analyze the titratable acidities of diluted samples, which were then reported as a percentage of anhydrous citric acid.

4.2. Measurement of Colour and Clarity

A Spectrophotometer was used to measure transmittance in diluted samples at wavelengths of 440 nm and 625 nm, respectively, to identify color and clarity changes in PJCs. The colour and clarity results were expressed as follows: colour (%T@440nm @11,9°Bx) and clarity (%T@625nm, @11,9°Bx).

4.3. Spectrophotometric Analysis of Hydroxy -Methyl- Furfural

HMF concentration in stored PJCs was obtained with employing a spectrophotometric method (Anonymous 1984). This practice is related to the reaction taking place among p-toluidine, barbituric acid, and HMF. Since the strengthens of red color occurred during this reaction, is correlated with the amount of HMF in the sample, spectrophotometer at 550 nm was used for the quantification of HMF.

5. KINETIC PARAMETERS COMPUTATION

Standard equation for a zero-order reaction model ($A = kt + A_0$) was used to analyze the differentiation in the HMF, colour, and clarity parameters of PJC that means HMF linearly rises, while colour and clarity decreases during storage.

Where; A_0, amount of criteria at zero-time; A, amount of criteria at moment t; k, rate constant of the reaction; t, storage period (week).

Arrhenius equation ($k = k_0 \times e^{-Ea/RT}$) was used for determination of temperature dependence of the HMF occurrence, and colour and clarity changes in PJC.

Where; k, speed constant of the reaction ($week^{-1}$); k_0, frequency factor ($week^{-1}$); Ea, activation energy ($kJ\ mol^{-1}$); R; universal gas constant ($8.314 \times 10^{-3}\ kJ\ mol^{-1}\ K^{-1}$); T, absolute temperature (°K). Besides, Q_{10} values were stated by the below formula:

$$Q_{10} = (k_2/k_1)^{(10/T_2 - T_1)} \tag{1}$$

where k_2, speed constant of the reactions at T_2 temperature (mg HMF $week^{-1}$ and colour T% @440 nm, clarity T% @625 nm); k_1 speed constant of the reactions at T_1 temperature (mg HMF $week^{-1}$ and colour T% at 440 nm, clarity T% at 625 nm) (Karadeniz et al., 2024b).

6. STATISTICAL ANALYSIS

This analysis has been performed using the IBM SPSS Statistics program. The correlations between HMF, colour, and clarity parameters have been determined, and a correlation test has been conducted at a significance degree of 0.01.

7. RESULTS & DISCUSSION

No significant changes were determined in physicochemical parameters of pear juice concentrates during storage at different temperatures. The initial °Bx value (70.36) was found as 70.45°Bx, 70.57°Bx and 70.55°Bx when the storage period ended at storage temperatures of 27°C, 37°C and 47°C, respectively. The value of pH was initially 3.9. At the end of storage, it was determined as 3.8, 3.9 and 3.8 at storage temperatures of 27°C, 37°C and 47°C, respectively. The titratable acidity (%, anhydrous citric acid) was found as 1.57 at the beginning of the storage while it was found as 1.60% at 27°C, 1.62% at 37°C and 1.59% at 47°C at the end of storage.

Changes in clarity, colour, and the formation of HMF in comparison with storage time had been described as a function of the temperatures (47°, 37°, 27°C) for pear juice concentrate’s nonenzymatic browning reaction. The most appropriate model was chosen by defining the determination coefficients (R^2) through regression analysis. Best-fit regression equations were used to calculate the rate constants. Variation in HMF quantity, colour values and clarity through the time of storage is presented in Figure 2, 3 and 4, respectively starting from the lowest storage temperature to the highest storage temperature in this research article.

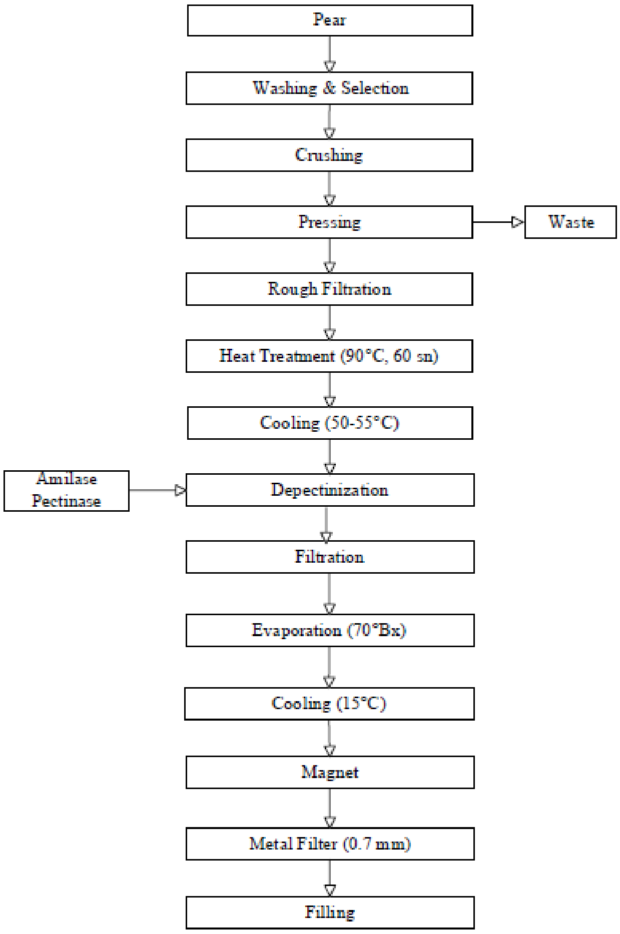

Figure 1. *Pear Juice Concentrate Processing Flow Chart*

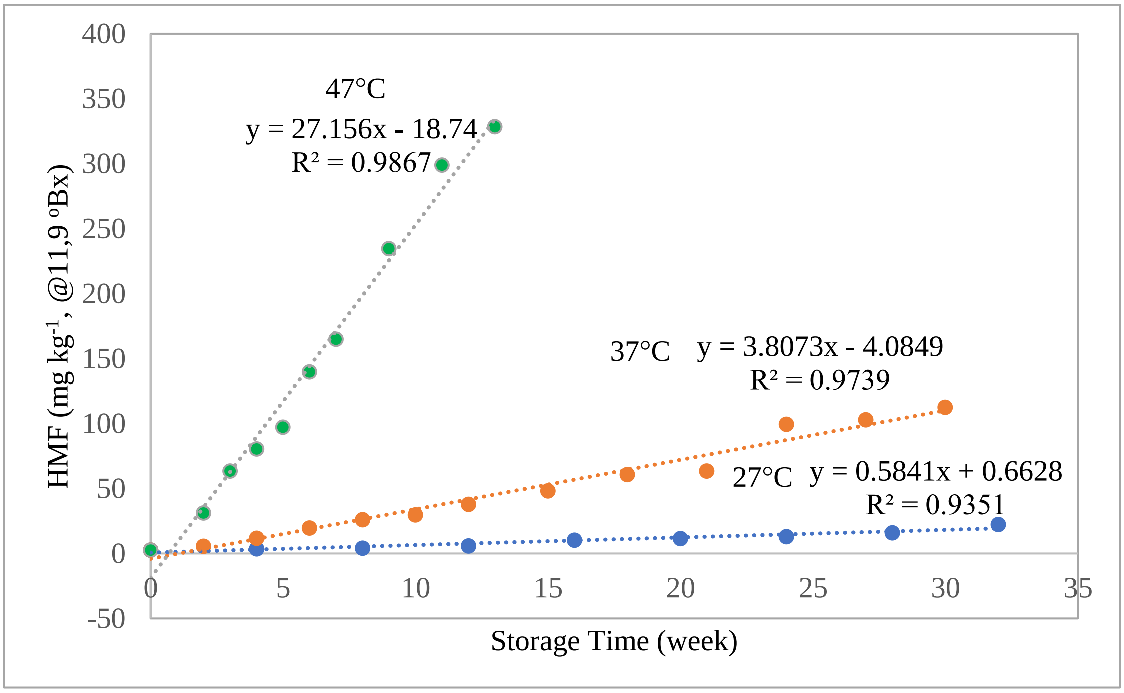

Figure 2. *HMF occurrence in PJC during storage*

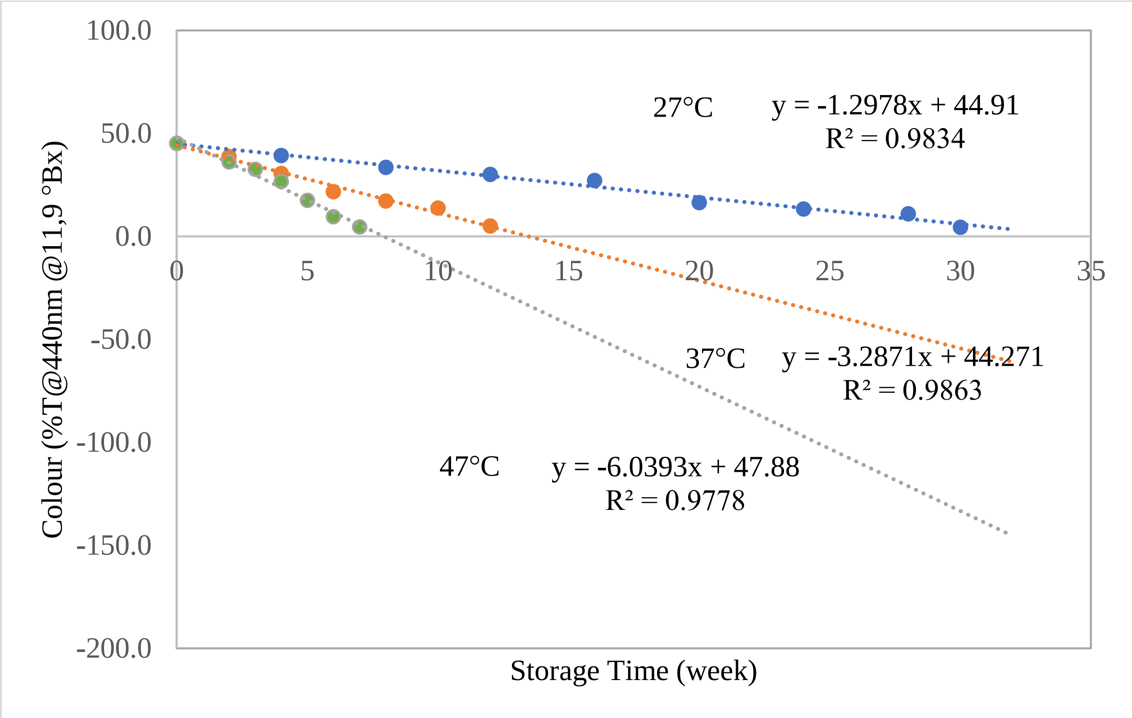

Figure 3. *Colour changes in PJC during storage*

The HMF content in pear juice concentrate increased over time, starting at 2.7 mg kg^{-1} and reaching 22.5, 112.5, and 328.5 mg kg^{-1} at 27°, 37°, and 47°C, respectively, at the end of storage time. The amount of HMF climbed by time and heat treatment applied in canned grapefruit juices and apple puree as indicated in the outputs of Lee and Nagy (1988) and Zhang et al. (2019) studies, respectively. The maximum increase for HMF content was detected at the rate of 12066%, this was followed by the value of 4066% at the storage temperatures of 47°C and 37°C, respectively. HMF amount in PJC, which showed a linear increase, stated that the reaction kinetics was in parallel with zero order model as presented in other research articles (Burdurlu et al., 2006; Duru et al., 2012). The model of sucrose–glutamic acid showed zero-order kinetics for HMF formation (Zhang et al., 2019). Beveridge and Harrison (1984) studied the effect of temperature and TSS on nonenzymatic browning reactions in PJC and reported that browning reaction occurred following zero order reaction kinetics.

The colour changes were evaluated for browning observed in PJC. It was detected that the colour value (%T@440nm) reduced by time at each storage temperatures examined (Figure 3) indicating that the brown colour intensity was increased. At the beginning of the storage the colour was found as 45,2 and it is less than 5 after 30 weeks of storage at 27°C, 12 weeks of storage at 37°C and 7 weeks of storage at 47°C. This is indicating that higher storage temperature increases the reaction rate. Reaction for colour intensity increase in PJC followed zero-order reaction kinetic which coincides with the findings of other studies (Beveridge & Harrison, 1984; Burdurlu et al., 2006). It has been demonstrated that the reactions of amino acids with reducing sugars have zero-order kinetics, leading to non-enzymatic changes (Ibarz et al., 2008).

Clarity change in PJC was found as 77% at 47°C stored samples. The reduction in clarity was found as 57% and 21% at 37°C and 27°C stored samples, respectively. The clarity changes in PJC also fit well with zero-order reaction kinetics which indicates there is a linear reduction of clarity during storage period.

Temperature dependence of the HMF formation, browning and clarity decrease was determined by Arrhenius equation and Arrhenius plots were given in Figure 5. Activation energy for HMF formation was found higher (153.14 kJ mol^{-1}) than that of both clarity (93.81 kJ mol^{-1}) and color (61.48 kJ mol^{-1}) changes which shows that the occurrence of HMF slow in comparison with color and clarity. Activation energy values for HMF increase in pear puree were reported as 115.14 kJ mol^{-1} by Tosi et al. (2002) and in modelling solution of apple juice found as 117.2-165.8 kJ mol^{-1} by the research of Resnik and Chirife (1979) which coincides with the result of this research.

Temperature quotient (Q_{10}) values were computed (Table 1) for three temperature ranges: 27–37°C, 37–47°C, and 27–47°C. Table 1 illustrates how temperature increases had a greater impact on HMF occurrence in PJC than on clarity and browning reactions. It was discovered that the rise in HMF at 47°C was 7.13 times greater than that at 37°C.

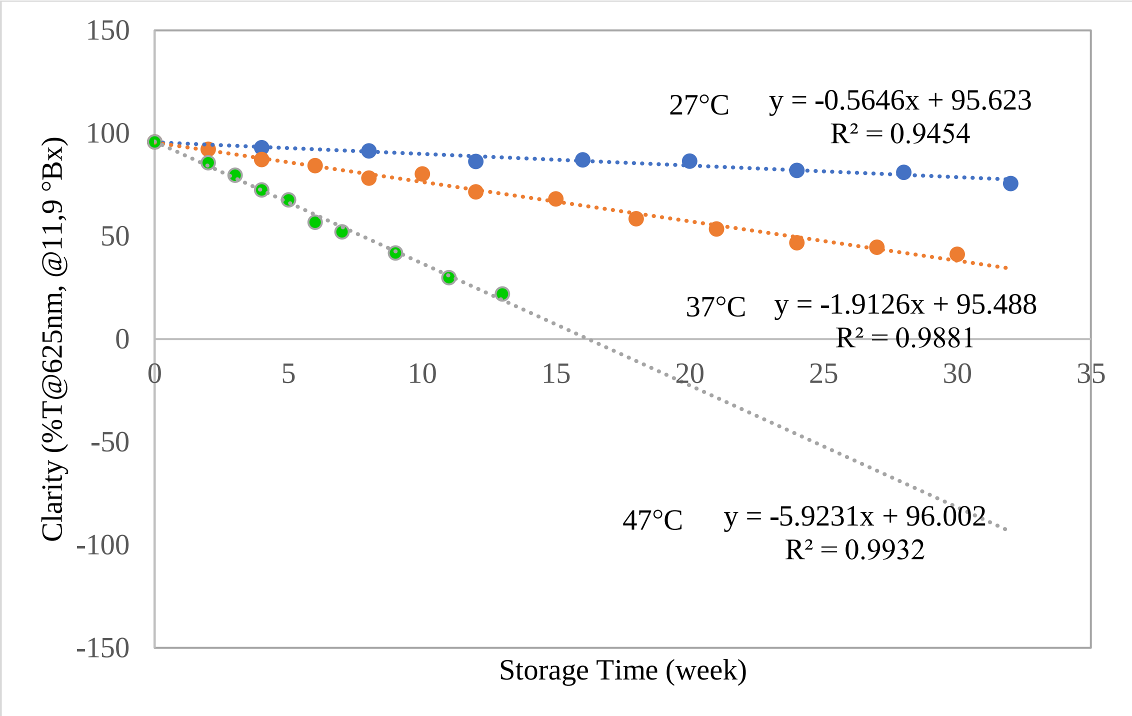

Figure 4. *Clarity changes in PJC during storage*

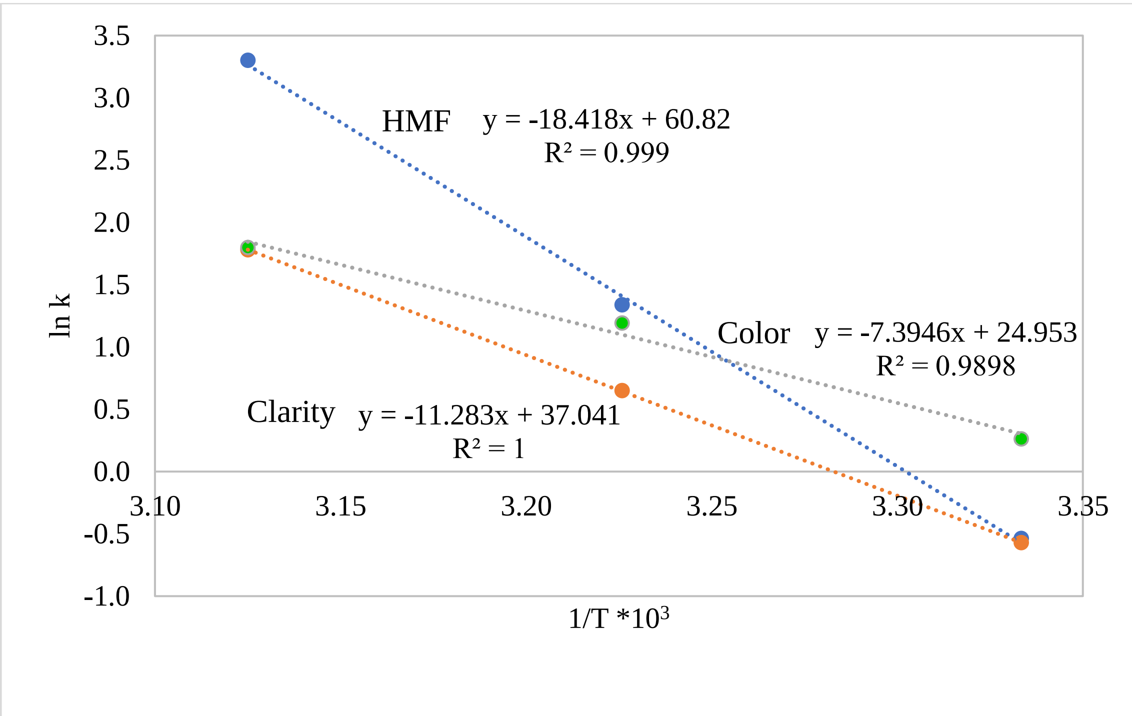

Figure 5. *Arrhenius plots of HMF, Color and Clarity parameters in PJC*

Table 1. *Kinetic criteria for Hydroxy methyl furfural, Clarity and Colour of PJC[*]*

Criteria	Storage Temperature (°C)	Reaction Equation	Activation Energy (kJ mol^{-1})	Q_{10}		
				27-37°C	37-47°C	27-47°C
Hydroxy methyl furfural	27	y = 0,5841x + 0,6628 (0,9351)	153,14 (0,999)	6.52	7.13	6.82
	37	y = 3,8073x - 4,0849 (0,9739)				
	47	y = 27,156x - 18,74 (0,9867)				
Clarity (%T@625nm, @11,9 °Bx)	27	y = -0,5646x + 95,623 (0,9454)	93,81 (1)	3.39	3.10	3.24
	37	y = -1,9126x + 95,488 (0,9881)				
	47	y = -5,9231x + 96,002 (0,9932)				
Colour (%T@440nm @11,9 °Bx)	27	y = -1,2978x + 44,91 (0,9834)	61,48 (0.9898)	2.53	1.84	2.16
	37	y = -3,2871x + 44,271 (0,9863)				
	47	y = -6,0393x + 47,88 (0,9778)				

[*] *The determination coefficients (R^2) of the reactions are given in the brackets*

Significant (P <0.01) negative correlations were noticed between HMF formation and colour changes in PJCs during storage (-0.959-(-0.992)). Clarity decrease, and HMF occurrence also shows significant (P <0.01) negative correlations in PJCs (-0.953-(-0.992)) (Table 2). Similar to the findings of this investigation, Capuano and Fogliano (2011) detected a positive correlation between the development of browning, color and HMF content.

Table 2. *Correlation coefficients among measured criteria in PJC[a]*

Criteria	HMF		
	27°C	37°C	47°C
Color	-0.959	-0.992	-0.989
Clarity	-0.953	-0.982	-0.992

[a] *P <0.01*

8. CONCLUSION

In order to evaluate the nonenzymatic browning reactions seen in kept PJC at 27°, 37°, and 47°C, hydroxy methyl furfural occurrence as well as colour and clarity changes were measured. The values of titratable acidity, pH, and TSS (°Bx) did not differ when the storage period ended. The kinetics of zero order reactions were followed by HMF formation, colour changes, and clarity changes. In all storage temperatures examined, the HMF content and colour changes displayed correlations in a negative way (r=-0.959-(-0.992)). Likewise, there is a significant negative correlation (r=-0.953-(-0.992)) between the decrease in clarity and the increase in HMF for all the reviewed temperatures. For HMF formation, colour, and clarity, the corresponding activation energy (kJ mol^{-1}) values were 153.14, 61.48, and 93.81, respectively.

AUTHOR CONTRIBUTIONS

Conceptualization, strategy, documentation and reviewing, F.K.; research & project management, B.I., laboratory work and formal analysis, S.K.; software, sources and funding, O.A., manuscript-review and editing, F.M. Publication of the final version of the article in this Journal has been read and legally accepted by all the authors.

CONFLICT OF INTEREST

The authors declare no conflict of interest.

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