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Response surface methodological study on HMF and fluorescent accumulation in red and white grape juices and concentrates

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Abstract

White and red grape juices and their concentrates were subjected to thermal treatments at different temperatures ranging from 50 to 70 °C at different times. 5-Hydroxymethylfurfural (5-HMF) and fluorescence relative index (FLRI) were measured. Response surface methodology (RSM) was applied to determine the effect of temperature and time on the HMF and FLRI formation at the different Brix (bx) degrees. An increase in temperature (from 50 to 70 °C) and time (from 12 to 192 h) for 15°, 45° and 65° Brix degrees was associated with an increase in HMF and FLRI development of white and red grape juices. HMF formation was higher in white grape juice and concentrates than in red ones. Optimum conditions were confirmed and these fitted the experimental data well. Thus, regression equations can be used to estimate HMF and FLRI values at various Brix degrees for white and red grape juices and concentrates.

Keywords: HMF; FLRI; Grape juice concentrate; Regression analysis; Response surface methodology

1. Introduction

Various thermal treatments are applied to foods during processing operations. One of the negative effects of these treatments is non-enzymatic browning. This includes Maillard reaction, caramelization, pigment destruction and ascorbic acid oxidation. The final product of non-enzymatic browning are melanoidins and 5-hydroxymethylfurfural (HMF), is one of the undesirable intermediates of the Maillard reaction (Ibarz, Pagan, & Garza, 1999). Types of sugars and their reducing capacity (Arena, Fallicio, & Maccarone, 2001; Eskin, 1990; Namiki, 1988), type of amino acids and pH (Ashoor & Zent, 1984; Buglione & Lozano, 2002; Göğüş, Bozkurt, & Eren, 1998; Nakama, Kim, Shinora, & Omura, 1993), temperature, acidity, water activity (Buera, Chirife, Resnik, & Lozano, 1987; Toribio, Nunes, & Lozano, 1984), and concentrations of metal ions, particularly Ca, K, Mg, Na^{+2}, Fe^{+2}, Fe^{+3} (Eskin, 1990; Lee & Nagy, 1988) have considerably significant effects on the Maillard reaction. Both heating procedures and storage conditions show synergy in non-enzymatic browning reactions. Longer storage time causes the more brown compounds (Buglione & Lozano, 2002; Toribio & Lozano, 1984). Maillard reaction rate is increased 4 fold by the increment of every 10 °C (Eskin, 1990). Several organic acids show catalytic effects on HMF accumulation, due to their destructive effects on sugars (Shinohara, Kim, & Omura, 1986). During the Maillard reaction, several compounds are formed, and they confer different taste and aroma properties on foods (Ninomiya, Matsuzaki, & Shigematsu, 1992). Reduced compounds, which have low molecular weight, cause aromatic changes which are similar to caramelization (Daniel & Whistler, 1985; Tressl, Rewicki, Helak, Kamperschröer, & Martin, 1985). Some Maillard reaction products are desirable for consumers, and they also have antibacterial and antioxidative effects

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(Lingnert & Waller, 1983; Pokorny, 1991; Shaker, Ghazy, & Shibanoto, 1995). The Maillard reaction, one of the most important chemical reactions, is generally explained using zero order reaction kinetics (Bozkurt, Göğüş, & Eren, 1999; Stamp & Labuza, 1983) or first order reaction kinetics (Rattanathanalerk, Chiewchan, & Srichumpoung, 2005; Toribio & Lozano, 1984). Temperature effect on the reaction rate is explained by using Arrhenius equations, and activation energy, which is necessary to start the reaction, is calculated by using that equation. From the Arrhenius equation, the most suitable storage conditions can be estimated (Ibarz et al., 1999). Correlation equations, obtained from the unstable foods against heat, may be used to determine the optimum temperature and time conditions (Pietrasik & Li-Chan, 2002). Besides HMF formation, some components, having fluorescence properties, are also formed during heat processing. The process of formation of fluorescence compounds is more sensitive than off-flavour, browning and colour development during processing and storage of foods, so this index has been suggested to determine, not only over-heating applications, but also final product quality (Labuza & Baisier, 1992; Umme, Asbi, Salmah, Junainah, & Jamilah, 1997). Chemical changes are of great importance during the production stages of foods. Determination of the reaction kinetics and mathematical modelling systems are very important for estimating the quality criteria, such as HMF and FLRI. Response surface methodology (RSM) is a collection of statistical and mathematical techniques useful for developing, improving and optimizing processes. It usually contains three stages: (i) design and experiments, (ii) response surface modelling through regression, (iii) optimization (Myers & Montgomery, 1995). The main advantage of RSM is the reduced number of experimental trials needed to evaluate multiple parameters and their interactions (Lee, Ye, Landen, & Eitenmiller, 2000).

The major disadvantage of single variable optimisation is that it does not include interactive effects among the various parameters for the reaction rate. In order to overcome this problem, optimisation studies have been done using response methodology. The main advantage of RSM is the reduced number of experimental trials needed to evaluate multiple parameters and their interactions. This paper aims to assess the effects of the main processing parameters on the HMF and FLRI formation in grape juices and to determine the optimum conditions using RSM analysis.

2. Material and methods

2.1. Material

Grape juice concentrates (GJC) obtained from Dimrit (red) and Emir (white) grape species, were provided from Taskobirlik Grape Juice Factory (Nevşehir, Turkey). HMF standard and all other chemicals used were obtained from Merck (Darmstadt, Germany).

2.2. Method

Red and white GJCs (total soluble solids = 65–72 as °Brix) were diluted to 15°, 45° and 65° Brix by using distilled water. A series of HDPE test tubes were filled with 5 ml of samples, sealed and subjected to heat in a water

Table 1
Experimental design matrix

No. experimental	Temperature (°C)	Time (h)
	X_1	X_2
1	60	12
2	70	6
3	70	42
4	50	48
5	50	120
6	60	84
7	50	192
8	70	24
Central run 1	60	48
Central run 2	60	48
Central run 3	60	48

Table 2
Experimental design responses

No. experimental	15° Bx				45° Bx				65° Bx			
	Y_1	Y_2	Y_3	Y_4	Y_1	Y_2	Y_3	Y_4	Y_1	Y_2	Y_3	Y_4
1	4.36	52.85	0.79	32.94	13.75	61.21	4.21	38.25	23	61	9.81	36.12
2	4.03	56.02	0.75	30.27	19.84	62.83	5.58	37.47	56	70	7.48	33.35
3	18.67	159.3	12.85	77.66	285.4	231.7	250.7	114.83	921	245	773.1	144.7
4	4.1	57.35	0.73	33.39	14.28	74.12	6.2	40.35	35	85	15.9	48.6
5	6.48	93.53	2.18	49.44	46.16	137.13	19.2	64.09	126	162	73.4	81.0
6	14.22	166.28	9.95	86.77	180.19	174.4	78.2	78.09	311	248	450.7	136.6
7	12.3	152.59	9.61	75.53	86.01	174.9	46.2	88.73	232	204	225.0	115.3
8	11.57	114.49	7.54	59.57	106.5	174.3	78.5	83.05	161	198	155.0	95.9
9	10.58	109.78	3.22	50.03	144.4	175.5	59.7	68.74	459	165	185.6	94
10	11.23	112.43	7.43	59.45	105.2	173.2	78.1	82.43	162	197	155.3	96.1
11	11.35	113.23	7.64	59.66	105.5	174.8	78.2	83.31	161	198	154.9	95.7

Y_1 (HMF, white grape), Y_2 (FLRI, white grape), Y_3 (HMF, red grape), Y_4 (FLRI, red grape).

Table 3
The fitted model equations

Concentration	Equations
15° Bx	$Y_1 = -6.555 + 0.1459\ T - 0.5589\ t + 0.01229\ Tt$
	$Y_2 = -35.4235 + 1.1375\ T - 4.3252\ t + 0.0997\ Tt$
	$Y_3 = -4.9079 + 0.0572\ T - 0.5092\ t + 0.0112\ Tt$
	$Y_4 = 15.9878 + 0.08627\ T - 2.2862\ t + 0.05123\ Tt$
45° Bx	$Y_1 = -226.35 + 3.505\ T - 9.69\ t + 0.2083\ Tt$
	$Y_2 = -35.41 + 1.535\ T - 6.041\ t + 0.135\ Tt$
	$Y_3 = -160.385 + 2.409\ T - 7.295\ t + 0.135\ Tt$
	$Y_4 = -5.902 + 0.636\ T - 2.464\ t + 0.0555\ Tt$
65° Bx	$Y_1 = 12965.15 - 427.225\ T - 56.365\ t + 3.4747\ T^2 + 0.0246\ t^2 + 1.027\ Tt$
	$Y_2 = 59.362 - 0.144\ T - 8.632\ t + 0.188\ Tt$
	$Y_3 = 9476.78 - 303.26\ T - 59.58\ t + 2.38\ T^2 + 0.0279\ t^2 + 1.0818\ Tt$
	$Y_4 = -4.525 + 0.451\ T - 4.558\ t + 0.101\ Tt$

Y_1 (HMF, white grape), Y_2 (FLRI, white grape), Y_3 (HMF, red grape), Y_4 (FLRI, red grape) T (Temperature, °C), t (Time, h).

bath (±0.1 °C) (Nuve BM 302, Turkey). Heating temperatures were 50, 60 and 70 °C; analysis samples were taken at 24, 12 and 6 h intervals; and total reaction times were 192, 120, 84, 48, 42, 12 and 6 h, respectively. The tubes were immediately cooled in an ice water bath in order to stop the heat accumulation. Samples were kept at −24 °C until the time of analysis. All samples were prepared in duplicate. HMF was determined quantitatively, following the procedure described by the IFFJP (1985) based on the colorimetric reaction between barbituric acid, *p*-toluidine and HMF, forming a red-coloured complex. The intensity of red colour is dependent upon the concentration of HMF, which was measured at 550 nm using a Shimadzu UV–VIS 1601 model double beam spectrophotometer. The fluorescence relative index (FLRI) was measured on the diluted samples (39-, 119- and 172-fold for 15°, 45° and 65° Brix degrees, respectively) by use of a fluorescence spectrophotometer (Perkin–Elmer, Model LS50B-Luminescence), utilizing maximum emission and excitation wavelengths measured at 400 and 459 nm, respectively. Freshly squeezed white grape juice was used as the reference (FLRI = 1) (Cohen, Birk, Mannheim, & Saguy, 1998).

2.3. Experimental design

According to prior experimental findings, the most influential factors on the HMF and FLRI formation in grape juices are temperature (X_1) and time (X_2). In order to evaluate the effects and interactions of these two factors, a central composite design was used. This design is constructed based on a 2^2 factorial design, one replicate of the central run with three coded levels, leading to 9 sets of experiments, allowing each experimental response to be optimised. The experimental conditions required by this design are defined in Table 1. The levels chosen for each of the two parameters are also presented; their values depend on results of preliminary experiments. The regression model is selected in order to predict each response (Y) in all experimental regions as follows:

Table 4
Coefficients and analysis of variance of regression models for HMF and FLRI of white and red GJC at 15°, 45° and 65° Bx

Factors		Y_1			Y_2			Y_3			Y_4		
		b	SE	Prob > F	b	SE	Prob > F	b	SE	Prob > F	b	SE	Prob > F
15 Bx	Constant	−6.555	1.43	0.0000	−35.423	4.04	0.0000	−4.908	1.68	0.0000	15.988	2.00	0.0000
	T (X_1)	0.146	1.71	<0.0001	1.137	4.86	<0.0001	0.057	2.01	0.0007	0.086	2.40	<0.0001
	t (X_2)	−0.559	2.09	<0.0001	−4.325	5.93	<0.0001	−0.509	2.46	0.0004	−2.286	2.93	<0.0001
	$T \times t$ (X_1X_2)	0.012	1.96	0.0006	0.099	5.55	<0.0001	0.112	2.30	0.0027	0.051	2.75	<0.0001
	R^2 (Model)	0.909		0.0005*	0.990		0.0001*	0.853		0.0027*	0.989		0.0001*
	CV (%)	17.02			4.42			34.71			4.23		
45 Bx	Constant	−226.35	28.14	0.0000	−35.41	25.27	0.0000	−160.385	41.10	0.0000	−5.902	11.91	0.0000
	T (X_1)	3.50	33.8	0.0008	1.536	30.35	0.0017	2.409	49.37	0.0089	0.636	14.30	0.0036
	t (X_2)	−9.69	41.25	0.0013	−6.041	37.05	0.0013	−7.299	60.25	0.0189	−2.465	17.76	0.0024
	$T \times t$ (X_1X_2)	0.208	38.63	0.0066	0.135	34.70	0.0086	0.154	56.44	0.0384	0.056	16.35	0.0159
	R^2 (Model)	0.885		0.0022*	0.803		0.0073*	0.659		0.0463*	0.765		0.0132*
	CV (%)	33.02			20.34			75.75			19.86		
65 Bx	Constant	12965.150	111.15	0.0000	59.362	16.19	0.0000	9476.78	89.09	0.0000	−4.525	7.11	0.0000
	T (X_1)	−427.220	215.40	0.0081	−0.144	19.45	<0.0001	−303.260	172.65	0.0035	0.451	8.54	<0.0001
	t (X_2)	−56.365	258.28	0.0147	−8.632	23.73	<0.0001	−59.580	207.02	0.0046	−4.558	10.43	<0.0001
	T^2 $(X_1)^2$	3.474	116.09	0.0303	–	–	–	2.380	93.05	0.25**	–	–	–
	t^2 $(X_2)^2$	0.025	231.68	0.4001**	–	–	–	0.028	185.70	–	–	–	–
	$T \times t$ (X_1X_2)	1.027	347.90	0.0405	0.189	22.23	<0.0001	1.081	278.85	<0.0154	0.101	9.47	<0.0001
	R^2 (Model)	0.877		0.0248*	0.942		<0.0001*	0.898		<0.0158*	0.964		<0.0001*
	CV (%)	53.27			11.48			51.22			9.4		

Y_1; (HMF, white grape), Y_2; (FLRI, white grape), Y_3; (HMF, red grape), Y_4; (FLRI, white grape), b; partial regression coefficient, SE; standard error, T; temperature (°C), t; time (h).

* Significant at 'Prob > F' less than 0.05.

** Nonsignificant term.

$$Y = b_0 + b_1X_1 + b_2X_2 + b_{11}X_1^2 + b_{22}X_2^2 + b_{12}X_1X_2,$$

where Y is the response calculated by the model; X_1 and X_2, are coded variables, corresponding to temperature and time, respectively; b_1, b_2, are the linear; b_{11}, b_{22} quadratic and b_{12} cross-product effects of the X_1, X_2 factors on the response.

The 'Design Expert' (version 6.0.11, Stat-Ease, Inc., Minneapolis, USA) software was used for regression and graphical analyses of the data obtained. The statistical significance of the regression coefficients was determined by using the F test and the applicability of the model was checked with significance coefficients of determination (R^2) and the coefficient of variation (CV) values. The optimum conditions of the process were obtained by using graphical and numerical analysis, using the software, based on the criterion of desirability.

3. Results and discussion

In unheated red GJCs at 65°, 45° and 15° Bx, average HMF values were measured as 1.10, 0.53, and 0.00 mg/kg, respectively. For the same concentrations, in white samples, average HMF values were 15.81, 9.14, 2.47 mg/kg, respectively. FLRI values were 20.1, 20.9 and 21.6 in red GJCs, and 26.2, 27.2 and 27.7 in white GJCs respectively. These differences between the red and white GJCs might originate from the their compositional variability. The experimental responses studied include: HMF concentrations and FLRI values. The experiments were carried out in a random order. The values obtained experimentally for these characteristics of the grape juices are given in Table 2. Table 3 shows the equation of fitted models for HMF and FLRI formation at 15°, 45° and 65° Bx concen-

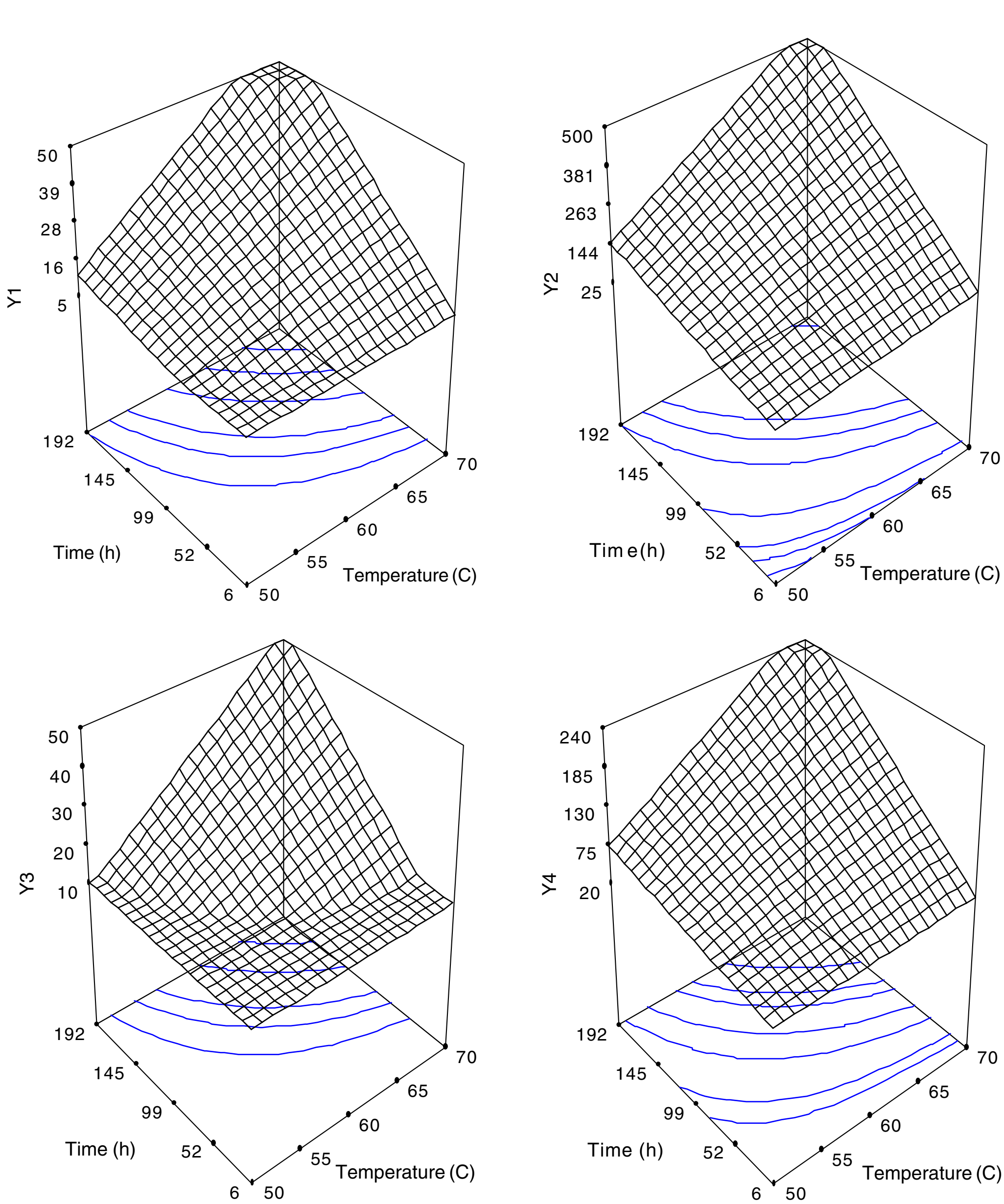

Fig. 1. Response surface plot showing effect of temperature and time on the HMF content and FLRI of white and red GJC at 15° Bx.

trations and the results for analysis of variance (ANOVA). The ANOVA confirms adequacy of the statistical models since their Prob > F values are less than 0.05 and statistically significant at the 95% confidence level. The models presented high determination coefficients (R^2) and low coefficients of variation (CV). These values were obtained as follows: $R^2 = 0.909$ and CV = 17.02 for Y_1; $R^2 = 0.99$ and CV = 4.42 for Y_2; $R^2 = 0.85$ and CV = 34.71 for Y_3; $R^2 = 0.9892$ and CV = 4.23 for Y_4. These results indicate a good precision and reliability for the experiments carried out. The significance and standard error of each coefficient were determined by *F*-value and Prob > *F* value which are listed in Table 4. The smaller the magnitude of the *F* value the more significant is the corresponding coefficient. This implies that the first order main effect of temperature and time (Prob $F < 0.0001$) is more significant than its quadratic main effect. The response surface plots described by the model equations (Y_1–Y_4) are represented in Fig. 1. The minimum HMF (10.8 mg/kg) and FLRI (107) contents were found at 70 °C and 23.61 h in white grape juices (15° Bx), while they were 11.6 mg/kg and 112 for HMF and FLRI in red grape juices, respectively. The maximum HMF concentration (12.9 mg/kg) and FLRI value (86.8) were found at 68.19 °C and 53.74 h in red grape juices.

Another statistical model was determined for HMF and FLRI values at 45° Bx concentration in Table 3 and the results for analysis of variance (ANOVA) are shown in Table 4. Although Prob > *F* values of HMF and FLRI (red grape) are less than 0.05, coefficients of determination ($R^2 = 0.6587$ and 0.7653) observed and lacks of fit were significant. If the model has a significant lack of fit, as indicated by an Prob > *F* value less than 0.05 at the 95% confidence level, this model should not be used to predict the response. As a result, models Y_3 and Y_4 can not be used for response at 45° Bx concentration. The significance and standard error of each coefficient of the regression models were determined by *F*-value and Prob > *F* value which are listed in Table 4 at 45 Bx concentration. The smaller the magnitude of the F value the more significant is the corresponding coefficient. This implies that the first order main effect of temperature and time (Prob $F < 0.0001$) is more significant than its quadratic main effect. Values greater than 0.10 indicate that the model terms are not significant.

The response surface plots described by the model equations (Y_1–Y_2) are shown in Fig. 2. The fitted surface has a true maximum and coordinates of the maximum point were the target values of HMF (white grape) concentration (60 mg/kg), and FLRI (white grape) which can be found to be $X_1 = 70$ °C and $X_2 = 8.38$ h. Finally, the last response studied was obtained at 65° Bx for HMF and FLRI concentration. The equations of fitted models are shown for HMF and FLRI formation at 65° Bx concentration in Table 3. Y_1 and Y_3 models were fitted quadratically according to Prob > *F* and R^2 values. The coefficients of correlation and variation and *F*-value are given in the Table 4. The mathematical models were very reliable with 0.877, 0.942, 0.898 and 0.9642R^2 values for Y_1, Y_2, Y_3 and Y_4, respectively. These values indicated the suitability of the respective models for adequately representing the real relationship among the parameters studied. Table 4 also lists the regression coefficients calculated by the model for b_0, b_1, b_2, b_{11}, b_{22} and b_{12}, along with significance levels of the terms. From Prob < *F* values of terms in Table 4, it can be seen that linear, cross product and quadratic terms are significant for models Y_1 and Y_3, quadratic terms were not significant for other models. Therefore, quadratic terms were cancelled for Y_2 and Y_4 models. Fig. 3 shows that the target value HMF (white grape) concentration (60 mg/kg), and FLRI (white grape) (147) can be obtained by working with 60 °C and 35.64 h; The target value of HMF (red grape) concentration (60 mg/kg), FLRI (red grape) (73.45) can be obtained by working with 60 °C and 33.45 h.

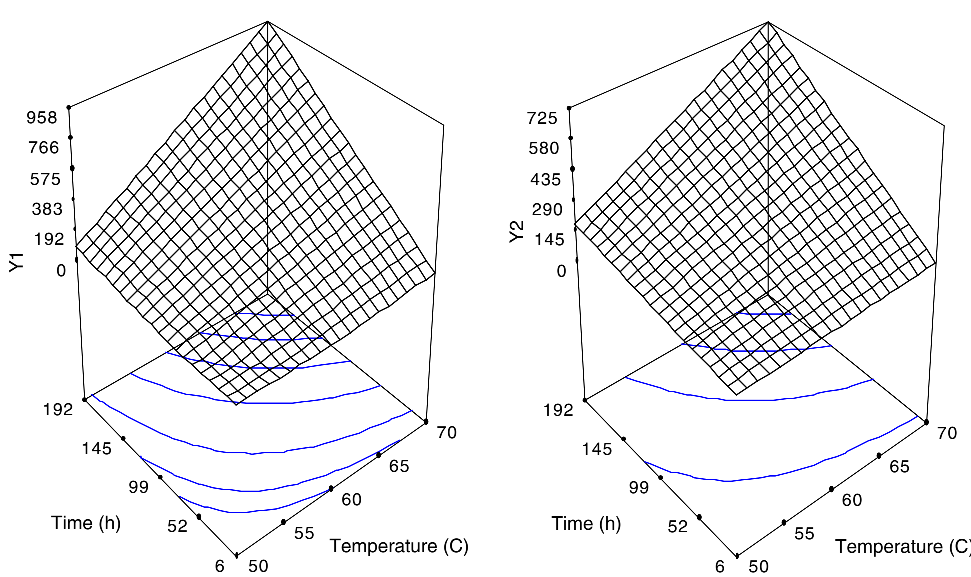

Fig. 2. Response surface plot showing effect of temperature and time on the HMF content and FLRI of white and red GJC at 45° Bx.

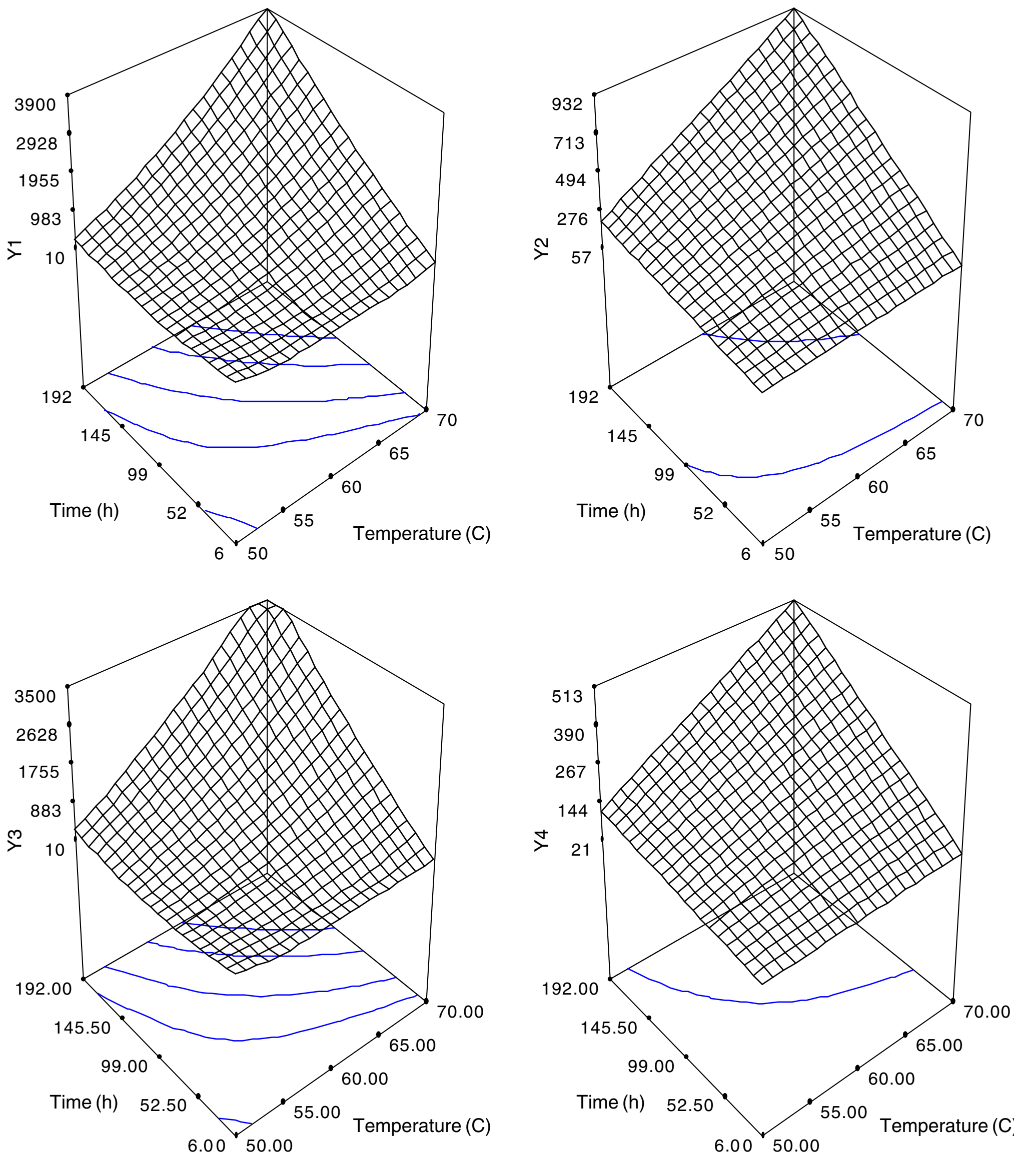

Fig. 3. Response surface plot showing effect of temperature and time on the HMF content and FLRI of white and red GJC at 65° Bx.

Table 5
The responses of the models at the lowest, middle and highest temperatures for different Brix degrees

	15° Bx, $t = 48$ h			45° Bx, $t = 48$ h			65° Bx, $t = 48$ h		
	50 °C	60 °C	70 °C	50 °C	60 °C	70 °C	50 °C	60 °C	70 °C
Y_1	3.4	10.76	18.12	−16.3	118.73	215.21	106.16	149.48	887.30
Y_2	53.12	112.35	171.58	75.37	155.52	235.65	89.02	177.82	266.62
Y_3	0.39	6.33	12.28	−66.09	22.79	98.73	64.54	169.20	749.86
Y_4	35.51	58.96	84.42	40.82	73.82	98.30	41.64	94.63	147.60

Table 6
Compared actual data and predicted values of the responses

	15° Bx, 60 °C, $t = 48$ h		45° Bx, 60 °C, $t = 48$ h		65° Bx, 60 °C, $t = 48$ h	
	Actual	Predicted	Actual	Predicted	Actual	Predicted
Y_1	11.23	10.76	105.2	118.73	162	149.48
Y_2	112.43	112.35	173.2	155.52	197	177.82
Y_3	7.43	6.33	78.1	22.79	155.3	169.20
Y_4	59.45	58.96	82.43	73.82	96.1	94.63

These results may be explained by the HMF and FLRI formation for the white and red grape juices concentration at different Brix degrees. The linear and interaction terms of temperature and time have the most significant effects in the production on HMF and FLRI accumulation, as is known. The optimum values of the temperature and time are determined for target HMF and FLRI formation. The common approach, to predict quality changes of a food system, is to define a parameter or an index of deterioration. This index has to be sensitive enough to express the effect of the process on the quality. Evidently, FLRI and HMF as quality indicators can be used under optimal conditions of time and temperature.

The models appear to be good for lowest, highest and also middle temperatures. Model results are determined for related temperatures at constant time, 48 h. These results are shown in Table 5 . At the middle temperature, responses are compared with the experimental data and shown in Table 6. These results agree with each other.

4. Conclusion

The response surface methodology was a useful tool for investigating the optimum conditions of temperature and time for target HMF and FLRI formation in red and white grape juices. The coefficients of determinations, R^2 values of the all parameters, show a good fit of the models with the experimental data at the 95% confidence level. When Brix degrees were altered from 15° to 65° by using statistical models, HMF and FLRI contents were increased for white and red grape juices. These results were well fitted with experimental data and models that are obtained can be used between the minimum and the maximum values of the variables.

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