

**MATHEMATICAL ANALYSIS OF COLOR CHANGES AND CHEMICAL
PARAMETERS OF ROASTED HAZELNUTS**

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**KAVRULMUŞ FINDIKLARIN RENK DEĞİŞİMİNİN VE KİMYASAL
PARAMETRELERİNİN MATEMATİKSEL ANALİZİ**

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PREFACE

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NOTATION

σ	Percent standard error (%)
a, a_1, a_2	Drying constant
a -value	Color dimension
AV	Average
b, b_1, b_2	Drying constant
b -value	Color dimension
β_i, β_{ij}	Model coefficients
C	Color
c	Coefficient
D	Diffusivity (m^2/s)
db	Dry basis
D_o	Diffusivity coefficient
df	Degree of freedom
E_a	Activation energy
e	Error term
f	Mathematical function
k	Reaction rate constant
k, k_1, k_2	Drying constant
k_o	Frequency constant
L -value	Color dimension
MC	Moisture content
MR	Moisture ratio ($(M-M_e)/(M_o-M_e)$)
MSE	Mean square error
n	Drying constant, order of reaction, number of observations
NS	Not significant
P	Mean relative deviation modulus (%)
R	Radius (m)
\mathcal{R}	Universal gas constant (J/mol K)
r^2	Correlation coefficient
R^2	Percent variability explained
SD	Standard deviation
SSE	Sum of square error
t	Time (min)
T	Temperature ($^{\circ}\text{C}$)
y	General second degree mathematical equation
X	Coded independent variables

Subscripts

e	Equilibrium
eff	Effective
i, m, n	nth observation
o	Initial
pr	Predicted



ABSTRACT

The main objective of the thesis was mathematical modeling of thin layer drying characteristics and to determine and analyze kinetics of color formation during roasting of hazelnuts over the temperature range of 100-160°C and up to 60 min roasting. Changes in some chemical quality parameters of hazelnuts during roasting were also studied. Moreover a consumer acceptance test was carried out.

So as to describe thin layer drying characteristics of hazelnut roasting several semi-theoretical and empirical mathematical models were evaluated. Effective diffusivity was calculated. Activation energy was also calculated using Arrhenius-type temperature dependence of diffusivity coefficient.

So as to determine kinetics of color formation, a generalized model, third degree polynomial with Arrhenius type temperature dependence of model coefficients, was developed. Activation energy for *L*-value of color was calculated over the temperature range of the study. Differences between whole-kernel, cut-kernel and ground-state measurements were analyzed using statistical techniques.

Color formation kinetics was also analyzed using response surface methodology to find out the effect of process variables on color development during roasting and to establish prediction models. A second degree prediction models, using RSM, was also developed to described color development as a function of roasting temperature and exposure time for *L*-value, *a*-value and *b*-value of whole-kernel, ground-state and cut-kernel measurements.

Besides mathematical modeling of moisture loss and color formation during roasting, effect of roasting on some of chemical parameters was also investigated over the

experimental range of 102 °C - 158°C and 16 min - 44 min just after roasting. The parameters used were protein content, sugar content and amino acid composition of hazelnuts, free fatty acid content and peroxide value, was also investigated. Effect of storage 1 month at 37°C on fatty acid composition, free fatty acid content and peroxide value of the roasted samples were also investigated. The results indicated that all of the parameters were affected by the roasting conditions. The longer roasting time at any roasting temperature resulted in the lower moisture, protein, sugar and amino acid contents. Similarly the higher roasting temperature at any roasting time resulted in the lower moisture, protein and sugar content. The lower roasting temperature produced the higher stability.

In addition to mathematical modeling of moisture loss and color formation; and analysis of changes in some chemical parameters during roasting, a consumer test were also performed to as to find out preference of consumers among the samples of the experimental study. Consumer acceptance test showed that samples roasted at 110°C for 40 min, at 130°C for 16 min; at 130°C for 30 min; at 130°C for 44 min and at 150°C for 20 min were preferred by the consumer.

ÖZET

Bu çalışmanın ana amacı kavurma sırasında fındıkların kuruma karakteristiği matematiksel olarak ifade etmek ve renk değişim kinetiği, 100°C - 160°C ve en fazla 60 dakikalık kavurma koşullarında, belirlenmektir. Bunlara ek olarak bazı kimyasal kalite parametrelerinin kavurma koşullarına göre değişimi de incelenmiştir. Ayrıca tüketici beğeni testi gerçekleştirilmiştir.

Fındıkların kavurma sırasındaki kuruma karakteristiği matematiksel olarak ifade etmek için bir kaç matematiksel denklem incelenmiştir. Etkin nem geçirim katsayısı hesaplanmıştır. Nem geçirim katsayısının sıcaklık bağımlılığı, Arrhenius tipi ilişkiyle tanımlanmıştır. Nem geçirimi için aktivasyon enerjisi de hesaplanmıştır.

Kavurma sırasında fındıkların rengindeki değişim kinetiğini matematiksel olarak ifade edebilmek için katsayıları sıcaklığa Arrhenius tipinde bağımlı üçüncü dereceden polinom kullanılmıştır. Çalışmada kullanılan kavurma sıcaklıkları için *L*-değerinin aktivasyon enerjisi hesaplanmıştır.

Fındıkların kavurma sırasındaki renk değişimine sıcaklık ve sürenin (süreç değişkenleri) etkisini belirlemek ve renk değişimi tahmin modelleri geliştirmek üzere, kavurma işlemi tepki yüzey yöntemiyle de incelenmiştir. Tepki yüzey yöntemiyle sıcaklık ve zamana bağlı, ikinci dereceden renk değişimi modelleri geliştirilmiş ve kavrulmuş fındıkların dış-, un- ve iç-renklerinin *L*-, *a*-, ve *b*-değerlerini başarıyla tahmin etmişlerdir.

Kavurma sırasındaki kuruma ve renk değişiminin modellenmesine ek olarak, kavurma sıcaklık ve süresinin bazı kimyasal parametreler üzerindeki etkisi de 102 °C - 158°C ve 16 dak. - 44 dak. kavurma koşullarında araştırılmıştır. Bu parametreler protein içeriği, şeker içeriği, amino asit bileşimi, serbest yağ asitliği içeriği ve peroksit değeridir.

Ayrıca, 37°C'de bir ay boyunca kavrulmuş depolanmış ve depolanmış örneklerde serbest yağ asitliği, peroksit değeri ve yağ asitleri bileşiminin değişimi incelenmiştir. Kavrurma koşulları bütün parametreleri önemli şekilde etkilemiştir. Fındıklar aynı sıcaklıkta daha uzun süre yada aynı sürede daha yüksek sıcaklıkta kavrulduklarında nem, protein ve şeker içeriğinde azalma gerçekleşmiştir. Daha düşük sıcaklıkta kavrulmuş fındıkların acılaşmaya dayanıklılığı daha fazla olmuştur.

Kavrurma sırasındaki kuruma ve renk değişiminin modellenmesine, ve kavrurma koşullarının bazı kimyasal parametreler üzerindeki etkisinin araştırılmasına ek olarak, kavrulmuş fındık örneklerinin tüketiciler tarafından beğeni seviyeleri tüketici beğeni testiyle araştırılmıştır. Beğeni testinde 110°C'de 40 dak, 130°C'de 16 dak; 130°C'de 30 dak; 130°C'de 44 dak ve 150°C'de 20 dakika kavrulmuş fındıklar tüketicilerce beğenildiği tespit edilmiştir.

1 INTRODUCTION

1.1 The Scope

Hazelnut is known in Anatolia since the ancient times but commercial cultivation start early in the 20th century (Köksal & Okay, 1996). Türkiye is the biggest hazelnut producer and exporter in the world with a production rate of around 550 000 ton/year and exports 83% of its production with a value of about one billion US\$ annually. But hazelnut surplus of Türkiye is more than 100 000 tons/year (Table 1.1.) which has a significant negative impact on the Turkish economy. Italy, USA and Spain are the other major hazelnut producing countries (Külünkoğlu, 1996; Akova, 1998) (Table 1.1).

Hazelnut products are mostly used in chocolate manufacture (80%), 15% in confectionery, biscuit, and pastry manufacture, and the remaining 5% are consumed without any further processing (Altundağ, 1989; Anonymous, 1995; Köksal & Okay, 1996). They are used to provide a sweet, delicate, yet definite flavor in the food products such as dairy, bakery, confectionery products and muesli. They are also used to enhance flavor of chocolate, ice cream, cookies, desserts, snack bars and side dishes (Labell, 1983; Kinderlerer & Johnson, 1992; Labell, 1992; Villarroel *et al.*, 1997a,b).

Türkiye exports in shell, natural (shell removed), blanched (skins removed) roasted (roasted whole kernels with maximum 3% moisture), sliced (sliced blanched kernels), diced (roasted kernels chopped into pieces of 2-10 mm), flour (blanched kernels chopped into pieces of maximum 2 mm), meal (roasted kernels chopped into pieces of maximum 2 mm) roasted paste (pressed mixture of roasted kernels, sugar and vanilla), puree (roasted kernels pressed into heavy syrup), nougats, fill-ups and dragee hazelnuts (Özdemir, 1997; Saklar, 1999).

Table 1.1. Production, export, import and stock rates (tons of in-shell hazelnuts) of important hazelnut producer countries (Anonymous, 2000)

Origin	Initial Stock	Production	Imports	Total Supply	Export	Domestic consumption	Ending Stocks
Turkiye							
1996/97	40 000	500 000	0	540 000	383 000	52 000	105 000
1997/98	105 000	515 000	0	620 000	440 000	50 000	130 000
1998/99	130 000	625 000	0	755 000	420 000	180 000	155 000
1999/00	285 000	550 000	-	835 000	440 000	140 000	255 000
2000/01	150 000	550 000	-	700 000	420 000	70 000	210 000
Italy							
1996/97	50 000	95 000	41 847	186 847	76 649	109 198	1 000
1997/98	1 000	87 000	45 000	133 000	27 000	103 000	3 000
1998/99	3 000	130 000	35 000	168 000	53 000	113 000	2 000
1999/00	4 000	100 000	50 000	154 000	38 000	114 000	2 000
2000/01	3 000	100 000	50 000	153 000	45 000	106 000	2 000
US							
1996/97	4.788	16.783	9.772	31.343	16.612	14.264	467
1997/98	467	42 640	10 765	53 872	16 084	26 788	1 000
1998/99	1 000	13 154	16 000	30 154	8 000	22 154	0
1999/00	109	34 000	12 000	46 309	23 000	23 000	309
2000/01	8 000	18 150	12 600	38 750	11 600	24 200	2 950
Spain							
1996/97	5 100	6 500	12 300	23 900	7 900	15 000	1 000
1997/98	1 000	18 900	7 000	26 900	10 400	16 000	500
1998/99	500	8 000	12 500	21 000	6 000	15 000	0
1999/00	-	16 000	6 000	22 000	7 000	14 000	1 000
2000/01	10 000	16 500	10 000	36 500	14 000	16 000	6 500

Most of the hazelnuts (>70%) were exported in shell until late 1980's. In 1990's, after establishment of new cracking factories, most of the hazelnuts (>70%) were exported as raw kernels. But ratio of processed hazelnuts in the exported hazelnuts was still <25% at the beginning of the year 2000 which means transition from natural hazelnut exportation to processed hazelnut products is very slow. So as to increase export of processed hazelnut products and extend its market in the world, improvement of quality of processed hazelnuts is necessary (Özdemir, 1997; Özdemir, 1998). Since roasting is among the most important steps of hazelnut processing, improvement of roasting process shall contribute improvement of quality of processed hazelnuts products.

Temperature (100-160°C) and time (<45 min) combinations are used to achieve desired level of moisture and color in the industry. Use of inappropriate temperature-time combination lead to quality defects such as short shelf life and poor flavor. Therefore prediction of roasting conditions (temperature-time combinations) more precisely prior to roasting contributes production of quality hazelnuts. Calculating and predicting a quality indicator such as color and moisture in food systems during processing or storage involves development of a mathematical model (Saguy & Karel, 1980; Samaniego-Esguerra *et al.*, 1991) which is not available for moisture loss and color development during hazelnut roasting. Flavor, crispy and crunchy texture is not usually monitored by the industry and sometimes required by the customer.

1.2 Objective of the Study

The main objective of the thesis was mathematical modeling of thin layer drying characteristics and to determine and analyze kinetics of color formation during roasting of hazelnuts over the temperature range of 100-160°C and up to 60 min roasting. Changes in some chemical quality parameters of hazelnuts during roasting were also studied. Moreover a consumer acceptance test was also carried out.

So as to describe thin layer drying characteristics of hazelnut roasting several semi-theoretical and empirical mathematical models were evaluated. Effective diffusivity and activation energy was calculated. So as to determine kinetics of color formation, a generalized model, third degree polynomial with Arrhenius type temperature dependence of model coefficients, was developed. Activation energy for *L*-value of color was calculated. Differences between whole-kernel, cut-kernel and ground-state measurements were analyzed using statistical techniques. Color formation kinetics was also analyzed using response surface methodology to find out the effect of process variables on color development during roasting and to establish prediction models.

Effect of roasting on protein content, sugar content and amino acid composition of hazelnuts, free fatty acid content and peroxide value was investigated. Effect of storage 1 month at 37°C on fatty acid composition, free fatty acid content and peroxide value of the roasted samples were also investigated. A consumer acceptance test was also carried out.

1.3 Turkish Hazelnuts

Wild species of hazelnut, genus *Corylus*, are distributed in nearly all parts of temperate zones of the Northern Hemisphere (Ayfer *et al.*, 1986). Economically important varieties in Türkiye have been selected from *C. Avellana* var. *pontica* (common hazelnut), *C. maxima* mill. (The giant hazelnut), and *C. Colurna* var. *glandulifera* (Turkish hazelnut) (Ayfer *et al.*, 1986).

1.3.1 Physical properties of Turkish hazelnuts

Turkish hazelnut is classified as round hazelnuts (the length to width ratio of 1.00 ± 0.19), pointed hazelnuts (the length to width of 1.3 ± 0.1) and long hazelnuts (the length to width ratio over 1.4). The major Turkish hazelnut varieties, their domestic synonymous names and annual production rates are given in Table 1.2. Round hazelnuts such as Tombul, Palaz, Çakıldak, Foşa are medium in size and have the highest quality and taste. Pointed hazelnuts such as Sivri, İncekara are medium, or large in size. Their texture, taste and other quality factors are moderate. Long hazelnuts such as Badem are undesirable in international trade, not only due to their shape but also their woody and dry texture and its low quality kernel. They have limited value only for fresh consumption in local markets (Ayfer *et al.*, 1986). Nut and kernel defects are serious problems in the hazelnut industry. The defects limit kernel ratio (weight percentage of good kernels to weight of the unshelled hazelnuts) and quality, reducing returns to growers and increasing cost to the handlers. Poorly filled nuts and shriveled kernels are usually smaller than the normal size.

Table 1.2. Synonymous names of Turkish hazelnut varieties and their production rates^a

Type	Variety	Synonymous names	Production (t/yr) ^b				
			Giresun	Ordu	Trabzon	Akçakoca	Total
Round	Tombul	Mehmet Arif ^c , Giresun Yağlısı ^d , Yağlı Fındık ^d	80,807	31,030	13,460	2,463	127,760
	Palaz			43,324			43,324
	Mincane	Sarıfındık ^d , Sarıyağlı ^d , Sırafındık ^c		1,260	26,092	30,224	57,576
	Foşa	Yomra ^c			2,336	18,149	30,485
	Çakıldak	Delisava ^d , Gökfindik ^c		31,124		11,037	42,161
	Kalınkara		1,484				1,484
	Karafındık	Karayaglı ^c					NA ^f
	Cavcava						NA
	Uzunmusa	Oskara Yağlısı ^{c,d} , Enişte Fındığı ^c					NA
	Kan						NA
Pointed	Kargalak						NA
	Sivri	Giresun Sivrisi	7,644		1,891		9,536
Long	İncekara			2,520		49,532	52,052
	Yuvarlak Badem	Değirmendere ^c					NA
	Yassı Badem	Değirmendere ^c					NA
Total			89935	117760	67300	120750	

^a Data are gathered from Ayfer *et al.*, (1986) and Anonymous, (1995).

^b Production rates in 1995.

^c Western Black Sea region.

^d Eastern Black Sea region.

^e Marmara region.

^f Not available.

Small kernels are most common when the crop load is heavy or trees are stressed during the period of rapid kernel growth. Black tips are found in varieties whose shells have weak sutures. Double kernels result from synchronous development and fertilization of both ovules (Mehlenbacher *et al.*, 1993). Early harvest also results in poorly filled nuts (Çakırmelikoğlu & Çalışkan, 1993). Brown centers has been associated with polyphenoloxidase activity in raw hazelnuts. It is more frequent in Spanish than Turkish and Italian hazelnuts (Keme & Messerli, 1976a). Physical properties and defects of Turkish hazelnut varieties are given in Table 1.3. Tombul is mostly produced in Giresun (about 130 000 t/yr). Tombul is not attractive in color. Its pellicle is light brown, clean, and easy to remove. Many kernels lose their pellicle even during transportation and storage. It is the best variety in terms of pellicle removal. The kernel is white, and center hallow is small. It has kernel ratio of 50-52%, and has low empty and double hazelnut percentages. Shelling of Tombul is rather difficult because of its lopped shape, relatively thin and elastic, and completely filled shell. İncekara is the second major variety of Türkiye, mainly produced in Akçakoca (about 55 000 t/yr). It has 51.9% kernel ratio but a relatively low pellicle removal (76.5%). Moreover, it has a slightly bitter taste. It is not preferred any more for cultivation due to their pointed shape. Mincane is the third major variety and mainly produced in Akçakoca and Trabzon (about 60 000 t/yr). Its kernel ratio is 48.2%. It has slightly bitter taste. Palaz and Çakıldak are among the major variety and mainly produced in Ordu (both about 45 000 t/yr). Mincane and Palaz are easy to remove the pellicle of the kernels (about 95%). Foşa is also one of the major variety and mainly produced in Akçakoca (about 30 000 t/yr). Both Çakıldak and Foşa have around 88% pellicle removal and 48.7% kernel ratio (Ayfer *et al.*, 1986). Harvest time affects kernel ratio and pellicle removal of hazelnut kernels. Harvesting the hazelnuts from tree at the right time increases kernel ratio from 46% up to 58%, increases pellicle removal after roasting from 56% to 93%, and decreases shriveled hazelnuts from 9.5% to around 1% for Tombul compared with early harvest. Similar improvements are obtained for Palaz and Çakıldak varieties. Çakıldak matures about 2 weeks later than Tombul and Palaz (Çakırmelikoğlu & Çalışkan, 1993).

Table 1.3. Some physical properties of the Turkish hazelnut varieties including the defects ^a

Variety	Length/ width ^b	Weight ^b (g)	Number of fruits/ cluster	Clearance at the center of the kernel ^c	Kernel fiber ^e	Testa removal after roasting (%)	Split shell (%)	Shriveled kernels (%)	Doubles (%)	Empty (%)	Decayed kernels (%)	Good kernels (%)	Yield (%) ^d
Tombul	1.11	1.46	3-4	+	-	97.70	1.13	13.79	0.82	7.91	0.80	74.58	51.70
Palaz	0.98	1.62	3-4	++	-	94.50	0.91	15.26	1.67	8.82	2.75	73.50	49.80
Mincane	1.15	1.55	2-3	+	-	96.60	1.69	17.71	1.36	5.81	0.99	75.65	48.20
Foşa	1.06	1.86	2-3	++	+	89.00	0.50	18.51	2.26	4.96	0.67	74.49	48.70
Çakıldak	1.17	1.60	1-2	++	++	87.80	0.00	41.72	0.58	6.03	0.73	51.73	48.70
Kalınkara	1.18	1.72	3-4	++	++	62.30	1.25	24.29	15.92	5.14	0.88	65.93	49.60
Cavcava	1.02	1.06	3-4	++	-	92.70	1.50	15.33	2.27	6.22	1.77	74.46	52.00
Uzunmusa	1.15	1.42	4-5	++	-	94.70	2.75	14.53	1.05	14.18	0.95	71.33	56.70
Sivri	1.36	1.70	3-4	+	-	72.30	0.17	19.00	0.37	10.40	0.86	69.55	48.90
Karafındık	1.18	1.42	3-4	+	++	83.50	2.14	36.31	4.61	7.77	1.13	60.81	49.20
Kargalak	0.86	2.82	1	++	++	NA ^e	0.00	NA	0.00	NA	NA	NA	35.00
Kan	1.16	1.59	3-4	+	-	88.50	2.00	40.04	0.90	9.65	0.38	49.43	52.30
İncekara	1.29	1.40	2-3	+	+	76.50	0.00	41.09	9.32	11.93	0.96	42.63	51.90
Yassı Badem	1.63	0.94	1-2	++	++	64.50	2.00	36.59	1.30	8.12	0.35	54.29	46.10
Yuvarlak Badem	1.68	1.76	2-3	++	++	61.50	0.00	55.05	0.97	14.22	0.00	30.07	46.10

^a Data are gathered from Ayfer *et al.*, (1986).

^b Unshelled hazelnut.

^c +++: much, ++: some, +: little, -: none.

^d Yield: Weight percentage of good kernel to weight of unshelled hazelnut.

^e Not available.

1.3.2 Composition of Turkish hazelnuts

The oil, protein, vitamin and carbohydrate content, iodine value, saponification value, refractive index and specific gravity, and mineral, amino acid, fatty acid and sterol composition of Turkish hazelnut varieties are given in Tables 1.4 - Table 1.7. The major Turkish hazelnut varieties contain about 55-66% oil, and 11-14% protein. Composition of hazelnuts is influenced from harvest time. Variety, geographical origin, growing practices and harvest time influence hazelnut fat composition (Gargano *et al.*, 1982; Bonvehi & Coll, 1993; Parcerisa *et al.*, 1993a,b; Garcia *et al.*, 1994; Parcerisa *et al.*, 1995a; Koyuncu *et al.*, 1996; Savage *et al.*, 1997; Özdemir *et al.*, 1998b; Parcerisa *et al.*, 1999; Yıldız *et al.*, 2000). Şahin *et al.*, (1990) stated that Turkish hazelnut varieties except for Tombul and Palaz have different oils content between years. Yıldız *et al.*, (2000) reported that the fat content, iodine value, saponification value, specific gravity, the fatty acid composition, the unsaturation/saturation ratio of the Turkish hazelnuts significantly differ between varieties. Iodine value, saponification value, specific gravity and refractive index of some Turkish hazelnut varieties were given in Table 1.5. Yıldız *et al.*, (2000) also reported sterol composition of the Turkish hazelnut varieties (Table 1.6.) as campesterol, stigmasterol, sitosterol, Δ^5 -avenasterol and Δ^7 -stigmasterol. The sitosterol was the major constituent (71.84%). The sterol composition was significantly different between varieties (Yıldız *et al.*, 2000). Spanish hazelnuts varieties are also influenced strongly by geographical origin and year but not variety (Parcerisa *et al.*, 1993a,b). Hazelnuts are rich in mono- and polyunsaturated fatty acids, especially oleic and linoleic (Baş *et al.*, 1986; Parcerisa *et al.*, 1997; Yıldız *et al.*, 2000). Unsaturated fatty acids are more susceptible to chemical autoxidation than saturated fatty acids. (Bonvehi & Coll, 1993; Garcia *et al.*, 1994; Bonvehi & Rosua, 1996). The rates of oxidation of fatty acids are approximately 1:10:100:200 for stearic ($C_{18:0}$), oleic ($C_{18:1}$), linoleic ($C_{18:2}$), linolenic ($C_{18:3}$) acids respectively (O'Keefe *et al.*, 1993). Therefore, varieties having lower level of linoleic acid and higher level of oleic acid at the same level of stearic acid are more stable to oxidative reactions.

Table 1.4. The moisture, carbohydrate, protein, mineral and oil content, fatty acid composition of the major Turkish hazelnut varieties^a

Variety	Water (%)	Carbohydrate ^b (%)	Protein ^c (%)	Mineral (%)	Oil (%)	Fatty acids (% of oil)					Unsaturated/ Saturated
						Palmitic	Palmitoleic	Steraric	Oleic	Lineoleic	
Tombul	4.83	15.72	13.78	2.07	64.77	4.50±0.23	0.22±0.04	1.02±0.24	82.61±0.51	11.65±0.70	17.12
Palaz	4.68	14.21	12.43	2.05	63.25	6.71±0.01	0.83±0.09	1.67±0.15	79.84±0.26	10.96±0.02	10.93
Mincane	4.56	12.22	13.29	1.90	63.64	7.88±0.16	0.69±0.07	2.32±0.35	76.87±0.35	12.49±0.10	8.83
Foşa	4.90	15.35	13.95	2.16	57.70	6.74±0.02	0.72±0.08	2.15±0.08	73.10±0.65	17.30±0.68	10.25
Çakıldak	5.19	22.32	14.91	2.55	55.07	5.62±0.02	0.49±0.03	1.12±0.13	71.27±0.01	21.36±0.06	13.82
Kalınkara	4.83	16.61	11.71	1.95	64.65	5.23±0.02	0.24±0.02	1.15±0.03	78.73±0.01	14.66±0.04	14.68
Cavcava	4.41	15.52	11.54	1.97	62.89	9.27±0.25	0.87±0.09	2.03±0.05	71.75±0.17	16.02±0.25	7.84
Uzunmusa	4.55	12.77	12.38	2.12	66.40	NA ^d	NA	NA	NA	NA	NA
Sivri	4.65	10.88	13.55	2.05	66.28	6.61±0.06	0.34±0.01	1.71±0.07	76.19±0.01	15.14±0.00	11.02

^a Data are gathered from Baş *et al.*, (1986).

^b Total carbohydrate.

^c Calculated as Nitrogen x 5.3.

^d Not available.

Table 1.5. Iodine value (IV), saponification value (SV), refractive index (RI) and specific gravity (SG) of some Turkish hazelnut varieties from different locations^a

Locations	Varieties	IV	SV	RI	SG
Akçakoca	Mincane	90.60 ± 1.53 ^a	193 ± 4.00 ^{c,d}	1.4678 ± 0.0086 ^a	0.9080 ± 0.0030 ^{a,b}
	Çakıldak	93.60 ± 1.08 ^{d,e}	183 ± 7.21 ^a	1.4687 ± 0.0080 ^a	0.9049 ± 0.002696 ^a
	Karafındık	94.10 ± 0.39 ^{e,f}	189 ± 2.65 ^{a,b,c,d}	1.4687 ± 0.0078 ^a	0.9088 ± 0.0013 ^{a,b}
Ordu	Foşa	91.40 ± 0.31 ^{a,b}	190 ± 4.36 ^{a,b,c,d}	1.4685 ± 0.0059 ^a	0.9120 ± 0.0028 ^{b,c,d}
	Palaz	92.80 ± 0.47 ^{c,d}	193 ± 2.65 ^{c,d}	1.4691 ± 0.0013 ^a	0.9172 ± 0.0023 ^{e,f,g}
	Çakıldak	97.90 ± 0.18 ^h	197 ± 8.54 ^d	1.4688 ± 0.0079 ^a	0.9173 ± 0.0015 ^{e,f,g}
Giresun	Sivri	97.50 ± 0.84 ^h	192 ± 5.29 ^{b,c,d}	1.4687 ± 0.0041 ^a	0.9213 ± 0.0052 ^g
	Tombul	92.40 ± 0.38 ^{b,c}	182 ± 4.36 ^a	1.4688 ± 0.0060 ^a	0.9202 ± 0.0013 ^{f,g}
	Kalınkara	94.90 ± 0.68 ^{f,g}	190 ± 2.65 ^{a,b,c,d}	1.4659 ± 0.0022 ^a	0.9103 ± 0.0036 ^{b,c}
Trabzon	Sivri	92.60 ± 0.55 ^{c,d}	192 ± 3.61 ^{b,c,d}	1.4687 ± 0.0017 ^a	0.9139 ± 0.0025 ^{c,d,e}
	Mincane	95.70 ± 0.33 ^g	188 ± 5.57 ^{a,b,c}	1.4690 ± 0.0048 ^a	0.9162 ± 0.0021 ^{d,e,f}
	Foşa	92.40 ± 0.34 ^{b,c}	184 ± 4.36 ^{a,b}	1.4687 ± 0.0024 ^a	0.9185 ± 0.0004 ^{f,g}

^a Data are gathered from Yıldız *et al.*, (2000).

Values in the same column with different lower-case letters (a-h) are significantly different at p<0.05.

Table 1.6. Sterol composition of some Turkish hazelnut varieties (% of unsaponifiable fraction of oil)^a

Locations	Variety	Campesterol	Stigmasterol	Sitosterol	Δ_5 -Avenasterol	Δ_7 -Stigmasterol	Unidentified
Akçakoca	Mincane	3.70 \pm 0.13 ^b	8.20 \pm 0.14 ^d	66.80 \pm 0.81 ^d	7.64 \pm 0.01	9.70 \pm 0.10	3.96
	Çakıldak	7.50 \pm 0.27 ⁱ	6.95 \pm 0.12 ^b	72.35 \pm 0.22 ^e	nd ^b	nd	12.90
	Karafındık	4.70 \pm 0.21 ^d	6.30 \pm 0.10 ^a	86.90 \pm 0.41 ^k	nd	nd	2.10
Ordu	Foşa	6.50 \pm 0.24 ^g	6.10 \pm 0.10 ^a	49.80 \pm 0.26 ^b	20.60 \pm 0.10	nd	17.00
	Palaz	8.01 \pm 0.08 ^j	8.04 \pm 0.17 ^d	78.80 \pm 0.41 ^g	nd	nd	5.15
Giresun	Çakıldak	2.80 \pm 0.11 ^a	10.30 \pm 0.13 ^h	84.50 \pm 0.22 ⁱ	0.70 \pm 0.10	nd	1.70
	Sivri	4.15 \pm 0.11 ^c	9.90 \pm 0.18 ^f	81.40 \pm 0.29 ^h	0.70 \pm 0.05	nd	4.40
	Tombul	5.60 \pm 0.28 ^e	8.25 \pm 0.07 ^d	78.00 \pm 0.40 ^f	nd	nd	8.15
	Kalınkara	4.02 \pm 0.10 ^c	7.50 \pm 0.13 ^c	86.08 \pm 0.28 ^j	nd	nd	2.40
Trabzon	Sivri	6.10 \pm 0.10 ^f	22.10 \pm 0.27 ⁱ	60.40 \pm 0.25 ^e	nd	nd	11.40
	Mincane	7.00 \pm 0.07 ^h	8.60 \pm 0.18 ^e	68.00 \pm 0.46 ^d	3.77 \pm 0.153	2.72 \pm 0.10	9.70
	Foşa	6.10 \pm 0.10 ^f	6.80 \pm 0.21 ^b	49.00 \pm 0.19 ^a	34.00 \pm 1.00	nd	4.10

^a Data are gathered from Yıldız *et al.*, (2000).

^b Not detected.

Values in the same column with different lower-case letters (a-k) are significantly different at $p < 0.05$.

Table 1.7. Amino acid composition of the major Turkish hazelnut varieties ^a

Amino acid (mg/100g db)	Tombul	Palaz	Mincane	Foşa	Variety Çakıldak	Kalınkara	Cavcava	Uzunmusa	Sivri
<i>Essential</i>									
Lysine	491.2	277.2	479.5	487.5	269.0	431.6	574.5	373.2	532.0
Isoleucine	720.1	516.8	369.6	621.8	488.9	670.1	606.5	529.0	438.0
Leucine	1,336.6	891.2	925.3	1,142.2	923.3	1292.9	1244.8	1003.3	929.6
Threonine	503.9	356.5	515.8	485.7	420.5	505.5	486.8	461.9	436.8
Valine	914.7	876.9	646.4	846.4	850.4	860.5	545.1	660.0	702.7
Methionine	255.2	144.7	179.6	234.0	120.6	244.1	171.5	164.4	202.9
Cystine	-	-	-	-	-	-	-	213.5	-
Methi. +Cyst.	255.2	144.7	179.6	234.0	120.6	244.1	171.5	377.9	202.9
Phenylalanine	798.7	570.6	746.6	724.7	614.3	731.5	691.9	419.4	635.3
Tyrosine	703.9	401.4	459.1	668.2	446.5	609.7	460.6	440.9	433.7
Pheyl. +Tyro.	1,502.6	972.0	1,205.7	1,392.9	1,060.8	1,340.2	1,151.5	859.3	1,069.0
Tryptophan	-	-	-	-	-	-	-	-	-
<i>Non-essentials</i>									
Histidine	454.4	648.5	441.8	429.6	774.3	421.0	355.2	363.0	337.7
Arginine	2,404.6	1,061.5	2,175.0	2,152.4	1,730.3	2,117.2	2,095.8	1,730.3	1,929.8
Aspartic acid	1,679.4	1,315.6	1,648.4	1,678.5	1,387.9	1,527.9	1,533.0	1,433.8	1,452.1
Serine	784.8	459.3	731.1	782.8	487.2	708.0	702.3	602.6	614.2
Glutamic acid	3,646.0	2,426.9	3,956.9	3,248.2	2,725.2	3,649.1	3,750.1	3,111.6	3,395.9
Proline	543.3	643.1	709.1	572.9	510.0	576.1	547.4	487.4	518.7
Glycine	691.6	441.9	782.7	665.0	483.6	672.2	743.9	629.2	681.8
Alanine	807.6	581.9	799.9	864.0	600.5	779.6	732.9	616.9	662.3

^a Data are gathered from Ayfer *et al.*, (1986).

During initial stages of fruit formation linoleic acid is predominant, whereas oleic acid and antioxidant components becomes dominant as maturity increases (Ayfer, 1972; Bonvehi & Coll, 1993; Koyuncu *et al.*, 1996). Pershern *et al.*, (1995) used unsaturation/saturation ratio (ratio of unsaturated fatty acids to saturated fatty acids) to predict of the shelf life of hazelnuts. As the the ratio gets lower the shelf life increases. The ratio increased in the following order: Cavcava, Mincane, Foşa, Sivri, Palaz, Çakıldak, Kalinkara and Tombul as shown in Table 1.4. However, shelf life is also affected by enzymatic activity (esterase, polyphenoloxidase, peroxidase and lipase), presence and concentration of pro-oxidant components (oxygen, iron, copper and manganese) and antioxidants such as tocopherols (Keme & Messerli, 1983a; Bonvehi & Coll, 1993; Bonvehi & Rosuo, 1996; Parcerisa *et al.*, 1995b). Therefore, it is recommended to use the varieties that are low in linoleic acid content and pro-oxidant compounds such as iron, manganese, and rich in anti-oxidant components such as tocopherols. Moreover light and oxygen should be eliminated from packages to increase the shelf life, and if possible, to reduce the preservation requirements of hazelnuts (Kinderlerer & Johnson, 1992; Bonvehi & Coll, 1993; Pershern *et al.*, 1995).

Glutamic acid, followed by arginine and aspartic acid are present in greatest concentrations in Turkish hazelnut varieties (Table 1.7.). The order in Chilean hazelnuts is, however, glutamic acid, aspartic acid and arginine (Villaroel *et al.*, 1987). Cystine is only present in the Uzunmusa variety. Lysine is the only limiting amino acid in the Chilean hazelnuts (Villaroel *et al.*, 1987). Amino acids are also play important role in the formation of color and aroma during roasting besides sugars (Basha & Young, 1985; Botta *et al.*, 1994). Organic acid composition in hazelnuts are reported to contribute to the taste and flavor of raw and roasted hazelnuts (Botta *et al.*, 1994; Botta *et al.*, 1996).

1.3.3 Importance of hazelnut for nutrition and health

Among the nut species, the hazelnut plays a major role for human nutrition, because of its special nutritional composition of proteins, fat, vitamins, and minerals (Woodroof, 1975; Villaroel *et al.*, 1987; Mattson, 1989; Elvevol *et al.*, 1990; Nicolosi *et al.*, 1990; Mehlenbacher, 1991; Sabate *et al.*, 1993; Villaroel *et al.*, 1993a,b; 1996; Ebrahim *et al.*, 1994; Alphan *et al.*, 1996a,b; Pala *et al.*, 1996; Özdemir *et al.*, 1998b; Parcerisa *et al.*, 1998; Açıktur *et al.*, 1999; Şimşek & Aslantaş, 1999). Hazelnuts are low in saturated fatty acid content (10%), even lower than olive oil (15%) and high in monounsaturated fatty acid (oleic acid). Monounsaturated and polyunsaturated fatty acids as well as natural sterols has been associated with decreased indices of cardiovascular diseases as a result of decreased serum cholesterol levels. They also favorably modified lipoprotein profile in normal persons when consumed frequently (Mattson, 1989; Elvevol *et al.*, 1990; Nicolosi *et al.*, 1990; Sabate *et al.*, 1993; Alphan *et al.*, 1996a,b). Hazelnuts also contain essential polyunsaturated fatty acids, daily requirement (1g) of which is satisfied with only 8 hazelnut kernels (Garcia *et al.*, 1994). Hazelnut can be used as a complementary protein source for combination with legume-based foods since they are low in cystine and methionine (Villaroel *et al.*, 1987).

Hazelnuts are very good source of vitamins B₆ and E (Mehlenbacher *et al.*, 1993; Pala *et al.*, 1996; Richardson, 1996; Açıktur *et al.*, 1999). 25 g of hazelnut is enough to supply 100% of vitamin E and 25% of vitamin B₆ of the daily requirements (Richardson, 1996). Among 17 hazelnuts variety, Tombul contained highest amount on vitamin E (453 mg/g oil) (Ebrahim *et al.*, 1994). Moreover, hazelnut is a good source of vitamins B₁, B₂. It is also very good plant source of iron, calcium and zinc that are required for growth. Potassium that is required for muscle and nerves system presents in hazelnuts at high level. Hazelnut is also a good source of phosphorus that is required together with calcium for bones and tooth (Alphan *et al.*, 1996b; Açıktur *et al.*, 1999; Şimşek & Aslantaş, 1999). Vitamin and mineral composition of Turkish varieties are given in Table 1.8. and Table 1.9.

Table 1.8. The vitamin composition of the major Turkish hazelnut varieties ^a

Variety	Vitamins (mg/100 g db)			
	B ₁	B ₂	B ₆	E
Tombul	0.410	0.051	0.18	20.627
Palaz	0.320	0.040	0.23	16.338
Mincane	0.363	0.051	0.33	16.482
Foşa	0.254	0.057	0.19	18.894
Çakıldak	0.328	0.056	0.31	19.532
Kalınkara	0.339	0.057	0.25	15.223
Cavcava	0.335	0.051	NA ^b	17.622
Uzunmusa	0.264	0.047	NA	18.218
Sivri	0.322	0.062	0.24	14.003

^a Data are gathered from Baş *et al.*, (1986) and Pala *et al.* (1996).

^b Not available.

Table 1.9. The mineral composition of the major Turkish hazelnut varieties ^a

Variety	Minerals (mg/100 g db)							
	Phosphor	Calcium	Magnesium	Manganese	Potassium	Zinc	Iron	Sodium
Tombul	304.0	118.7	157.0	7.32	618.6	5.94	3.32	4.76
Palaz	284.0	121.0	151.5	8.56	613.7	6.42	1.90	3.32
Mincane	272.0	95.8	158.5	5.64	550.7	3.46	2.19	2.42
Foşa	246.0	99.5	154.0	7.47	730.2	3.02	2.42	1.53
Çakıldak	55.07	147.2	181.0	7.60	875.7	5.28	2.58	3.25
Kalınkara	264.0	105.7	167.5	8.02	623.5	3.74	2.05	2.93
Cavcava	224.0	96.9	168.0	6.43	676.8	8.38	2.86	3.83
Uzunmusa	312.0	93.2	158.5	7.30	628.3	4.10	2.42	4.21
Sivri	256.0	100.1	160.0	8.40	618.6	3.82	1.96	4.21

^a Data are gathered from Baş *et al.*, (1986) and Pala *et al.* (1996).

1.3.4 Other benefits of hazelnuts or its production

In Türkiye, hazelnut is cultivated in 500 000 hectare area by 370 000 family (Külünkoğlu, 1996). Almost eight million of people are involved into production and processing of Turkish hazelnut (Akdağ & Öztürk, 1993). Hazelnut cultivation in Eastern Black Sea region of Türkiye also contributes to prevent erosion in high sloped and shallow fields under heavy rain (Ayfer, 1984; Baş, 1990; Pınar & Beyhan, 1991).

Besides hazelnut tocopherols, hazelnut phenolic substances such as gallic acid, *p*-hydroxy benzoic acid, epicatechin and/or caffeic acid, sipanic acid, and quercetin was reported to be possible natural antioxidant to use in foodstuff (Andreoni, 1996; Yutan *et al.*, 2000).

Contaminated hazelnuts are used in oil and cosmetic industry. Hazelnut shells are used for fuel and mulching, furfural manufacturing; artificial wood, plywood and linoleum manufacturing (Woodroof, 1967); production of methanol and acetic acid through pyrolysis (Demirtaş, 1999).

1.4 Roasting of Nuts

Purpose of roasting is to increase overall palatability of the products. Roasting alters and significantly enhances the flavor, color, texture and appearance of nuts. The resulting product is delicate, uniquely nutty and widely enjoyed compared to raw nuts (Pattee *et al.*, 1982a,b; Mayer, 1985; Sanders *et al.*, 1989; Pattee *et al.*, 1995; Saklar, 1999). Like for the other nuts and beans, roasting is one of the common form of processing of hazelnuts (Buckholz *et al.*, 1980; Moss & Otten, 1989; Jayalekshmy & Mathew, 1990; Hashim & Chaveron, 1996; Perren & Escher, 1996a,b,c; Shimoda *et al.*, 1997; Jung *et al.*, 1997; Jinap *et al.*, 1998).

Roasting also removes pellicle of hazelnut kernels, inactivates enzymes that speeds up nutrient damage and destroys undesirable microorganisms and food contaminants (Buckholz *et al.*, 1980; Hashim & Chaveron, 1996; Köksal & Okay, 1996; Richardson & Ebrahim, 1996; Atakan & Bostan, 1998). Roasting causes decreases in vitamin B₁ and vitamin B₂ of roasted hazelnuts (Özdemir *et al.*, 2000b); vitamin E of roasted hazelnuts (Richardson & Ebrahim, 1996); carotene, vitamins B₁, B₂, E and C and of roasted maize (Ayatse *et al.*, 1983); potassium and calcium content of roasted maize (Ayatse *et al.*, 1983).

Temperature and time are the main factors controlled during industrial roasting process. But initial moisture content and air velocity also affects heat transfer rate and subsequently drying and physicochemical changes in proteins (Chiou & Tsai, 1989; Saklar, 1999).

Drying and chemical changes occur during roasting (application heat treatment, $>100^{\circ}\text{C}$) which bring about generation of flavor and aroma, textural changes, color formation and lipid oxidation (See Figure 1.1). The changes involves changes in the carbohydrates, proteins, fats or physiologically active substances, such as vitamins or essential amino acids in correlation to the temperature-time treatment of the product. Proteins and amino acids can be cross-linked or decomposed, fats can be decomposed or oxidized, nutritional substances such as vitamins and amino acids may be destroyed or they can be blocked by reactions with other ingredients. Oligosaccharides can react twice, decompose hydrolytically or caramelize. Sucrose inverted to fructose and glucose during the reactions. All chemical reactions contribute to the change in the original quality properties of a dry product such as color, taste, smell, nutritional value and shelf life (Muller & Bauer, 1990). Therefore it is necessary to understand these changes during roasting so as to obtain better quality roasted hazelnut.

1.4.1 Non-enzymatic browning reactions

The changes in color, flavor, texture and appearance during roasting of nuts are mainly related to non-enzymatic browning (Buckholz *et al.*, 1980; Mayer, 1985; Perren & Escher, 1996a,b,c; Lopez *et al.*, 1997a). Non-enzymatic browning involves condensation of carbonyl group of a reducing sugar with free, uncharged amine group of amino acid or protein with the loss of one mole of water (Danehy, 1986; Ames, 1988; Troller, 1989; Labuza & Braisier, 1992; Jinap *et al.*, 1998).

The non-enzymatic browning reaction can be broken into three primary reactions that generate color and flavor: Maillard reaction, Strecker degradation, and sugar caramelization (Buckholz *et al.*, 1980; Danehy, 1986).

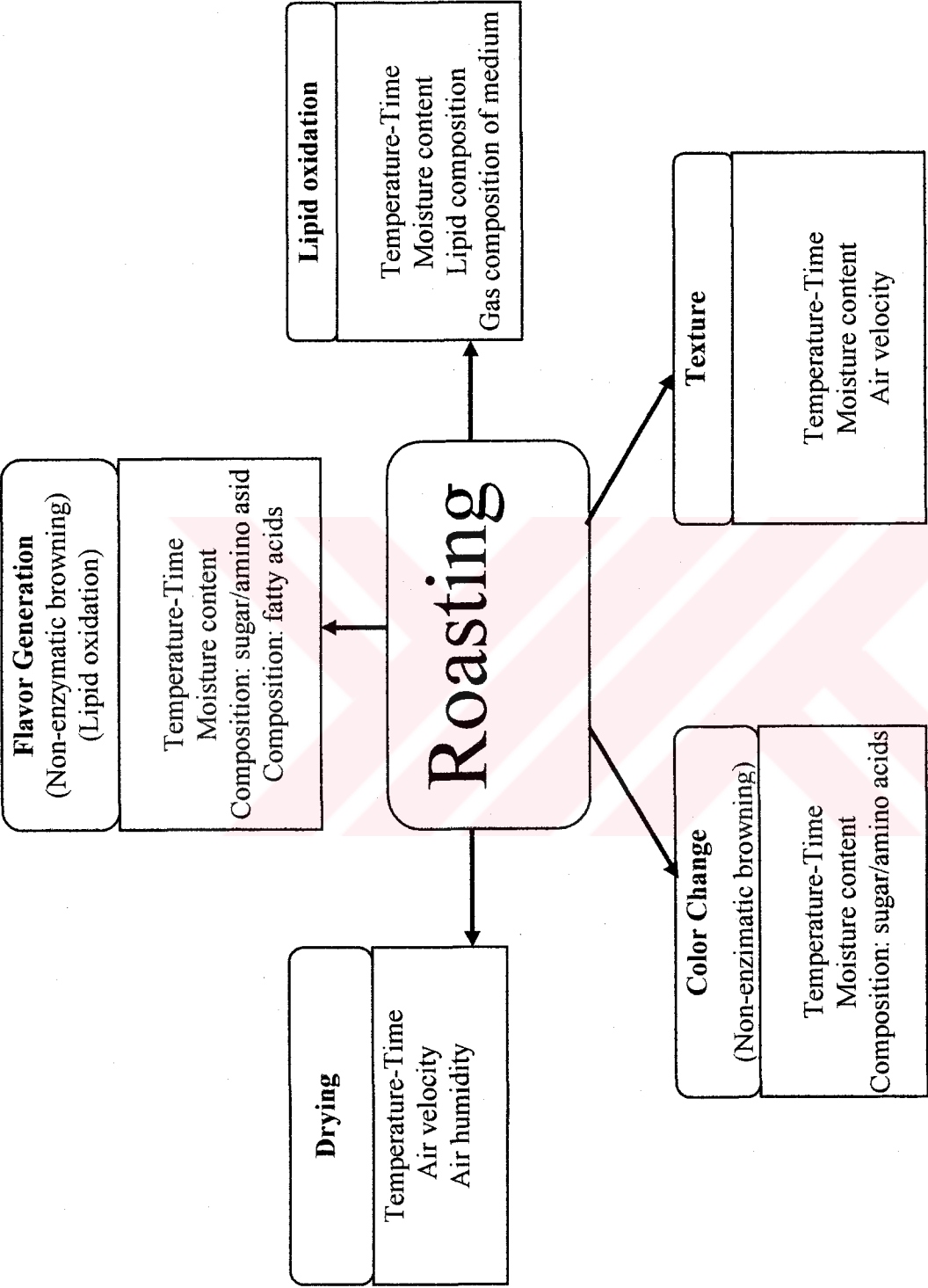


Figure 1.1. Effect of roasting on nuts

The Maillard reaction and Strecker degradation are similar because they require a reducing sugar (or sugar decomposition products), amino acids, and a small amount of water reactants. Reaction of carbohydrates with amino acids produces amadori compounds that are built as precursors of the Maillard reaction. In peanuts and coffee, naturally low level of reducing sugar presents and hydrolysis of sucrose to reducing sugars (fructose and glucose) occur during roasting (Trugo & Macrae, 1986; Danehy, 1986; Rodriguez *et al.*, 1989).

Non-enzymatic browning products have anti-oxidant and anti-nutritional properties. Anti-oxidant properties were related to the formation of phenolic type structures and/or the metal chelating properties of melanoidins. Non-enzymatic browning, however, causes a decrease in nutritive value due to decreased protein digestibility and loss of essential amino acids (Danehy, 1986; Ames, 1988; O'Brien & Morrissey, 1989; Nicoli *et al.*, 1991).

1.4.2 Moisture loss/drying during roasting of nuts

Drying is one of the processes occurring during roasting operation and was related with textural changes during roasting (Mayer, 1985; Perren & Escher, 1996a,b; Saklar, 1999; Saklar *et al.*, 2001). In spite of low initial moisture content of the nuts, which is generally in the range of 5-9%, moisture loss occurs during roasting due to high roasting temperature ($>100^{\circ}\text{C}$). Therefore theory of drying would also apply roasting process. Moisture loss during roasting are affected by roasting temperature, roasting time, air velocity, product characteristics, roaster characteristics which are related with heating performance (Saklar, 1999).

Initial moisture content also effect nonenzymatic browning reactions which are related with color and flavor characteristics of roasted nuts (Pattee *et al.*, 1982a,b; Moss & Otten, 1989; Sanders *et al.*, 1989; Troller, 1989; Lopez *et al.*, 1997a).

Therefore control and monitoring of moisture content prior to and during roasting is essential to obtain desired color at specified moisture content. But there is limited study on moisture loss in nuts during roasting (Moss & Otten, 1989; Bhattacharya & Prakash, 1997).

1.4.2.1 Mathematical modeling of moisture loss during roasting

The behavior of the food during drying/roasting depends on the heat and mass transfer characteristics of the product being dried. A knowledge of temperature and moisture distribution in the product is vital for equipment and process design, quality control, choice of appropriate storage and handling practices. Mathematical models that describe drying mechanisms of foods can provide the required temperature and moisture information (Parry, 1985; Parti, 1993). Among mathematical models, thin layer drying equations have been found wide application due its ease of use and lack of required data in complex theoretical models (such as phenomenological and coupling coefficients) (Madamba *et al.*, 1996). Isothermal conditions within the grain, but not with time are assumed in thin layer drying equations due to fact that the rate of heat equalization within the grain is two orders of magnitude greater than the rate of moisture equalization. Therefore only moisture diffusion is used to describe mass transfer in the medium (Whitaker *et al.*, 1969; Young 1969).

Thin layer drying equations fall into three categories namely, theoretical, semi-theoretical, and empirical. The first takes into account only internal resistance to moisture transfer while the other two considers only external resistance to moisture transfer between product and air (Henderson, 1974; Whitaker *et al.*, 1969; Fortes & Okos, 1981; Bruce, 1985; Parti, 1993). The most widely investigated theoretical drying model has been the Fick's second law of diffusion. Drying of many food products such as rice (Ece & Cihan, 1993) and hazelnut (Demirtaş *et al.*, 1998), soybean (Suarez *et al.*, 1980a), rapeseed (Crisp & Woods, 1994), pistachio kernel (Karataş & Battalbey, 1991)

have been successfully predicted using Fick's law with Arrhenius type temperature dependent diffusivity. Nevertheless, many assumptions necessary required to use this law to describe falling-rate drying period of foods has been proven to be invalid (Moss & Otten, 1989).

Semi-theoretical equations offer a compromise between theory and ease of use (Fortes & Okos, 1981). Semi-theoretical models are generally derived by simplifying general series solution of Fick's second law or modification of simplified models. But they are only valid within the temperature, relative humidity, air flow velocity and moisture content range for which they were developed. They require small time compared to theoretical thin layer models and do not need assumptions of geometry of a typical food, its mass diffusivity and conductivity (Parry, 1985). Among semi-theoretical thin layer drying models, Henderson & Pabis model, two-term model, Lewis model, Page model and modified Page model are used widely. Henderson & Pabis model (E.1) is first term of a general series solution of Fick's second law (Henderson & Pabis, 1961). Henderson & Pabis model was used to model drying of corn (Henderson & Pabis, 1961), wheat (Watson & Bhargava, 1974), rough rice (Wang & Singh, 1978), peanut (Moss & Otten, 1989) and mushroom (Gürtaş, 1994). A poor fit during first 1 or 2 hr of drying of corn was, however, reported due to the greater temperature difference between the kernel and air, and loss of accuracy due to the truncation of the series solution (Henderson & Pabis, 1961). Slope of Henderson & Pabis model, coefficient k , is related to effective diffusivity when drying process takes place only in the falling rate period and liquid diffusion controls the process (Suarez *et al.*, 1980b; Madamba *et al.*, 1996).

$$MR = a \exp(-kt) \quad (E\ 1)$$

The two-term model (E 2) is the first two term of general series solution to Fick's second law and has also been used to describe drying behavior of agricultural products, regardless of particle geometry. It was used to model corn drying (Henderson, 1974; Sharaf-Eldeen *et al.*, 1980), white beans and soybeans drying (Hutchinson & Otten,

1983), and drying of macadamia nut in-shell and kernel (Palipane & Driscoll, 1994). However, it requires constant product temperature and assumes constant diffusivity.

$$MR = a \exp(-k_1 t) + b \exp(-k_2 t) \quad (E 2)$$

Lewis model (E 3), where intercept is unity, is a special case of Henderson & Pabis model. It is analogous to Newton's law of cooling: the rate of moisture loss of a food surrounded by a medium at a constant temperature (thermal equilibrium) is proportional to the difference between the kernel moisture and its equilibrium moisture content (Brooker *et al.*, 1974). Lewis model was used to describe drying of barley (Bruce, 1985), wheat (O'Callaghan *et al.*, 1971), shelled corn (Sabbah *et al.*, 1972), cashew nuts and kernels (Chakraverty, 1984) and walnut (Anigbankpu *et al.*, 1980). The model, however, tends to overestimate the early stages and underestimate the later stages of the drying curve (Bruce, 1985).

$$MR = \exp(-kt) \quad (E 3)$$

Page model (E 4) is modification of Lewis model to overcome its shortcomings (Page, 1949, cited in Bruce, 1985). Page model has produced good fits in predicting drying of short grain and medium rough rice (Wang & Singh, 1978), soybean (White *et al.*, 1981; Hutchinson & Otten; 1983), white bean (Hutchinson & Otten; 1983), shelled corn (Agrawal & Singh, 1977; Misra & Brooker, 1980), corn (Flood *et al.*, 1972), barley (Bruce, 1985), rapeseed (Pathak *et al.*, 1991) and sunflower seeds (Syarif *et al.*, 1984).

$$MR = \exp(-kt^n) \quad (E 4)$$

Page model was modified (E 5) by Overhults *et al.*, (1973) to describe drying of soybean.

$$MR = \exp((-kt)^n) \quad (E 5)$$

Empirical models derive a direct relationship between average moisture content and

drying time, and neglect fundamentals of the drying process. Therefore they can not give a clear accurate view of the important processes occurring during drying although they may describe the drying curve for the conditions of the experiment (Keey, 1972; Irudayaraj *et al.*, 1992). Among them, Thompson and Wang & Singh models has been found application in the literature.

Thompson model (E 6) was used to describe shelled corn drying for temperatures between 60°C to 149°C (Thompson *et al.*, 1968), and Wang & Singh model (E 7) was used to describe drying of rough rice (Wang & Singh, 1978).

$$t = a \ln MR + b (\ln MR)^2 \quad (E\ 6)$$

$$MR = 1 + a t + b t^2 \quad (E\ 7)$$

Since moisture content is among the quality indicator of the roasting process, calculating and predicting the moisture content requires mathematical models (Saguy & Karel, 1980; Samaniego-Esguerra *et al.*, 1991; Saklar, 1999). But there is limited study on mathematical modeling of moisture loss in nuts during roasting (Moss & Otten, 1989; Bhattacharya & Prakash, 1997).

1.4.3 Color change during roasting of nuts

Roasting enhance color of the nuts through non-enzymatic browning reactions that ultimately increase overall palatability of the products. Non-enzymatic browning Maillard and Strecker reaction products include a variety of products with complex structures, many of which are unsaturated. The double bonds in these structures absorb light, causing them to behave as brown pigments and contribute to a darker color of the roasted products (Trugo & Macrae, 1986; Danehy, 1986; Rodriguez *et al.*, 1989; Cammarn *et al.*, 1990; Lopez *et al.*, 1997a).

Sugar caramelization, the thermal dehydration and fragmentation of sugars also yield brown pigments besides organic acids and various aldehydes and ketones. Burnt flavors are commonly associated with the caramelization reaction products.

Since the numerous classes of aromatic products with complex structures from the Maillard and Strecker reactions, such as aldehydes and pyrazines forms during roasting, control of roasting process with flavor is difficult and/or very expensive because require complex instrumentation and time requiring analysis. But color is among the most important quality attribute of the dehydrated foods for consumers (Driscoll & Madamba, 1994), and empirically, color is also an effective quality indicator because the brown pigments increase as the browning and caramelization reactions progress (Moss & Otten, 1989; Cammarn *et al.*, 1990). However, Moss & Otten (1989) was stated that selection of a roast on the basis of color alone could lead to flavor defects. Because nonenzymatic browning, subsequently color and flavor are dependent on temperature, water activity, composition, and pH of the food.

Among sugars, glucose and fructose are active in browning reactions besides pyrazine formation. Sucrose and starch may also be involved in the roasting reactions through hydrolysis. Table 1.10. summaries the changes in sugar components of nuts during roasting.

Table 1.10. Changes in sugar during roasting of nuts

Food	Sugar			Reference
	Fructose, glucose	Sucrose	Starch	
Hazelnut		Hydrolysis	Hydrolysis	Kırbaşlar, 1998
Peanut	Decrease	Hydrolysis		Qupadissakoon & Young, 1984
Coconut	Decrease	Hydrolysis	Hydrolysis	Jayalekshmy & Mathew, 1990
Cocoa	Decrease	Hydrolysis		Rohan & Stewart, 1966
Pistachio	Decrease		Hydrolysis	Kashani & Valadon, 1984
Soybean	Increase			Kato <i>et al.</i> , 1981

Intensity of browning is correlated with amino acids and sugars. Degree of browning decreases in the following order: ribose, fructose, glucose and lysine, glycine, tryptophan, tyrosine (Ashoor & Zent, 1984). Among sugars, pentoses were found to be more reactive than hexoses and fructose reacted more rapidly than glucose (Koehler *et al.*, 1970).

Temperature and moisture may be different within the food due to drying which results in localized concentration of reactants (Warmbeir *et al.*, 1976; Saguy & Karel, 1980; Labuza & Saltmarch, 1981a; Muller & Bauer, 1990; Driscoll & Madamba, 1994; Rapusas & Driscoll, 1995; Lopez *et al.*, 1997a; Göğüş *et al.*, 1998). Lower content of reducing sugars (fructose and glucose) within the sample and among the different sizes of the product bring about lower browning rates (Lopez *et al.*, 1997a; Pattee *et al.*, 1982a). Consequently, varying reaction rates in different section of the sample and the local development of Maillard reaction or lighter color in the smaller sizes samples may be observed (Pattee *et al.*, 1982a; Göğüş *et al.*, 1998). Peanuts stored at 9% rather than 6% reported to produce a darker color after roasting with reduced flavor quality. Due to compositional differences between varieties temperature-time required to achieve a specific color is different between varieties (Pattee *et al.*, 1982a,b; Sanders *et al.*, 1989). Harvesting practices and maturity also reported to affect color of the roasted peanuts (Chiou *et al.*, 1992). Maximum browning rate observed at 0.4-0.6 water activity levels. After browning critical moisture content, dilution of reactants decreases rate of non-enzymatic browning reaction as the moisture content increases (Troller, 1989; Lopez *et al.*, 1997a) as also observed by Moss and Otten (1989) who stated that color develops faster after rapid drying in peanut roasting.

Although changes in sugar components of several nuts during roasting were studied (See Table 1.10.), there is limited study about changes in sugar components of hazelnut during roasting (Kırbaşlar, 1998).

1.4.3.1 Kinetics of color changes

Calculating and predicting a quality indicator in food systems during processing or storage involves development of a mathematical model (Saguy & Karel, 1980; Samaniego-Esguerra *et al.*, 1991). A quality indicator such as color is usually modeled using general rate equation (E 8):

$$\pm dC/dt = kC^n \quad (\text{E } 8)$$

When	$n > 1$,	$C/C_1 = (1 + (n-1) kt)^{1/(1-n)}$	(E 9)
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	$n = 1$ (1 st order),	$C = C_o \exp(-kt)$	(E 10)
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	$n = 0$ (Zero order)	$C = C_o - kt$	(E 11)
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The order of a chemical reaction is generally between 0 and 3 for a food system. The reaction for nonenzymatic browning of foods is generally first order (E 10) or zero order (E 11) (Mizrahi *et al.*, 1970; Warmbeir *et al.*, 1976; Labuza & Saltmarch, 1981b; Mishin *et al.*, 1983; Singh *et al.*, 1983; Toribio *et al.*, 1984; Aguerre & Suarez, 1987; Pagliarini *et al.*, 1990; Bhattacharya, 1996; Samaniego-Esguerra *et al.*, 1991; Driscoll & Madamba, 1994; Rapusas & Driscoll, 1995; Shin & Bhowmilk, 1995).

The water activity and temperature dependence of the indicator should be related to deterioration kinetics of indicator compounds (Muller & Bauer, 1990). Effect of temperature is usually considered using Arrhenius-type (E 12) relationship (Saguy & Karel, 1987; Cammarn *et al.*, 1990; Samaniego-Esguerra *et al.*, 1991; Driscoll & Madamba, 1994; Bhattacharya, 1996; Göğüş *et al.*, 1998):

$$K = k_o \exp(-E_a/\mathcal{R}T_a) \quad (\text{E } 12)$$

where k is reaction rate constant of nonenzymatic browning, k_o is a frequency constant (independent of temperature), E_a is the activation energy, \mathcal{R} is the universal gas constant, T_a is the absolute temperature. Linear, exponential and hyperbolic functions were also employed to correlate browning with temperature but were found to be valid only over a limited range (Karel, 1983). Saguy & Karel (1980) reviewed activation

energies of some of the typical reactions: diffusion control (0-33 kJ/mole); enzyme activation (41-125 kJ/mole); lipid oxidation (41-104 kJ/mole); color, texture and flavor (41-125 kJ/mole); non-enzymatic browning (104-209 kJ/mole). Aguerre & Suarez, (1987), Samaniego-Esguerra *et al.*, (1991), Pagliarini *et al.*, (1990), Driscoll & Madamba, (1994), Rapusas & Driscoll, (1995) and Bhattacharya, (1996) used zero order rate equation with Arrhenius-type dependence on temperature to describe kinetics of nonenzymatic browning during drying of corn, drying of onions, heat treatment of milk, drying of garlic, onion storage and drying of parboiled rice, respectively.

The effect of water activity on the nonenzymatic browning kinetics were described with a quadratic polynomial by Rapusas & Driscoll, (1995) for onions drying, with a first-degree polynomial by Samaniego-Esguerra *et al.*, (1991) for onion storage and with a first-degree-polynomial by Driscoll & Madamba (1994) for garlic drying.

Mizrahi *et al.*, (1970), Mishin *et al.*, (1983), Singh *et al.*, (1983) and Shin & Bhowmilk (1995) employed first-degree with Arrhenius-type temperature dependence model to describe nonenzymatic browning of cabbage, potatoes, intermediate moisture apples and pea puree, respectively. Mizrahi *et al.*, (1970) considered effect of both solid content and moisture content while Mishin *et al.*, (1983) and Singh *et al.*, (1983) considered effect of water activity or moisture content on model coefficients.

Zero order kinetics with Arrhenius-type temperature dependence was suggested to be applied for browning kinetics during roasting (Cammarn *et al.*, 1990). For peanut roasting, however, Moss & Otten (1989) used a second-degree polynomial in describing *L*- and *a*-value in peanut roasting, and a third-degree model in describing *b*-value.

Although color formation kinetics during roasting in several nuts were studied (Cammarn *et al.*, 1990; Moss & Otten, 1989), there is limited no study about color formation kinetics of hazelnuts during roasting.

1.4.3.2 Color formation kinetics using response surface methodology

Response surface methodology (RSM) is a statistical technique for investigation of processes (Kaleoğlu, 1996; Thomson, 1982). It was successfully applied to food processes (Guerrero *et al.*, 1996; Kaleoğlu, 1996; Shieh, C-J *et al.*, 1995; Mudahar *et al.*, 1990). It was developed by Box and Wilson (1951) to study the output or response (dependent variables) of a system as a function of explanatory variables (independent variables) (Thomson, 1982). The main advantage of RSM is the ability to reduce the experimental runs needed to provide sufficient information for statistically acceptable results. It is also fast and less expensive (Shieh *et al.*, 1995). The response can also be thought of as a surface over the independent variables in experimental space. Therefore, experiments, identifying or evaluating one or more response variables as a function of explanatory variables, has been associated with the term response surface. Generally, RMS are used to mathematically model the experimental space or to optimize the system response (Thomson, 1982). So as to mathematically estimate a response y with k number of independent variables (factors, x_i) and coefficients β_i with a true function f , simple mathematical equations such as polynomials can be used. Since polynomials are simple, can provide a curvilinear relationship between a large number of variables, posses a optimum and utilize simple computational algorithms (using the least square method) for estimation of coefficients β_i , they are extensively used in food processes. The most commonly polynomials are the first degree (E 13) and second degree (E 14) response functions while there are limited amount of work with third degree polynomials (Draper, 1985; Thompson, 1982). Even if the second order are found to be inadequate higher order models are not employed. Moreover, first degree polynomials are not accurate and mostly used for parameter estimation (Draper, 1985). The limitations of using polynomials as a approximating functions can be easily overcome by application of appropriate mathematical transformations of the independent or dependent variables (Draper, 1985).

$$y = \beta_0 + \sum_{i=1}^k \beta_i x_i \quad (E 13)$$

$$y = \beta_0 + \sum_{i=1}^k \beta_i x_i + \sum_{i=1}^k \beta_i x_i^2 + \sum_{i=1}^{k-1} \sum_{j=i+1}^k \beta_{ij} x_i x_j \quad (E 14)$$

Experimental designs of RSM codes of 0, ± 1 , α are used. 0 donates center of a independent variable range, ± 1 donates 1 unit lower and higher points from the center point, and α are used to make the design rotatable which has uniform variance at any given radius from the center of the design. So that experimental designs can be written without knowing the interest range for each independent variable. Moreover, it is possible to compare magnitude of each variable since the range of the variables are identical (all have a range of ± 1). So that response variable can be better estimated. Among several experimental designs, central composite design is usually employed for experiments of second order models. Central composite designs includes three types of experimental points. Cube points is the points at which independent variables are coded as ± 1 . Star points is the points at which two of independent variables is coded as 0 while the other has a code of α . Center points are replicated points at the center of the design (0,0,0) (Draper, 1985, Thompson, 1982).

Response surface methodology was used to find out the effect of process variables on color formation kinetics during roasting and to establish a second degree prediction models, as a function of roasting temperature and exposure time for L -value, a -value and b -value of whole-kernel, ground-state and cut-kernel measurements.

1.4.4 Flavor generation during roasting of nuts

Roasting promotes flavor of the nuts that ultimately increase overall palatability of the products (Buckholz *et al.*, 1980; Mayer, 1985; Perren & Escher, 1996a,b,c; Lopez *et al.*, 1997a). Monosacchararides and free amino acids are essential precursors of flavor

generating Maillard reactions to give rise pyrazine compounds. Free amino acids and monosaccharides are released from polypeptides and complex carbohydrates through undefined processes during roasting process. Among free amino acid aspartic acid, glutamic acid, phenylalanine and histidine are typical flavor precursors and sucrose participates the flavor and color generating reaction through its inversion to glucose and fructose (Newell *et al.*, 1967; Koehler & Odell, 1970). Among the Maillard reaction product, pyrazines have been well characterized as the volatiles contributing the roasted and aromatic odor in high-temperature-processed food products. They are mainly absorbed in the oils and comprising highest proportion of the total volatiles (Shimoda *et al.*, 1997) and are not as volatile as in aqueous system (Hashim & Chaveron, 1996).

The numerous classes of aromatic products with complex structures from the Maillard and Strecker reactions, such as aldehydes, pyrazines and sugar fragments, often depend on the amino acid composition (Cammarn *et al.*, 1990). Changes in amino acid content in peanuts during roasting are significantly affected by the nature and extent of heat treatment, internal temperature, and moisture content of kernels (Chiou *et al.*, 1991a). The free amino acids decreased significantly with time of roasting. Newell *et al.*, (1967) classified amino acids as typical (aspartic acid, glutamic acid, phenylalanine and histidine) and atypical (threonine, tyrosine, lysine) peanut flavor precursors. The involvement of atypical flavor precursors does not contribute positively flavor formation. In model studies, asparagine, aspartic acid and glutamic acid gave highest yields of pyrazines (Koehler & Odell, 1970). Asparagine, glutamine and certain peptides, involved in the flavor generation reactions, disappeared after 6 months of storage. Maturity and seed size affects flavor characteristics of the roasted peanut due to compositional differences between maturity classes and seed size (Rodriquez *et al.*, 1989). Changes in free amino acid content of nuts during roasting was summarized in Table 1.11.

Table 1.11. Free amino acids of nuts involved during roasting

Food	Amino acids involved	Reference
Hazelnut	Losses in total amino acids	Kırbaşlar, 1998
Peanut	Aspartic acid, glutamic acid, alanine, isoleucine, histidine, phenylalanine	Qupadissakoon & Young, 1984
Coconut	<i>Color:</i> Lysine, glycine, tryptophan, <i>Aroma:</i> Glutamic acid, aspartic acid, alanine <i>Other:</i> Theonine, valine, arginine, methionine, isoleucine, proline, serine <i>Total amino acid:</i> lysine, arganine	Jayalekshmy & Mathew, 1990
Cocoa	Threonine, glutamic acid, phenylalanine, cysteine, histidine, arginine	Rohan & Stewart, 1966
Pistachio	Lysine, arginine and methionine	Kashani & Valadon, 1984

Although changes in free/total amino acid composition during roasting of several nuts were studied (Table 1.11.), there is limited study about changes in amino acid composition of hazelnut during roasting (Kırbaşlar, 1998).

1.4.5 Lipid oxidation during roasting of nuts

Roasting involves high temperature heat treatment which decreases oil stability of nuts that ultimately decrease overall palatability of the products. Most nuts contain around 50% oil. Moreover foods containing unsaturated fatty acids are susceptible more to rancidity due to lipid oxidation that bring about the production of off odors and off flavors, and the production of toxic or physiologically active compounds that can damage proteins, enzymes and amino acids. Hazelnut and peanut oils are composed of around 90% and 80% unsaturated fatty acids, respectively. Oleic acid constitutes about of 80% of the hazelnut oil and 50% of the peanut oil while linoleic make up of about 10% of hazelnut oil and about 30% of the peanut oil (Bett & Boylston, 1992; Braddock *et al.*, 1995; Mate *et al.*, 1996; Yıldız *et al.*, 2000). Like other nuts, peanut and hazelnuts are susceptible to the lipid oxidation.

Rancidity involves free radical mechanism, initiated by oxidative rancidity and hydrolytic rancidity both of which leading to fatty acid hydroperoxides. Oxidative rancidity develops in the presence of oxygen either by metal ion catalysis (autoxidation via the classical free radical route) or by enzyme-initiated oxidative degradation (peroxidase, lipoxygenase) (Keme *et al.*, 1983a; Bonvehi & Rosua, 1996). Autoxidation has three basic steps: initiation (addition of oxygen to the fatty acids), propagation (generation of hydroperoxides and free radicals) and termination (combination of free radicals with each other or with other compounds, formation of further peroxides and the release of oxygen back to the system). Once initiated, the reaction is self-propagating, forming more hydroperoxide and more free radical and/or breakdown products, depending upon conditions (St. Angelo & Ory, 1975). Autoxidation in the absence of oxygen slow downs even at room temperature of 18-25°C (Keme *et al.*, 1983a; Mate *et al.*, 1996). Oleic acid and linoleic acid autoxidation produces most of the rancid substances in hazelnuts (Bergner *et al.*, 1974; Grosch *et al.*, 1983; Keme *et al.*, 1983a; Kinderlerer & Johnson, 1992; Fourie & Basson, 1989) and linoleic acid in peanuts (Mate *et al.*, 1996). Free fatty acids or triglycerides are the substrates for these reactions. However, enzymatic splitting of fatty acids by peroxidase and lipoxygenase can not occur in the absence of oxygen because the enzymes are oxygen dependent. Peroxidase activity in the damaged surfaces is more pronounced (Hadorn *et al.*, 1977; Keme *et al.*, 1983a,b).

Lipases, esterases, lipoxygenase and peroxidase are involved in enzyme-catalyzed lipid oxidation reactions (hydrolytic rancidity). Lipases and esterase splits off fatty acids from the lipids and produces free fatty acids. Then the formed free fatty acids can be substrates of the oxidation reactions (Lopez *et al.*, 1997b,c). But these lipolytic enzymes which are situated closely below pellicle cannot attack the fats in the undamaged cells (Riedl & Mohr, 1979). Lipase and esterase are oxygen-independent enzymes. Moreover, lipase activity mainly depends upon moisture content. Maturity and age of the seed influences lipase content of a seed besides climatic conditions. Esterase is heat stable

and may be still active even after roasting (Keme *et al.*, 1983a). Roasting substantially reduces activity of lipase and eases activity of peroxidase (Grosch *et al.*, 1983). High roasting temperature deactivates partly lipoxygenase in hazelnuts (Lopez *et al.*, 1997b). Lipoxygenase promotes oxidation of peanuts stored at 4°C after a lag period of several months (St. Angelo & Ory, 1975) but its activity eased after 25 min of roasting (Chiou *et al.*, 1991b). Therefore oxidation of roasted peanuts at 4°C was possibly catalyzed by metals or metalloproteins (e.g. peroxidase, tyrosinase) through peroxidation of unsaturated fatty acids (St. Angelo & Ory, 1975).

Enzymatically catalyzed peroxidation in raw peanuts is a more specific process than the hemoprotein or autoxidation processes that appear to take place in roasted nuts. Peanut lipoxygenase attacks linoleic acid to produce hydroperoxide. Then, breakdown of the hydroperoxide produces hexanal, a carbonyl compound that can also combine with certain protein functional groups (St. Angelo & Ory, 1975). Role of enzymes in hazelnut oxidation in both raw and roasted hazelnut products were not studied yet.

The oxidation products, namely hydroperoxides, are active oxidants and have tendency to react with other compounds at room temperature, during storage and processing to form carbonyl compounds such as monocarboxylic acids, aldehydes, ketones, hydrocarbons, esters and lactons. These breakdown compounds are related with the rancid flavor (Chang *et al.*, 1978; St. Angelo *et al.*, 1979; Stevenson *et al.*, 1979; Serim, 1990; Fourie & Basson, 1989; Bett & Bobylston, 1992; Liu & White 1992; Ünal & İşçioğlu, 1992). Moreover, these degradation products as well as peroxides and lipid free radicals can react with vitamins, amino acids and proteins which impairs flavor, and/or lower nutritive value of food products besides staling (e.g., reaction of lysine and threonine with the oxidized linoleic acid) and toughening (St. Angelo & Ory, 1975; Gardner, 1979; St. Angelo *et al.*, 1979; Senter *et al.*, 1984; Anonymous, 1993). Although heat denatures proteins but apparently does not dissociate the lipid-protein complexes. Therefore improperly packaged roasted nuts may undergo lipid

peroxidation with subsequent lipid-protein interactions during storage (Lopez *et al.*, 1997c). They have also been associated with possible carcinogenic effect and cause of many diseases (Gardner, 1979; Fourie & Basson, 1989; Pariza, 1990; Duthie, 1993).

Temperature, water activity, type of substrates, oxygen content, relative humidity, presence of metals, presence of anti-oxidants and enzymatic activity affect the rate of lipid oxidation (Cavaletto & Yamamoto, 1971; Harris *et al.*, 1972; Shewfelt & Young, 1977; Prabhakar & Amla, 1978; Lopez *et al.*, 1997c; Mate *et al.*, 1996). Since the activation energy of the lipid oxidation is lower than other food reactions such as nonenzymatic browning reactions, lipid oxidation can progress very rapidly at moderate temperatures. Moreover, water activity is among the major factor affecting the rate of lipid oxidation in foods and can progress even at very low water contents in fat-containing foods (Lopez *et al.*, 1997c). Below and above 0.3-0.5 water activity, rate of lipid oxidation is high (Troller, 1989). Evranuz (1993) stated that roasted peanuts peroxidized more rapidly at low ($1.4 \pm 0.02\%$) and high ($3.9 \pm 0.06\%$) moisture content compared to intermediate moisture content ($2.2 \pm 0.04\%$) due to protective action of water against lipid oxidation near or at monolayer moisture contents. (Monolayer moisture content of peanut is 2.1% and about 0.3 water activity). The rate decreased up to 0.4 water activity (about 3% moisture content) and increased with further increase in moisture content. Since crispness is lost above 3% moisture, moisture content of peanut should be kept near to monolayer value but not at minimum oxidation moisture content (Shewfelt & Young, 1977; Evranuz, 1993; Mate *et al.*, 1996). In contrast to roasted peanut, oxidation rate of roasted walnut increased more at moisture content above monolayer compared to moisture contents lower than monolayer value. This was attributed to enzymatic mechanism of lipid oxidation in walnuts (Mate *et al.*, 1996). Therefore, initial evaluation of moisture content prior to roasting were stated to be a prerequisite to determine temperature and time combinations for optimizing roasted peanut quality (Chiou & Tsai, 1989).

Free fatty acids (FFA) have undesirable flavor characteristics, and FFA above 0.5-0.7% indicates onset of rancidity (Radtke & Heiss, 1971; Harris *et al.*, 1972; Hadorn *et al.*, 1977; Keme *et al.*, 1983a; Lopez *et al.*, 1997c). FFA limit for the processed hazelnut kernels was set to be 1.0-1.3% in the Turkish standards (TS-1917, 1993). FFA values which is measure of hydrolytic rancidity, should be used in conjunction with diene-extinction, which is measure of auto-oxidative rancidity, because the long chain fatty acids have lower organoleptic influence than the short-chain fatty acids (C₆-C₁₂). The latter become noticeable on account of their soapy taste even at lower concentrations. n-Octanal is the most important constituent of the rancid off-flavor of the hazelnuts with a aroma threshold of 0.04 ppm (Bergner *et al.*, 1974; Prabhakar & Amla, 1978; Grosch *et al.*, 1983; Keme *et al.*, 1983a; Kinderlerer & Johnson, 1992).

Peroxide value was recommended as a measure of onset of rancidity in nuts (Fourie & Basson, 1989; Braddock *et al.*, 1995; Mate *et al.*, 1996). Peroxide value below 1.4 meq/kg correlated with good quality peanut, almond, macadamia nuts (Braddock *et al.*, 1995; Fourie & Basson, 1989). Rancid flavors were determined in the roasted hazelnut with peroxide values above 2 meq/kg (Richardson & Ebrahim, 1996). Walnut and milk powder also develop undesirable flavor at only 2 meq/kg peroxide value (Phabhakar & Amla, 1978). Peroxide value limit for the processed hazelnut kernels was set to be 7-8 meq/kg in Turkish Standard TS-1917 (1993). The limiting peroxide values for acceptable roasted peanuts or peanut oil is 20-30 meq/kg (St. Angelo *et al.*, 1977; Evranuz, 1993). Edible quality of roasted peanuts is lost at 42-47 meq/kg (Evranuz, 1993). But even lower peroxides values (8-10 meq/kg) was found to be a flavor quality end point of roasted peanuts (Braddock *et al.*, 1995). Among the rancid flavors, threshold of hexanal and nonanal in air is 10 ppm (Braddock *et al.*, 1995). Hexanal is associated with oxidation of linoleic acid and with intense green, grassy off-aroma while nonanal has a powerful floral note (Braddock *et al.*, 1995; Mate *et al.*, 1996).

Roasting initiates lipid oxidation and the formation of carbonyl compounds in peanuts (Bett & Bobylston, 1992), but roasting also renders oils of peanuts more stable against oxidation during storage due to anti-oxidative effect of Maillard reaction products (Chiou *et al.*, 1991b; Chiou, 1992; Mate *et al.*, 1996) through enediol-structure reductones, greatly slowing down the oxidation rate of fats by breaking down the radical chain by donation of a hydrogen (Nicoli *et al.*, 1997). The products have also metal chelating properties, can reduce hydroperoxides to nonradical products. The products can also act as oxygen scavengers so that they contribute to inhibit the formation of hydrogen peroxide (Nicoli *et al.*, 1997). Oxidative effect of roasting was related with destruction of natural antioxidants, breakdown of fatty acids and physical changes such as disruption of cellular compartmentalization (Gardner, 1979; Mate *et al.*, 1996; Perren *et al.*, 1996a).

Increasing temperature and exposure time increase the peroxide value and decreases acid value and iodine value of peanut oil. This decrease in iodine value may be due to either peroxidation of unsaturated bonds, saturation or isomerization of unsaturated fatty acids. Peroxides are not heat stable, and decomposes to carbonyl and hydroxyl acids. The roasting also changes refractive index and flow time of peanut oil which shows presence of polymeric material (Mostafa, 1987). Elevated drying temperature lead to formation of carbonyl compounds from the autoxidation of the unsaturated fatty acids (Chiou *et al.*, 1991b). Roasting time-temperature combination, temperature of hazelnut at the exit of roaster and exposure time to air prior packaging and storage influence significantly shelf life of hazelnuts. Roasting temperature should not exceed 150°C and temperature of the hazelnut at the exit of the roaster should be around 20°C (Perren & Escher, 1996a,b,c; Perren *et al.*, 1996a).

Although effect of roasting conditions on the stability of hazelnuts were studied previously (Hadorn et al., 1977, Perren & Escher, 1996a,b,c; Perren et al., 1996a,b; Richardson & Ebrahim, 1996; Köksal & Okay, 1996), studies about nut roasting should include these parameters to assess effect of experimental conditions of the study on the quality of the nuts.

1.4.6 Textural changes during roasting of nuts

Texture can be defined as the sensory manifestation of the structure or inner makeup of the products in terms of their mechanical and geometrical characteristics. Mechanical characteristics are manifested by the reaction of the food to stress. These are measured organoleptically by pressures exerted on the teeth, tongue, and roof of the mouth during eating and by the kinesthesia sense in the muscles of the hand, fingers, jaw or lips. Hardness/firmness, cohesiveness, brittleness, chewiness, adhesiveness, gumminess, elasticity, springiness/resilience, viscosity and adhesiveness are mechanical characteristics. Geometrical characteristics refer to the arrangement of the constituents of the food and are reflected mainly in the appearance of the food product and measured as by the tactile nerves in the surface of the skin of the hand, lips, or tongue. Examples of geometrical characteristics are smoothness, chalky/powdery, fibrous, grainy, gritty, crystalline, flaky, lumpy/bumpy besides moisture properties (wetness, oiliness, moistness, dryness) (Szczesniak, 1963; Meilgaard *et al.*, 1999).

Food texture is ultimately assessed by the consumer through sensory understanding. The main stimuli originate in the oral cavity as a result of nerve impulses from biting and crushing the food with the teeth and the action of tongue and palate besides tactile and auditory organs. These responses are processed in the brain and provide an integrated concept that is termed texture. It is common to use human subjects so as to measure food texture for sensory evaluations. Instrumental methods of texture analysis have also become popular due to reproducibility (Aguilera & Stanley, 1990).

Crispness and crunchiness are widely used in hazelnut as texture attributes (Saklar, 1999). Crispness appears to be the most versatile and universally liked single texture while crunchiness, indicator of pleasure and fun, is linked with well-liked foods and is closely related to crispness (Szczesniak & Kahn, 1971; Vickers, 1981). Crispness and crunchiness is related to essentially non-deformable, easily and abruptly breakable materials which release energy and leads to characteristic sound effects during breaking (Szczesniak, 1990). Potato chips may be example of a crispy product and ice may be example of a crunch product while celery may be example of a “snap” product. A snap product emits a “crunchy” sound and is also crispy. A snap product is characterized by a very sudden, clean and total fracture which has a bearing on the quality and the short duration of the sound (Szczesniak, 1988). Hung and Chinnan (1989) studied the crispy and crunchy quality of roasted peanuts and found that fracture point and the work inversely correlated with the sensory crispness and crunchiness, respectively. Vickers and Bourne (1976) stated that crispy and crunchy texture of roasted hazelnuts make them delicious, energetic and full of pleasure for substantial eating. Saklar (1999) studied crispy, crunchy and mechanical texture properties of roasted hazelnuts and stated that crispness and crunchiness are correlated with mechanical texture properties. A positive correlation between crispness and crunchiness of roasted hazelnuts was also demonstrated.

1.4.7 Sensory evaluation and consumer acceptance test

Sensory evaluation is used to evoke (guidelines for the preparation and serving of samples under controlled conditions so that biasing factors are minimized), measure (numerical data are collected to establish lawful and specific relationship between product characteristics and human perception), analyze (use of statistical methods, including experimental design to analyze data) and interpret reactions to those characteristics of foods and materials as they are perceived by the senses of sight, smell, touch and hearing (IFT, Sensory Evaluation Division, 1981).

Sensory tests are divided into two: analytical and affective. Analytical tests are used for laboratory evaluation of products in terms of differences or similarities and for identification and quantification of sensory characteristics. Affective tests are used to evaluate preference and/or acceptance of products.

Among analytical tests, descriptive analyses are used to specify the sensory attributes of a single product or a comparison among several products, using statistical analysis to determine the appropriate terms, procedures and panelists. It is useful for flavor profile, texture profile and quantitative descriptive analysis. Saklar (1999) performed a descriptive analysis for roasted hazelnuts using response surface methodology. Acceptable sensory characteristics for a 9 scale hedonic scale were found to be 5.52-11.41 for roasted hazelnut flavor, 0.87-4.52 for burnt flavor, 2.44 for painty flavor, 5.22-9.78 for crispness and 6.78-10.24 for crunchiness (Saklar, 1999; Saklar *et al.*, 2001). Acceptable physical characteristics for roasted hazelnuts were found to be 57.71-75.26 for L-value, 0.91-6.60 for a-value, 18.42-21.18 for b-value of color (measured by UV visible spectrophotometer, Shimadzu, UV2100); 0.93-19.60 for ΔE value; 0.26-1.81 for moisture content (%), 20.56-34.30 for first fracture point (measured by Loyd Compression apparatus) (Saklar *et al.*, 2001).

Affective tests are used to assess the personal response preference and/or acceptance by current or potential customers of a product idea, or specific product characteristics. Among affective tests, consumer acceptance tests are performed to maintain product, or to improve/optimize product, to develop new products or to assess a market potential. Consumer tests are carried out with random selected, untrained minimum 24 panelist who are representative of target population and consumers of test product. 50-100 panelists are considered adequate (Meilgaard *et al.*, 1991; Saklar, 1999). Saklar (1999) also performed a consumer acceptance test for the roasted hazelnuts to find out acceptable samples over the experimental conditions. Saklar *et al.*, (2001) stated that physical characteristics such as L-, a- and b-value of color, moisture and first fracture

point can be used to determine optimum process conditions. Because physical and sensory data resulted in approximately the same optimum process conditions and physical characteristics is easier and more practical than the sensory characteristics. Nevertheless a consumer test was also performed to as to find out preference of consumers among the samples of the experimental study.



2 MATERIALS AND METHODS

2.1 Hazelnuts

Freshly harvested and sun dried hazelnuts (season 1998) were supplied from Hazelnut Research Center (Giresun, Turkiye) and stored in-shell at 4°C in vacuum plastic bags until used (at most two months). The major Turkish hazelnut variety, Tombul, was used in the study. The samples were temperature equilibrated overnight and cracked using a laboratory scale modified grain mill to crack shells. After calibrating the samples, 11-13 mm of hazelnut samples were used in the experiments. Proximate composition of the raw hazelnut, determined using standard analytical methods (AOAC, 1990; AOCS, 1990), was 5.0% moisture, 15.4% protein, 4.5% sugar, 2.4% ash and 65.4% oil.

2.1.1 Roasting system

The forced air pilot scale dryer-roaster (73 cm x 205 cm x 161 cm) (APV, Pasilac, England) was used during experiments. The apparatus consisted of a heater, a centrifugal fan for generating an air stream, and a drying chamber (Figure 2.1.). The each nut sample was held in a rectangular (10 cm x 15 cm) wire mesh tray on the support (60 cm x 60 cm). Each tray could hold approximately 100 g of kernels. The size of the perforations (6 mm diameter) and the open area (>50%) were sufficiently large to reduce pressure drop due to perforations. Appropriate sliding gates of the dryer were opened so that air movement was downwards and uniformly distributed in the drying chamber using baffles.

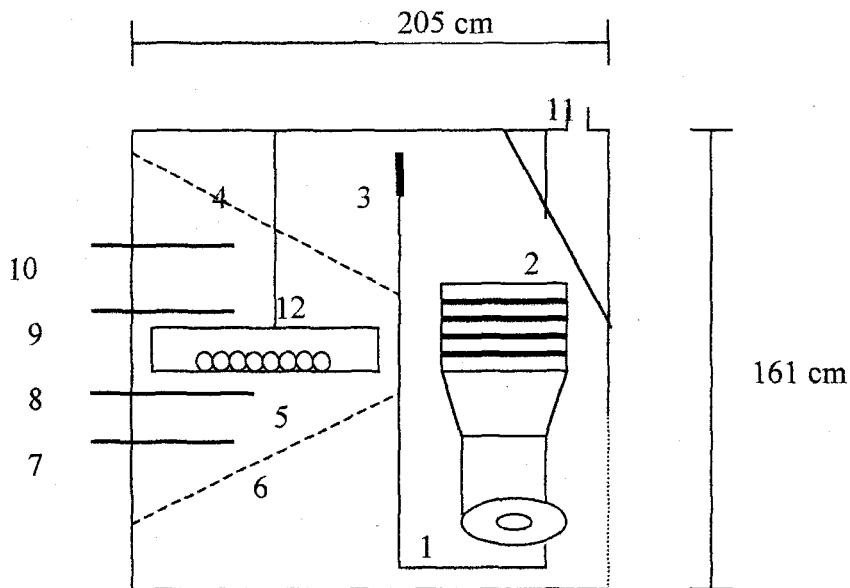


Figure 2.1. Schematics of pilot plant roaster in vertical axis and its instrumentation (1- Air intake; 2,3-Baffle; 4,6-Perforated plate; 5-Sample tray; 7,10-Pressure drop; 8,9-Temperature sensors; 11- Air exhaust; 12-Velocity measurement)

2.2 Mathematical Modeling of Drying and Color Formation During Hazelnut Roasting

2.2.1 Experimental conditions

Hazelnuts were roasted using a forced air pilot scale roaster (Pasilac, APV, England) at roasting air temperatures of 100°C 120°C, 140°C and 160°C which represents the range, commonly used in the hazelnut industry.

In general, the drying process of a food may be divided into a constant-rate period and one or more falling rate periods (Husain *et al.*, 1972). Almost all of the drying of grain and nut products occurs in the falling rate periods (Parry, 1985; Moss & Otten, 1989; Palipane & Driscoll, 1994; Shivhare *et al.*, 1994) during which drying rate is mainly controlled by internal diffusion of moisture and effect of air velocity on drying rate is insignificant above a critical air velocity value (Treybal, 1984; Palipane & Driscoll, 1994; Madamba *et al.*, 1996; Li & Morey, 1984). Furthermore, Henderson & Pabis

(1962) showed that resistance to moisture movement at the surface of grains is negligible compared to internal resistance. Moreover, colloidal and hydrophilic nature of food products was stated to cause the water molecules to be tightly held by the material (Mazza & Le Maguer, 1980). Critical air velocity, below which drying rate is affected, was stated to be 0.102 m/s for grains (Henderson & Pabis, 1962) and 0.14 m/s for soybean and white beans (Hutchinson & Otten, 1983). Hence, air velocity was kept constant at 0.8 m/s throughout experiments not to affect drying rate by air velocity. Air velocity was measured (Testo, Model 400, England) at the outlet of the drying chamber. Moreover, equilibrium moisture content was assumed to be zero (Moss & Otten, 1989) since roasting temperatures (100-160°C) were higher or very close to the temperatures used in moisture content determination in which samples are dried at 103°C (Keme & Messerli, 1976b; TS-3074, 1978).

2.2.2 Experimental procedure

Prior to placing the sample in the roasting chamber, roaster (APV, Pasilac, England) was run for at least 2 hr to obtain steady state conditions. The kernels as single layer were placed in the roasting chamber in 12 small drying trays. Then, every 5 min for a period of 1 hr, one tray was removed from the roasting chamber in less than 10 s. So that steady state conditions were maintained during sampling. The trays were cooled to room temperature in a desiccators. Then moisture content and color measurements were carried out as described below.

2.2.3 Color measurements

Roasted samples were stored in plastic bags at 4°C until the color measurements. All color measurements were conducted within 10 days of roasting experiments. The measurements were performed after manual blanching the samples to remove skins. The poor quality hazelnuts were also removed. The color of the roasted samples was measured using Minolta Chroma Meter II Reflectance system (Model CR 300). The

instrument is a tristimulus colorimeter which measures four specific wavelengths in the visible range, specified by the CIE (Commission Internationale de l'Esclairage). Tristimulus values give a three dimensional value for color in which equal distances approximate equal perceived color differences. The L -, a -, and b -values are the three dimensions of the measured color which gives specific color value of the material. L -value represents light-dark spectrum with a range of 0 (black) to 100 (white). a -value represents green-red spectrum with a range of -60 (green) to +60 (red). b -value represents blue-yellow spectrum with a range of -60 (blue) to +60 (yellow) (Moss & Otten, 1989; Driscoll & Madamba, 1994). These values are dependent on measurement factors such as the type and size of the material, angle of the measurements and stability of the reference standards (Driscoll & Madamba, 1994).

Outside color of the 20 randomly selected hazelnut kernels were measured for every sample. Moreover, the measurements were conducted after milling each sample to constant grind size at 5 different parts of the resulting sample. The former measurement method was referred as whole-kernel measurements and the latter method was referred as ground-state measurements throughout the thesis.

2.2.4 The statistical procedure for mathematical modeling of drying during hazelnut roasting

Analysis of variance (ANOVA) was performed to find out effect of temperature on the drying of hazelnuts during roasting. Henderson & Pabis, Two-term, Lewis, Page model, the modified Page, Wang & Singh and Thompson model were fitted to the experimental drying data. Correlation coefficient and the mean square error (MSE) were used as criteria for adequacy of fit. The average of the relative percent difference between the experimental and predicted values or the mean relative deviation modulus (P) defined by the equation (E 15) was used as a qualitative measure of the equation adequacy (Lomauro *et al.*, 1985; Madamba *et al.*, 1996; Palipane & Driscoll, 1994).

$$P = \frac{100}{n} \sum \frac{|(M_i - M_{pri})|}{M_i} \quad (E 15)$$

where M_i is the moisture content at observation; M_{pri} is the predicted moisture content at observation; and n is the number of observations.

Initial selection of thin layer drying models was done using regression procedure. The drying coefficients or constants of the selected models were then related to the temperature to obtain functional relationships, using one-step regression technique.

The best model describing the thin-layer drying characteristics of hazelnut kernels during roasting was chosen as the one with the highest correlation coefficient and the least error sum of squares and the least mean relative deviation modulus (Lomauro *et al.*, 1985; Madamba *et al.*, 1996; Palipane & Driscoll, 1994).

2.2.5 The statistical procedure for mathematical modeling of color formation during hazelnut roasting

Analysis of variance (ANOVA) was performed to find out effect of temperature on the color of roasted hazelnuts. Zero order, first order, quadratic equation and third equation were evaluated to describe the experimental data.

Correlation coefficient, the mean square error (MSE), and percent standard deviation, defined by the equation (E 16), were used as criteria for adequacy of fit (Lomauro *et al.*, 1985; Rapusas & Driscoll, 1995; Madamba *et al.*, 1996).

$$\sigma = \frac{100}{C_{ave} \sqrt{n}} \sqrt{\sum_{i=1}^n (C_i - C_{pri})^2} \quad (E 16)$$

where C_i is color dimension at observation; C_{pri} is the predicted color dimension content at observation; and n is the number of observations. Initial selection of mathematical

models was done using regression procedure. The model coefficients or constants of the selected equations were then related to the temperature to obtain functional relationships, using one-step regression technique. The best model describing color formation kinetics of hazelnut kernels during roasting was chosen as the one with the highest correlation coefficient and the least error sum of squares and the least percent standard error (Lomauro *et al.*, 1985; Palipane & Driscoll, 1994; Madamba *et al.*, 1996).

2.3 Experimental procedure for Color Formation Kinetics Using Response Surface Methodology

The independent variables (factors) of this study was time and temperature of the roasting process. They are coded as X_1 and X_2 , respectively. For responses of color a second degree polynomial was employed. Coded and uncoded values of the experimental design was given Table 2.1. The data was analyzed for analysis of variance and regression coefficient calculation, using statistical analysis software package SPSS.

2.4 Analysis of Chemical Changes During Hazelnut Roasting and Storage at 37°C

Effect of roasting conditions on the moisture, protein, total sugar, non-reducing sugar content, peroxide value (PV) and free fatty acids (FFA) were investigated at 9 different roasting conditions, determined by central composite design of RSM.

Stability of roasted hazelnuts was also studied by storing hazelnuts at 37°C for one month (Harris *et al.*, 1972; Labuza *et al.*, 1972; Fourie & Basson, 1989; Budin & Breene, 1993; Perren & Escher, 1996c). PV, FFA and fatty acid composition was determined.

2.4.1 Moisture content

Moisture content was determined according to TS-3074 (1978) at 103 ± 2 °C for 4 hr.

Table 2.1. The coded and uncoded the two factors for a central composite design for two factors: Temperature (X_1) and time (X_2)

No	Block	Code		Uncoded	
		X_1	X_2	X_1	X_2
1	1	-1.0	-1.0	110	20
2	1	1.0	-1.0	150	20
3	1	-1.0	1.0	110	40
4	1	1.0	1.0	150	40
5	1	0.0	0.0	130	30
6	1	0.0	0.0	130	30
7	2	-1.41	0.0	102	30
8	2	1.41	0.0	158	30
9	2	0.0	-1.41	130	16
10	2	0.0	1.41	130	44
11	2	0.0	0.0	130	30
12	2	0.0	0.0	130	30

2.4.2 Oil extraction

The samples were wrapped in a cheese cloth and oils were cold extracted using hydraulic press, operated at 280-300 kg/cm² (Lopez *et al.*, 1997c; Prabhakar & Amla, 1978; Chiou, 1992). The extracted oils were kept at -30°C until analyzed.

2.4.3 Fat content

Fat content was determined using Soxhlet extraction as described in AOCS (1990).

2.4.4 Peroxide value (PV)

Standard method of AOCS Cd 8-53 (1990) were used for the determination of PV. Sample was dissolved in 30 ml acetic acid-chloroform solution (3/2 v/v) and 0.5 ml of KI solution was added. After 1min, 30 ml H₂O was added and the mixture was titrated with 0.01 N sodiumthiosulfate until yellow color was lost. Then 5 ml of starch indicator was added and the solution was titrated again with 0.01 N sodiumthiosulfate until blue color

disappeared. Finally peroxide value was calculated using the formula given below.

$$\text{Peroxide value (PV, meq/kg)} = ((V-B) * N_f / w) * 1000$$

Where V: Volume of the sodiumthiosulfate consumed

B: Volume of the sodiumthiosulfate consumed during blank titration

w: Weight of oil sample, g

N_f : Normality of sodiumthiosulfate * Factor

2.4.5 Free fatty acid (FFA)

Standard method of AOCS Ab 5-49 (1990) were used for the determination of FFA. Sample was dissolved in 50 ml of alcohol and 2 ml of phenolphthalein was added. The solution was titrated with 0.1 N NaOH until pink color persisted. The amount of free fatty acid was calculated as % of oleic acid using formula given below.

$$\text{FFA (\% of oleic acid)} = ((V-B) * N_f * 28.2) / w$$

Where V: Volume of the NaOH consumed

B: Volume of the NaOH consumed during blank titration

w: weight of oil sample, g

N_f : Normality of NaOH * Factor

2.4.6 Fatty acid composition

The fatty acid methyl esters of total lipids were obtained by direct transesterification according to a standard method of AOCS (1990). 0.1-0.2 g oil from the sample were mixed with 5 ml 0.5 N methanolic NaOH and boiled until the droplets of the fat disappears (about

for 10 min) using a condenser in order to allow saponification. Then, 5 ml of BF_3 were added to the flask from the pulp or automatic pipette through the top of the condenser, and boiled for 1 min. Next, 5 ml of the heptane was added from the top of the condenser and boiled for 1 min. Then, the flask was removed from the condenser and left for cooling. Then, the solution was transferred into the 25 ml flask, and saturated NaCl solution was added to the flask and shaken gently. Saturated NaCl solution was added until the solution in the flask was 25 ml. 1 ml of solution from upper layer was transferred into a bottle after phase separation. The bottle was placed into deep freezer until the analysis. Fatty acids methyl esters were analyzed using gas chromatography (Perkin Elmer, Model Autosystem, USA) with a flame ionization detector. The carrier gas was helium at a flow rate of 1-1.5 ml/min. A capillary column, Carbowax 20M (25 m x 0.22mm i.d.) was used for the fatty acid analyses. Injector, detector and column temperatures were 220°C, 240°C and 180°C, respectively. Injection quantity was 1 μl . Fatty acids were identified by comparison with retention times of known standards.

2.4.7 Protein content

Protein analyzer (Keltex Auto 1030) was used for protein analysis. The analysis was carried out according to method of AOAC (1990). 1 g of sample was burnt at 420°C for 45 min after addition of a catalyzer (3.5 g K_2SO_4 and 0.0038 g Se), 12 ml of 95% H_2SO_4 and 5 ml of H_2O_2 . After that, the sample was cooled to room temperature and 75 ml of distilled water was added. Then the sample was put into protein analyzer. Amount of 0.1 M HCl consumed was read from the analyzer. The protein content was calculated using the formula given below.

$$\text{Protein (\%, db)} = (1.401 \times V \times 5.3) / w \times (100 / (100 - \text{MC}_i))$$

Where V: Volume of the 0.1 M HCl consumed

w : weight of the sample

2.4.8 Total amino acid composition

Each sample was hydrolyzed at 110°C for 24 hr in 6 N HCl. Then liquid part of the sample solutions was evaporated in rotavapor at 65°C. The residual was washed with 20 ml buffer solution at 2.2 pH and stored in refrigerator. After temperature equilibrium in room conditions, samples were injected into the analyzer. Separation of acidic, neutral and basic amino acids were carried out with buffer solutions at 3.0, 3.5, 3.85, 4.30, 5.50, and 10.50 pH with Eppendorf amino acid analyzer (Model LC 3000, Germany).

2.4.9 Total sugar, reducing and non-reducing sugar content

Total sugar and non-reducing sugar content were determined according method of Lane-Eynon (AOAC, 1990). 150 ml distilled water was added into 250 ml container, containing 25 gr of sample (W) and mixed. Then, 10 ml of Carez I and II were added and mixed. Next, distilled water was added until 250 ml of the solution was obtained. After 10 min, the solution was filtered. Supernatant obtained was used for the analysis of reducing sugar as titration solution. For the analysis of total sugar, the supernatant was further modified as the following: 50 ml of the supernatant and 5 ml of 37% HCL were boiled at 67-70°C for 5 min and cooled. Next, pH of the solution was brought to 8.1-8.3 with 5N NaOH and distilled water was added until volume of the solution was 100 ml.

For the titration, 5 ml of Fehling A and B, and 50 ml of distilled water were poured into another 250 ml of container which was, then, kept on the flame. At the beginning of boiling, 1 ml of methylene blue was added and titrated with the titration solutions indicated above depending on the analysis until a red color was observed.

Reducing sugar content (R, g/100g, db), total sugar content (T, g/100g, db) and non-reducing sugar content (NR, g/100g, db) was, then, calculated as:

$$R = (F/[V_R * (W*100/ 250)]) (100/(100-MC_i))$$

$$T = (F/[V_T * (W*50/ 250)]) (100/(100-MC_i))$$

$$NR = (T-R) * 0.95$$

Where F is factor of Fehling solutions, V_R is consumed titration solution of reducing sugar, V_T is consumed titration solution of total sugar, and MC_i is moisture content of the sample.

2.5 Consumer Acceptance Test

The panellists were employees of the TÜBİTAK-Marmara Research Centre. Most of the panellist had no previous experience in sensory evaluation. 84 panellist, 36 female and 48 male, aged among 20-59 years participated in the consumer evaluation test. Education level varied from secondary school to university. Samples used in this part of the study were prepared with hazelnuts from harvest season of 2000.

A balanced incomplete block design (see Table A.9.), as described by Cochran and Cox (1957), was used in the test because panellists would find it increasingly difficult to evaluate a product as the number of the samples increased. As described in the design, each consumer evaluated three samples out of 9 (excluding replicates at the centre points). Each of 9 samples was evaluated 28 times.

The samples were presented to the panellists in closed glass jars, coded with three-digit numbers. The panellists were provided with odourless water between tests. Consumers were typically asked to give judgements on how much like or dislike color, flavor, texture and overall of the samples. A 9-point hedonic scale (Figure A.1) was used. Mean values for each attribute of each sample were obtained. Samples having the scores of 6.05 and above were evaluated as acceptable (Saklar, 1999; Meilgaard *et al.*, 1999). Scores given by the consumer for each attribute of each sample were also summed so as to find out total score of each attribute of each sample. Scores above 168 (2/3 of the maximum score, 252) was evaluated as acceptable.

3 RESULTS AND DISCUSSION

3.1 Mathematical Modeling of Drying During Roasting of Hazelnuts

Temperature significantly effected drying during roasting of hazelnuts as shown in Figure 3.1. As the roasting temperature increased a higher faster drying occurred in a given time. A. During first 25 min of roasting, 44.1%, 50.6%, 73.4%, 90.1% of the moisture were removed at roasting air temperatures of 100°C, 120°C, 140°C, 160°C, respectively (Figure 3.2.). Similar high initial drying rates were reported by Madamba *et al.*, (1996) during garlic drying and by Palipane & Driscoll, (1994) during macadamia drying. Moreover, many researchers reported drying air temperature to be the single and the most important factor affecting drying rate. They pointed out that use of higher drying air temperature increases drying rate significantly. These included Puiggali *et al.*, (1987) and Demirtaş *et al.*, (1998) for hazelnuts, Crisp & Woods (1994) for rapeseed, Karataş & Battalbey (1991) for pistachio kernel, Mazza & Le Maquer (1980) for onions, Sharaf-Eldeen *et al.*, (1980) for ear corn, Suarez *et al.*, (1980b) for grain sorghum, Hutchinson & Otten, (1983) and Suarez *et al.*, (1980a) for soybean, Hutchinson & Otten, (1983) for white beans, Chinnan (1984) for in-shell pecans, Syarief *et al.*, (1984) for sunflower seeds, Verma *et al.*, (1985), Sharma *et al.*, (1982), Ece & Cihan (1993) for rough rice, Lebert & Bimbenet (1991) for plum drying.

As expected drying process during roasting of hazelnuts took place in the falling rate period (Figure 3.3.) as initial moisture content (around 6% db) was already very low at the beginning of roasting. Almost all the drying of grains and nuts products occur in the

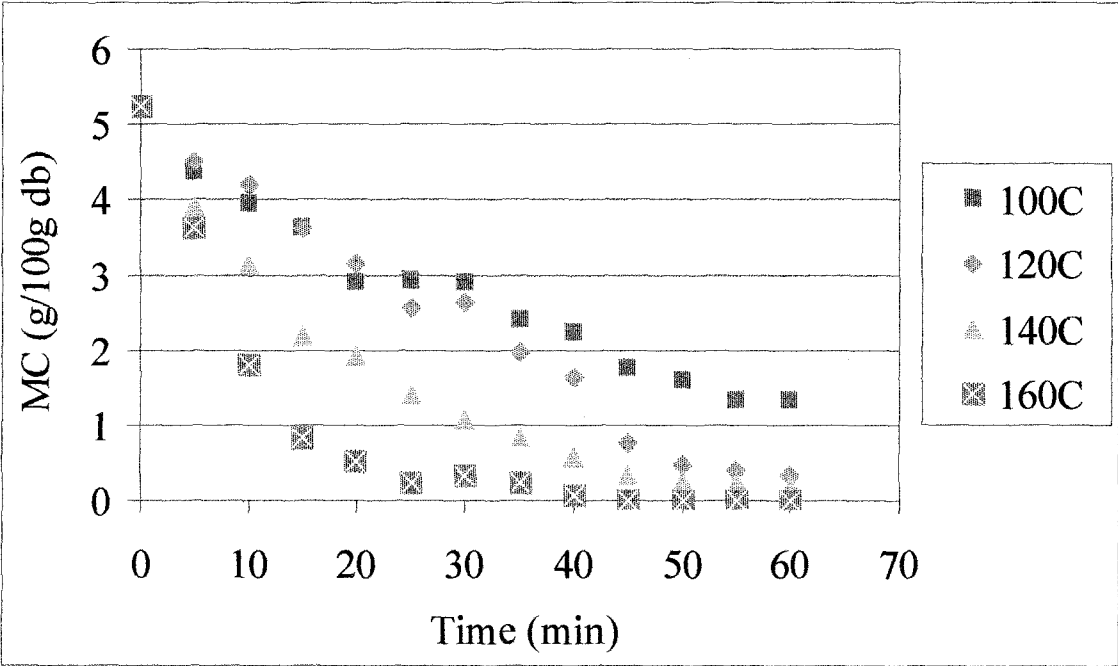


Figure 3.1. Effect of temperature on the moisture content of the hazelnuts during roasting

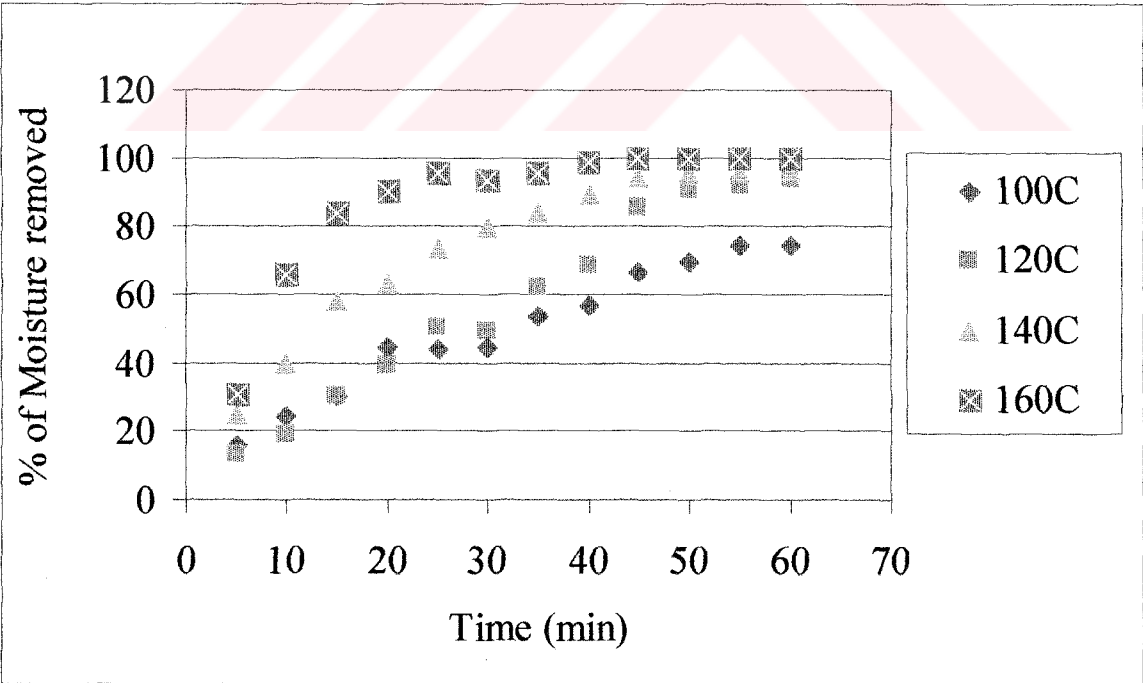


Figure 3.2. Percentage of moisture removed during roasting of hazelnuts

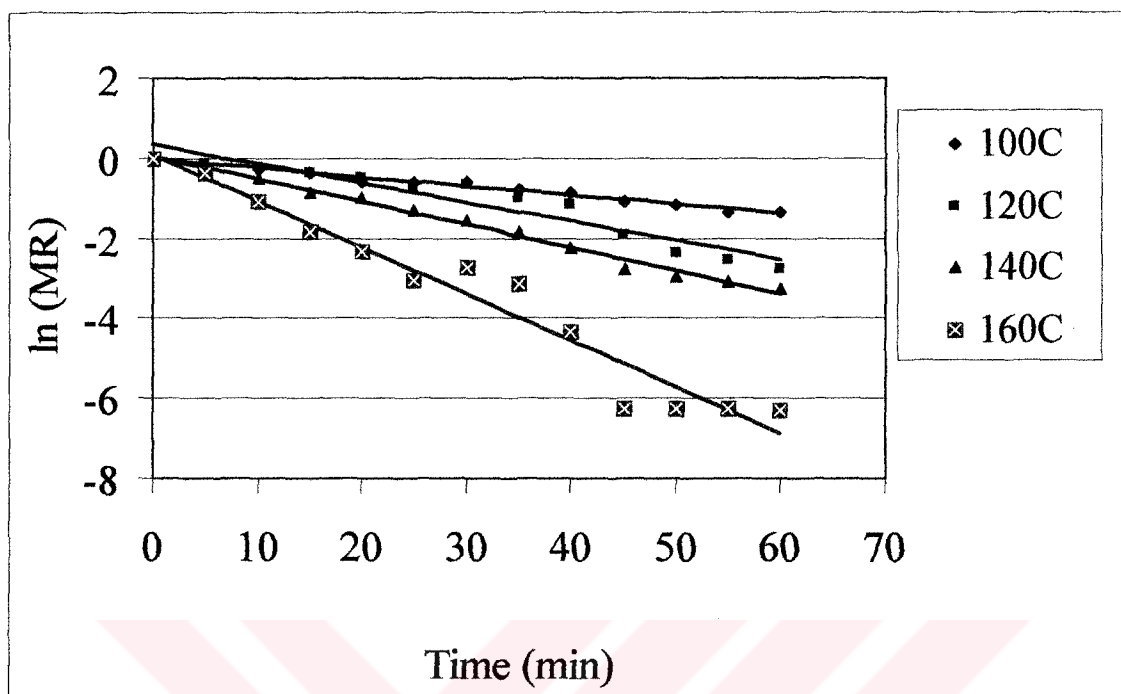


Figure 3.3. Experimental and predicted $\ln(MR)$ vs. time

falling rate periods during drying/roasting (Husain *et al.*, 1972; Suarez *et al.*, 1980a,b; Chinnan, 1984; Syarief *et al.*, 1984; Parry, 1985; Moss & Otten, 1989; Karataş & Battalbey, 1991; Lebert & Bimbenet, 1991; Pathak *et al.*, 1991; Crisp & Woods, 1994; Palipane & Driscoll, 1994; Shivhare *et al.*, 1994; Demirtaş *et al.*, 1998).

At such high roasting temperatures, nonenzymatic browning reaction is favored which occurs between carbonyl group of a reducing sugar with free, uncharged amine group of amino acid or protein with the loss of one mole of water. The reaction was related to formation of color and aroma (Ames, 1988; Troller, 1989; Labuza & Braisier, 1992; Jinap *et al.*, 1998). Since aroma compounds are volatiles and lost during roasting, some of the dry matter loss can be attributed to non-enzymatic browning reaction, especially at higher roasting air temperatures. Further research, however, is necessary to find out effect of non-enzymatic browning reaction on dry matter loss during roasting

3.1.1 Calculation of effective diffusivity and activation energy

Since the drying during roasting of hazelnuts occurs in the falling rate period only and liquid diffusion controls the process, Fick's second law can be used to describe drying process during roasting hazelnuts. General series solution of Fick's second law in spherical coordinates is given below (E 17) in which constant diffusivity and spherical hazelnut with a diameter of 0.01 m was assumed:

$$\frac{\bar{M} - M_e}{M_o - M_e} = \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left(-\frac{n^2 D \pi^2}{R^2} t\right) \quad (\text{E } 17)$$

where D is the effective diffusivity (m²/s) and R is the radius of the hazelnut. A first term of the series solution of equation (E 17) is generally known as The Henderson & Pabis model (E 1) where k is related to the effective diffusivity:

$$k = \frac{D\pi^2}{R^2} \quad (\text{E } 18)$$

The Henderson & Pabis model obtained r^2 greater than 0.92 in experimental moisture ratio prediction (Table 3.1.). Similar findings were reported by Moss & Otten (1989) for peanut roasting, by Watson & Bhargava (1974) for wheat drying and by Suarez *et al.*, (1980b) for grain sorghum drying. Average of intercept value, constant "a", of The Henderson & Pabis model was 1.131 over the experimental conditions used in this study. But theoretical intercept value, estimated with first term of equation (E 17), has a value of $\ln(6/\pi^2)$ and is equal to -0.498. This deviation can be attributed to the short roasting time employed in the study since Henderson & Pabis model is generally recommended for long drying times (Madamba *et al.*, 1996).

Effective diffusivity was calculated by equation (E 18), using slopes derived from the linear regression of $\ln(MR)$ vs. time data shown in Figure 3.3. Generally, an effective diffusivity is used due to limited information on the mechanism of moisture movement

during drying and complexity of the process (Madamba *et al.*, 1996). The effective diffusivity (D_{eff}) during roasting of hazelnuts varied from 2.301×10^{-7} to $11.759 \times 10^{-7} \text{ m}^2/\text{s}$ over the temperature range 100-160°C. These values higher than the reported diffusivity for food materials during drying which is 10^{-9} and $10^{-11} \text{ m}^2/\text{s}$ (Madamba *et al.*, 1996). The higher diffusivity can be attributed to the higher temperatures employed in the study. Rizvi (1986) stated that effective diffusivity depend on drying air temperature besides variety and composition of the material. Isosteric heat of sorption which is a measure of moisture mobility within the food is another factor that affects effective diffusivity (Madamba *et al.*, 1996).

Effect of temperature on effective diffusivity is generally described using Arrhenius-type relationship (E 19) to obtain better agreement of the predicted curve with experimental data (Henderson, 1974; Mazza & Le Maguer, 1980; Suarez *et al.*, 1980a; Steffe & Singh, 1982; Pinaga *et al.*, 1984; Carbonell *et al.*, 1986; Crisp & Woods, 1994; Gürtaş, 1994; Madamba *et al.*, 1996). Crisp & Woods (1994) reasoned that temperature is not function of radial position in the grain under normally experienced drying conditions, and diffusivity varies more with temperature than moisture content.

$$D_{\text{eff}} = D_o \exp\left(-\frac{E_a}{RT_a}\right) \quad (\text{E } 19)$$

where D_o is a diffusivity constant equivalent to the diffusivity at infinitely high temperature and E_a is the activation energy (kJ/kg). A plot of $\ln D$ vs. reciprocal of the absolute temperature (T_a) gives the energy of activation as a slope and constant D_o as the intercept (Figure 3.4.). Then, Arrhenius-type temperature dependence of effective diffusivity can be expressed as:

$$D_{eff} = 0.014 \exp\left(-\frac{4099.8}{T_a}\right) \quad (E 20)$$

from which the activation energy for water diffusion can be found to be 1891.6 kJ/kg. It is higher than activation energies of onion drying (1200 kJ/kg) (Mazza & Le Maquer, 1980), garlic slices drying (989 kJ/kg) (Madamba *et al.*, 1996), rice drying (1183 kJ/kg) (Paniga *et al.*, 1984), mushroom drying (1680 kJ/kg) (Gürtaş, 1994) and pistachio nut drying during the first falling rate period (1252.6 kJ/kg) (Karataş & Battalbey, 1991) but lower than activation energy of paprika drying (2036 kJ/kg) (Carbonell *et al.*, 1986) and pistachio nut drying during the second falling rate period (2412.5 kJ/kg) (Karataş & Battalbey, 1991).

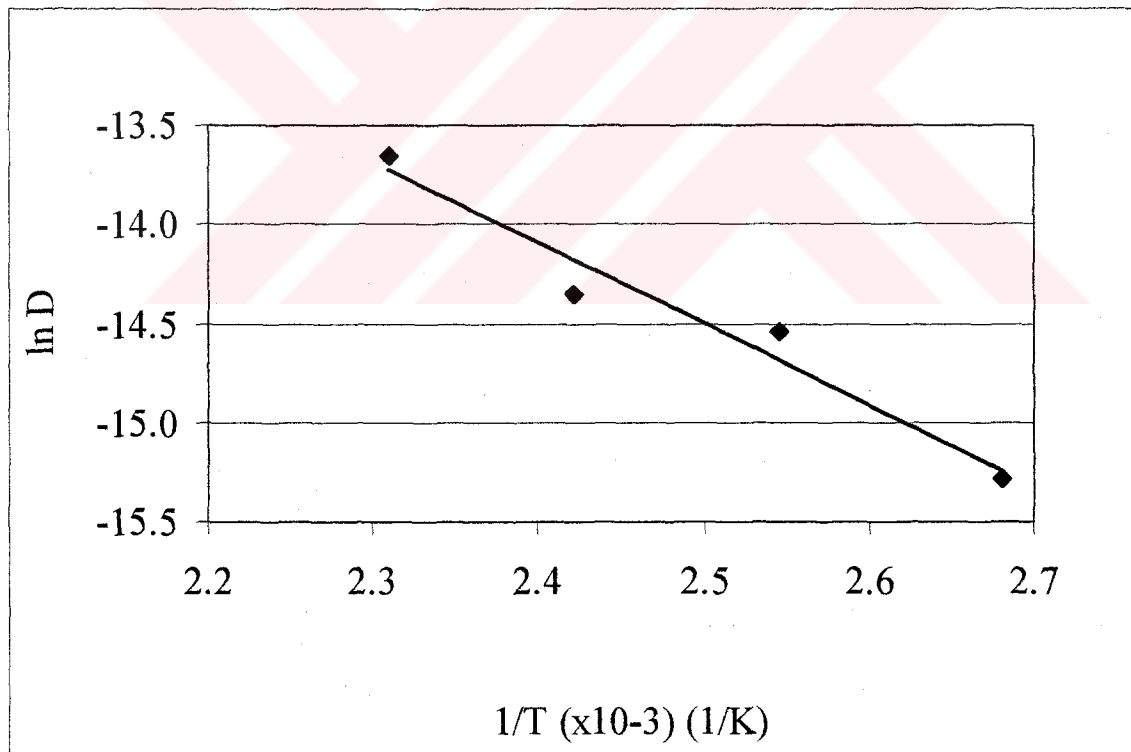


Figure 3.4. Arrhenius-type relationship between effective diffusivity and temperature

3.1.2 Modeling of the thin layer drying characteristics of hazelnut during roasting

Thin layer drying models, the Henderson & Pabis model, the two-term model, the Lewis model, the Page model, the modified Page model, the Wang & Singh model and the Thompson model were used to describe drying process during roasting of hazelnuts. The models were evaluated based on mean square error (MSE), correlation coefficient (r^2), and the mean relative deviation (P) modulus (Lomauro *et al.*, 1985; Madamba *et al.*, 1996; Palipane & Driscoll, 1994). These curve fitting criteria for the seven model was shown in Table 3.1. and Table 3.2.

The Henderson & Pabis, the two-term, the Page, the modified Page and the Thompson models obtained r^2 greater than acceptable r^2 value of 0.90 (Madamba *et al.*, 1996) at all roasting air temperatures. However, the Lewis model at 120°C roasting air temperature and the Wang & Singh model at 160°C roasting air temperature produced r^2 value lower than 0.9. Among the thin layer drying models, Two-term model obtained the highest r^2 values in the temperature range of the study. The Thompson model produced the highest MSE which was in the range of 7-17. The Wang & Singh model produced the lowest MSE. The percent mean relative deviation modulus (P), indicating deviation of the experimental data from the predicted line, were in the range of 4.95 and 59.82 in the semi-theoretical models except for the Page model. A higher variability between 11.75 and 217.24 was observed in terms of P for the Page model. Empirical models produced lower P values expect for the Wang & Singh model at 160°C. At that temperature, the Wang & Singh model predicted MR lower than zero which caused to increase P considerably after 30 min. The range of P for the Wang & Singh model and for the Thompson model was 4.82-1363.1 and 5.41-11.73, respectively. Semi-theoretical models were rejected in spite of their high r^2 due to their high P values. Because a P value lower than 10% is recommended for the selection of models and r^2 was stated not to be a good criteria for evaluating non-linear mathematical equations (Lomauro *et al.*, 1985; Chen & Morey, 1989; Madamba *et al.*, 1996). Moreover, the Wang & Singh

model were rejected due to its high P value at roasting air temperature of 160°C despite its low MSE and high r^2 at other temperatures. The Thompson model was selected due to its lower P value and comparable r^2 values to fit the experimental data on roasting of hazelnuts. The model coefficients were calculated using Levenberg-Marquard estimation method. The drying coefficients a and b were then related to the roasting air temperature to obtain functional relationships, using one-step regression procedure as recommended by Madamba *et al.*, (1996). Drying coefficients of the Thompson model were related to roasting air temperature using first degree polynomial:

$$a \text{ or } b = c_0 + c_1 T \quad (E 21)$$

where c_0 and c_1 are model coefficients. The linear temperature dependence of drying constants was also used by Madamba *et al.* (1996) for garlic drying, Hutchinson & Otten (1983) and Overhults *et al.*, (1973) for soybean drying, Syarief *et al.*, (1984) for sunflower seed drying (Bruce, 1985) for barley drying.

The results of the one-step regression procedure together with curve fitting criteria of r^2 , MSE and P-value were shown in Table 3.4. The Thompson model described thin layer roasting of hazelnuts with drying constant as a linear function of temperature with acceptable MSE and P-value, and high r^2 . The model with its coefficients is:

$$t = (-116.05 + 0.656 T) \ln MR + (-19.89 + 0.122 T) (\ln MR)^2 \quad (E 22)$$

Figure 3.5. shows drying curve predicted by the Thompson model for the experimental data of thin layer roasting of hazelnuts for the temperature range of 100-160°C. Figure 3.6. shows comparison of actual and predicted values for the model (E 22). The experimental data generally banded around 45°C straight line which shows the suitability of the model (E 22) in describing behavior of hazelnuts during roasting.

Table 3.1. Curve fitting criteria for semi-theoretical thin layer drying models for the roasting of hazelnuts

Models	T (°C)	r ²	MSE ^a	P (%) ^b
The Henderson&Pabis MR = a exp(-kt)	100	0.98	0.0045	4.95
	120	0.92	0.0849	23.34
	140	0.99	0.0130	8.62
	160	0.95	0.2922	41.39
The Lewis MR = exp(-kt)	100	0.979	0.0043	5.00
	120	0.882	0.1112	27.15
	140	0.990	0.0127	8.27
	160	0.950	0.2708	40.66
The Page MR = exp(-kt ⁿ)	100	0.973	0.0125	33.67
	120	0.949	0.0537	186.19
	140	0.993	0.0044	11.75
	160	0.969	0.0252	217.24
The modified Page MR = exp(-(kt) ⁿ)	100	0.973	0.0125	6.57
	120	0.949	0.0537	24.06
	140	0.993	0.0044	8.47
	160	0.969	0.0252	44.44
The two-term MR = a exp(-k ₁ t) + b exp(-k ₂ t)	100	0.99	4.978	0.0122
	120	0.974	40.18	0.0631
	140	0.999	10.13	0.0032
	160	0.995	59.821	0.0129

^a Mean square error

^b Mean relative deviation modulus (P)

Table 3.2. Curve fitting criteria for empirical thin layer drying models for the roasting of hazelnuts

Models	T (°C)	r ²	MSE ^a	P (%) ^b
The Wang & Singh MR = 1 + at + bt ²	100	0.975	0.0015	4.8
	120	0.986	0.0015	15.3
	140	0.982	0.0018	19.9
	160	0.879	0.0129	1363.1
The Thompson T = a (lnMR) + b (lnMR) ²	100	0.983	7.07	9.6
	120	0.972	11.62	8.7
	140	0.987	5.26	5.4
	160	0.959	17.00	11.7

^a Mean square error; ^b Mean relative deviation modulus (P)

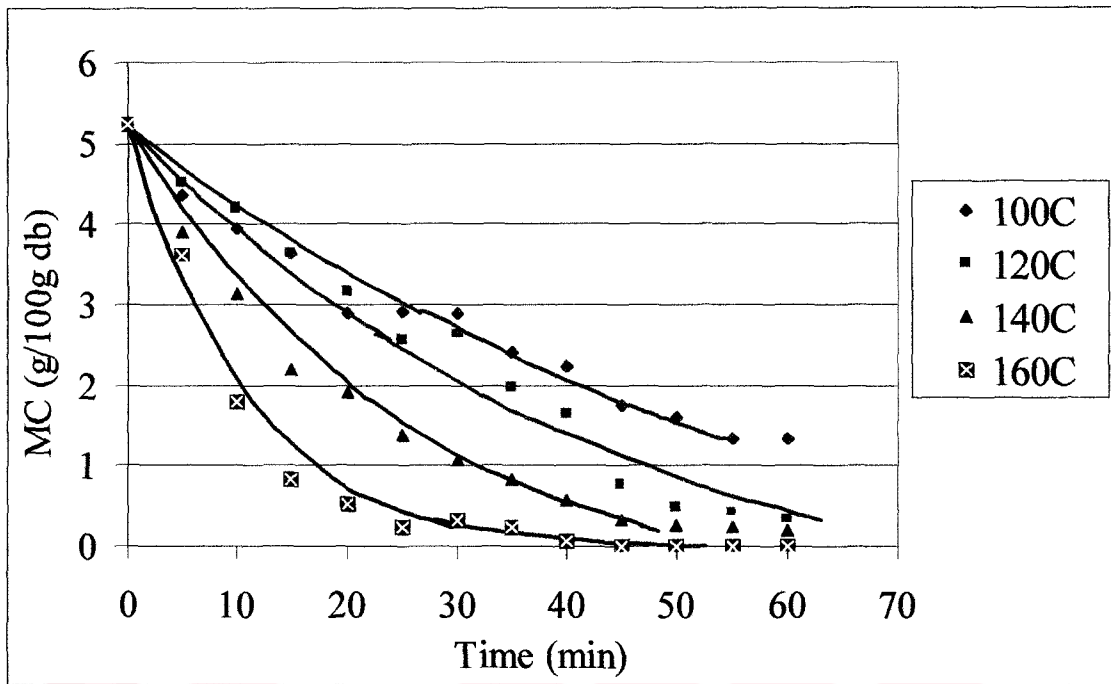


Figure 3.5. Thomson model fitted to drying during hazelnut roasting

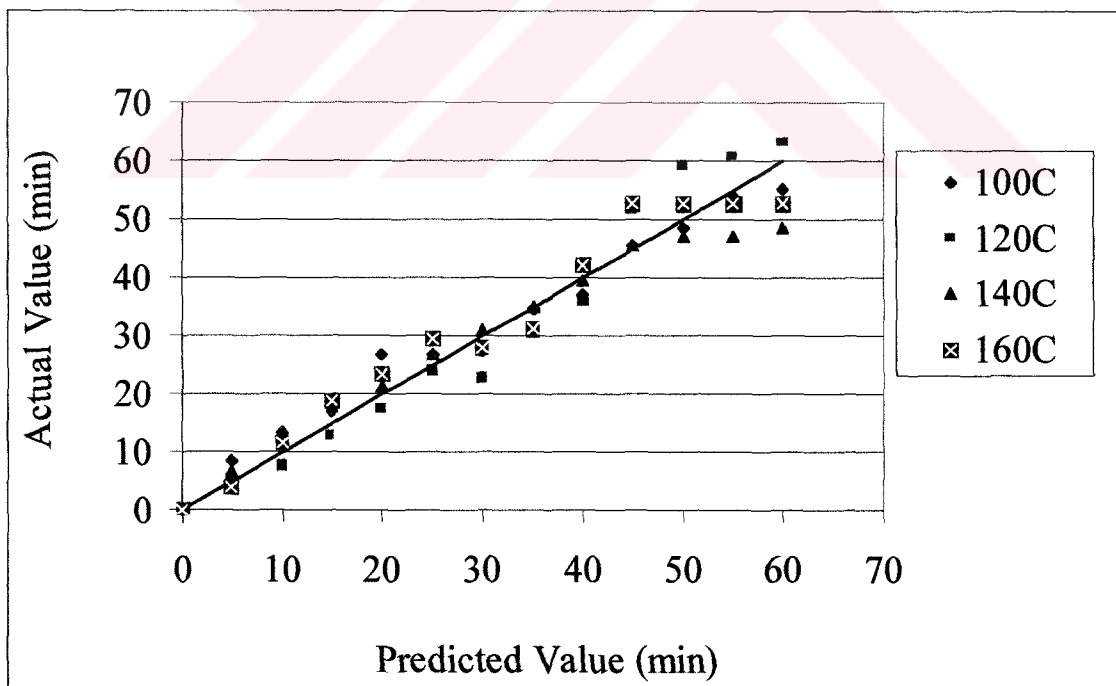


Figure 3.6. Comparison of actual and predicted value by the Thompson model

Table 3.3. Selected thin-layer drying model and its constants

The Thompson Model	r^2	MSE ^a	P (%) ^b
$t=a (\ln MR)+b (\ln MR)^2$	0.954	17.29	14.43
$A=-116.05+0.6560T$			
$B=-19.89+ 0.1217T$			

^a Mean square error; ^b Mean relative deviation modulus (P)

3.2 Kinetics of Color Change

Browning, enzymatic or nonenzymatic, is a complex reaction. Since the enzymes responsible for browning are denatured due to high temperatures employed during industrial roasting of nuts (>100°C), possibility of enzymatic browning was considered to be negligible (Troller, 1989; Driscoll & Madamba, 1994) and color changes during roasting of both peanut and hazelnut was previously classified as nonenzymatic (Moss & Otten, 1989; Perren & Escher, 1996c).

Analysis of variance (ANOVA) was performed to determine the factors affecting the color changes of roasted hazelnuts. For both whole-kernel and ground-state measurements, one-way ANOVA indicated that temperature and time significantly affected L -, a - and b -values of hazelnut color during roasting ($p<0.0001$) over the temperature range studied (Figure 3.7.- Figure 3.9.).

A detailed analysis with one-way ANOVA was conducted to find out effect of each temperature on the color changes. For whole-kernel measurements, there was no significant differences changes over exposure time in L -, a - and b - values at roasting air temperature of 100°C and L -, b -values at roasting air temperature of 120°C. At roasting air temperatures of 140°C and 160°C, effect of time on L -, a -, and b -values of color were, however, significant ($p<0.0001$) for whole-kernel measurements. On the other hand, for ground-state measurements that effect of time on L -, a -, and b -values of color were significant ($p<0.0001$) over all the temperature range of study. Only b -value had a lower level of significance ($p<0.013$) at 100°C roasting for ground-state measurements.

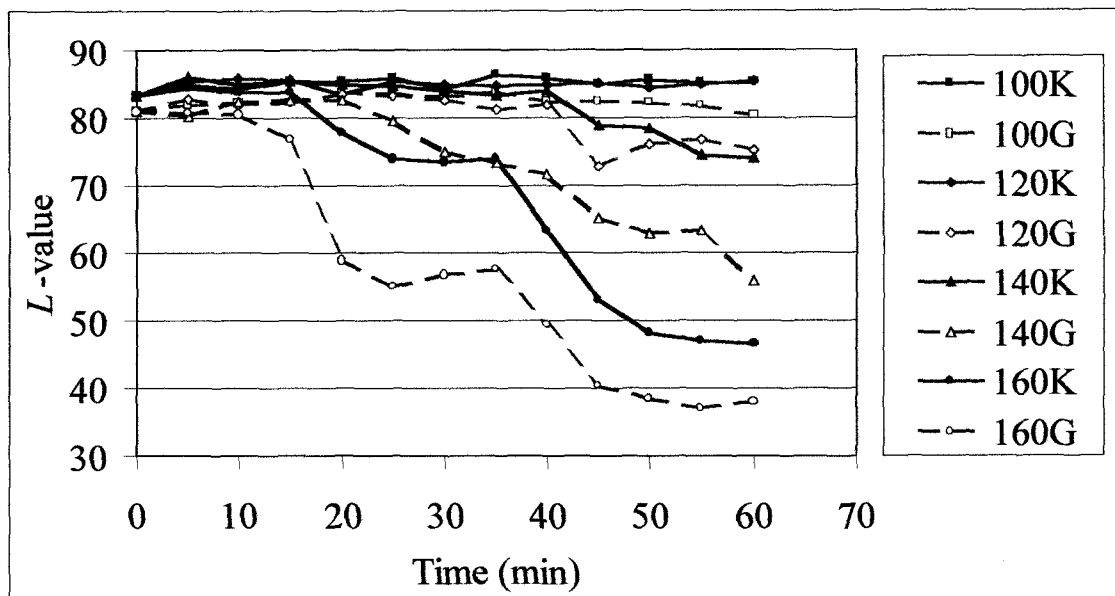


Figure 3.7. Changes in L -value of hazelnuts during roasting (100, 120, 140, 160 denotes roasting air temperature in degree Celsius; K: whole-kernel measurements, G: Ground-state measurements)

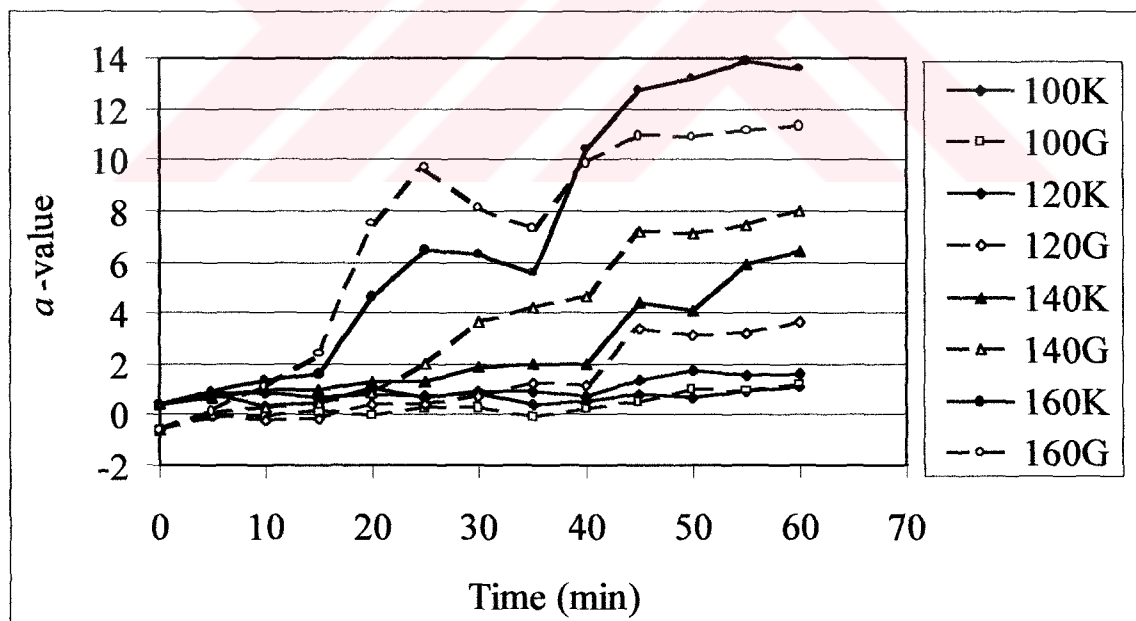


Figure 3.8. Changes in a -value of hazelnuts during roasting (100, 120, 140, 160 denotes roasting air temperature in degree Celsius; K: whole-kernel measurements, G: Ground-state measurements)

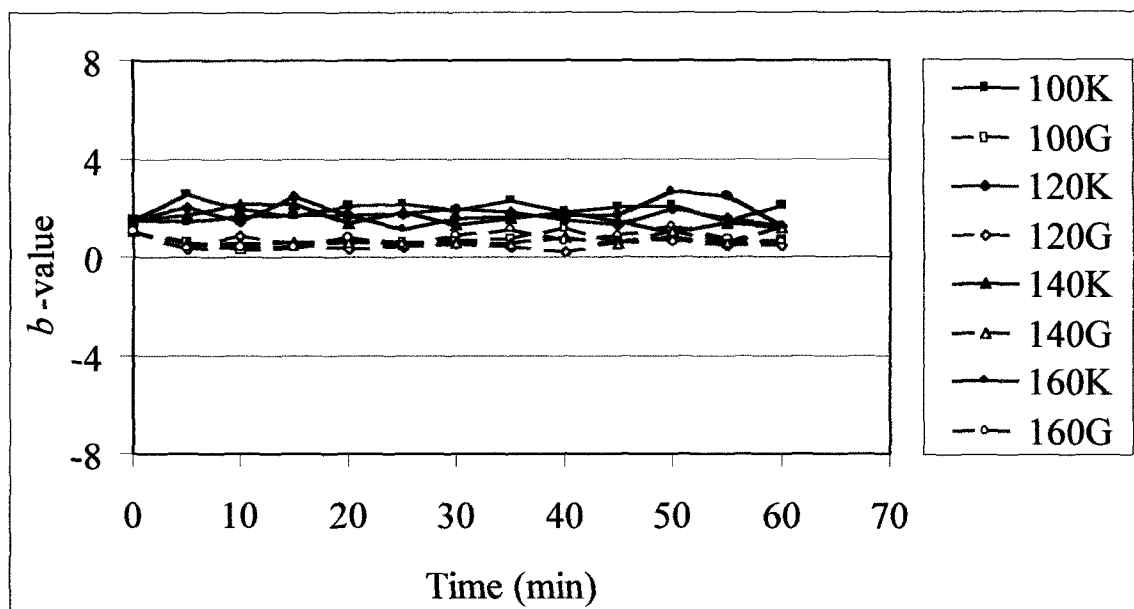


Figure 3.9. Changes in b -value of hazelnuts during roasting (100, 120, 140, 160 denotes roasting air temperature in degree Celsius; K: whole-kernel measurements, G: Ground-state measurements)

The Duncan's multiple range test at 95% level of significance was used for comparison of means. L -value tended to be constant for a particular time period before a significant color change was sensed by the instrument (Figure 3.7.). A similar induction period was reported for browning of garlic during drying (Driscoll & Madamba, 1994) and for peanut roasting (Moss & Otten, 1989). In fact, a slight lightening of the nuts at the beginning of the roast was observed. Moss & Otten, (1989) reasoned the lightening due to glazed appearance of the slightly-roasted nuts after grinding. This explanation is not valid for roasted hazelnuts since the lightening was also observed in whole-kernel measurements. Initial lightening was also observed in milk and it was attributed to denaturation of heat labile soluble proteins and their subsequent coagulation (Rhim *et al.*, 1988; Pagliarini *et al.*, 1990). Although further investigation is necessary, denaturation of soluble proteins may also be reason of initial lightening in roasted hazelnuts.

The induction period were preceded the main browning period near the half way point of a full roast due to concentration of substrates at lower moisture content. During the induction period significant chemical changes occur in which colorless intermediates are formed. The length of the induction period was found to be inversely proportional to temperature. Moisture content also reported to affect induction period (Lopez *et al.*, 1997a). After a sufficient quantity of intermediate products have been produced, the reaction proceeds to its final stage in which brown pigments –melanoidins- are formed (Troller, 1989; Villota & Hawkes, 1992; Lopez *et al.*, 1997a). The results are in agreement with the results reported by Moss & Otten (1989) for peanut roasting and by Driscoll & Madamba, (1994) for garlic drying.

A similar to induction period was also observed in *a*-value. Upon continued roasting, a sharp increase in the curve of *a*-value observed due to increased rate of formation brown pigments through Maillard reaction. Like *L*- value, the length of the induction period was found to be inversely proportional to temperature. Similar results were reported by Moss & Otten (1989) for peanut roasting. They also stated that both *L*- and *a*-values, representing degree of lightness and the red-green range, respectively depends on the characteristics of unroasted nuts, especially maturity of nuts but *b*-value does not. Moss & Otten (1989) reported an induction period in *b*-value of roasted peanuts at initial stages of roasting followed by an increase. During roasting of hazelnuts, no trend was, however, observed in *b*-value. The range of *b*-value was 1 to 3 for whole-kernel measurements while that of ground-state measurements was 0 to 1.2 over the temperature range of the study.

Measurement type, whole-kernel or ground state measurement, significantly affected *L*-value ($p < 0.0001$) and *b* value ($p < 0.005$) over the temperature range of study but there was no significant difference between types of measurement for *a*-value ($p < 0.799$) (See Figure 3.7. -Figure 3.9.). *L*- and *b*-value were significantly lower in ground-state measurements, which indicated a darker color due to decreased lightness and

yellowness, compared with whole kernel. This may be due to brown centers observed in roasted samples (internal browning). Similar brown centers were also reported for almonds and pecans after roasting (King *et al.*, 1983). Therefore, level of roasting and/or color of the roasted sample should not be monitored by measuring only outside color of whole-kernels.

3.2.1 Modeling of color formation

Initial evaluation of zero-order equation, first-order equation, quadratic polynomial and third degree polynomial, based on mean square error (MSE), correlation coefficient (r^2), and percent standard deviation (σ) modulus, pointed out that the best fits was obtained with third degree polynomial. Results of curve fitting criteria for the third degree model were shown in Table 3.4. and Table 3.5.

Ground-state measurements gave equal or better correlation coefficient, mean square error and percent standard deviation results than whole-kernel measurements over the temperature range studied (Table 3.4. and Table 3.5.). b -Value results for both type of measurement gave a low level of correlation coefficient and percent standard deviation. No trend in b -values for both type of the measurements was observed throughout during roasting treatment over the temperature range studied. Therefore, b -values for both type of measurements were rejected from further modeling analysis but L - and a -values of color was used to describe color formation during roasting.

Correlation coefficients of L -, and a -values of ground-type measurements were around 0.9. L -, and a -values for whole-kernel measurements obtained lower correlation coefficients at 100°C and 120°C roasting air temperatures but their MSE was also considerably low. Therefore, L - and a -values of both type of measurements were accepted for modeling with third-degree modeling.

The coefficients of the third degree model were calculated using Levenberg-Marquard estimation method. The model coefficients were then related to the roasting air temperature with Arrhenius type relationship (E 12) to describe temperature dependence using one-step regression procedure, as recommended by several authors (Haralambu *et al.*, 1985; Saguy & Karel, 1987; Driscoll & Madamba, 1994; Madamba *et al.*, 1996).

Table 3.4. Curve fitting criteria for third degree polynomial for whole-kernel measurements

Color Dimension	T (°C)	r^2 ^a	MSE ^b	σ (%) ^c
L-value	100	0.519	0.40	0.56
	120	0.229	0.57	0.74
	140	0.947	1.22	1.12
	160	0.963	11.29	4.07
a-value	100	0.628	0.02	15.79
	120	0.779	0.07	22.40
	140	0.961	0.22	15.64
	160	0.956	1.59	14.98
b-value	100	0.068	0.12	14.78
	120	0.289	0.11	16.23
	140	0.476	0.09	15.89
	160	0.277	0.18	20.40

^a Correlation coefficient; ^b Mean square error; ^c Percent standard deviation

Table 3.5. Curve fitting criteria for third degree polynomial for ground-state measurements

Color Dimension	T (°C)	r^2 ^a	MSE ^b	σ (%) ^c
L-value	100	0.854	0.20	0.45
	120	0.745	4.32	2.16
	140	0.973	2.94	1.94
	160	0.941	23.06	6.93
a-value	100	0.898	0.03	58.14
	120	0.930	0.22	31.38
	140	0.982	0.24	11.77
	160	0.917	2.25	18.05
b-value	100	0.442	0.04	26.27
	120	0.418	0.04	32.44
	140	0.475	0.04	24.11
	160	0.518	0.05	26.82

^a Correlation coefficient; ^b Mean square error; ^c Percent standard deviation

The results of the one-step regression procedure as the curve fitting criteria of r^2 , MSE and percent standard deviation were shown in Table 3.6. For L -value correlation coefficient, MSE and percent standard error coefficient were better for ground-state measurements than whole-kernel measurements. L -values of the whole-kernel measurements were over estimated at roasting air temperature of 100°C and under estimated at 120°C and 140°C at later stages of roasting (Figure 3.10.). Curve fitting criteria results were comparable for a -value results for both type of measurement. However, a -value of the whole-kernel measurements was over estimated at roasting air temperature of 100°C at the beginning of roasting process (Figure 3.11.). Therefore, ground-state measurements were selected to describe color changes during roasting of hazelnuts. Then, the overall mathematical model for L - and a -value for ground-state measurements as a function of temperature and time can be written:

$$L = 83.5\exp(-1.4/T) - 9.7 \times 10^{17} \exp(-18305.7/T) t - 1.92 \times 10^8 \exp(9848.7/T) t^2 + 2.5 \times 10^{15} \exp(-18826.1/T) t^3 \quad (E\ 23)$$

$$a = 3.4 \times 10^{16} \exp(-16653.8/T) - 0.0013 \exp(917.6/T) t + 1.2 \times 10^6 \exp(-7916.7/T) t^2 - 1.3 \times 10^7 \exp(-10884.1/T) t^3 \quad (E\ 24)$$

Table 3.6. One-step regression results for the third degree polynomial

Color-dimension	Measurement type	r^2 ^a	MSE ^b	σ (%) ^c
L -value	Whole-kernel	0.83	20.7	5.21
	Ground-state	0.97	7.49	3.43
a -value	Whole-kernel	0.96	0.57	24.97
	Ground-state	0.95	0.88	28.95

^a Correlation coefficient; ^b Mean square error; ^c Percent standard deviation.

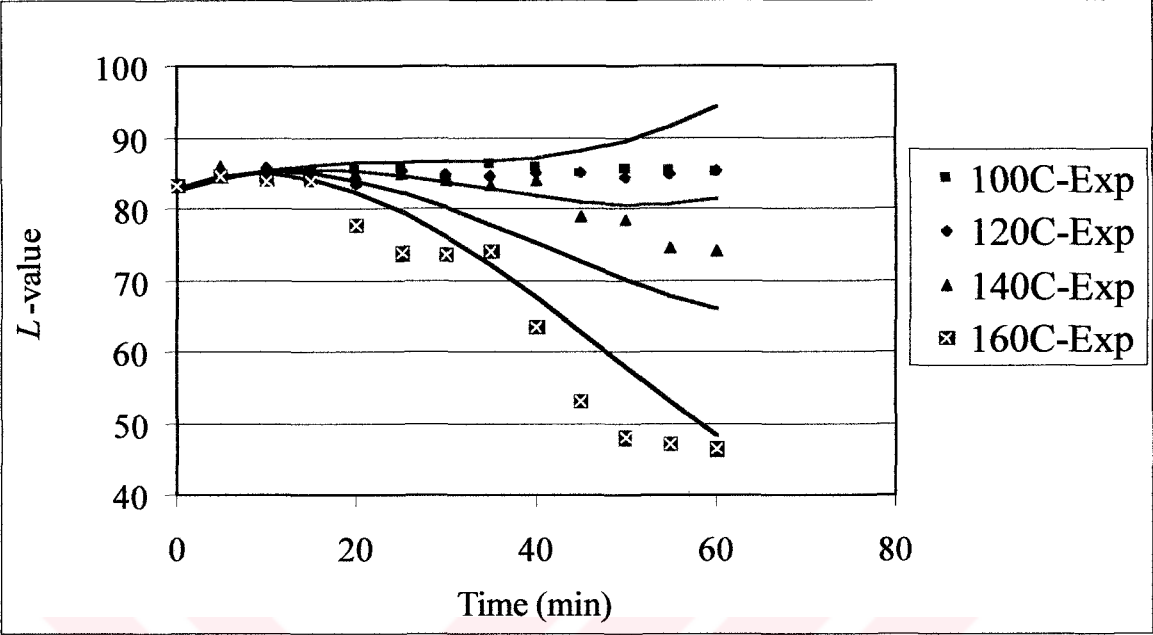


Figure 3.10. Predicted and experimental L -value for whole-kernel measurements (Exp: Experimental data; Continuous lines: Prediction data)

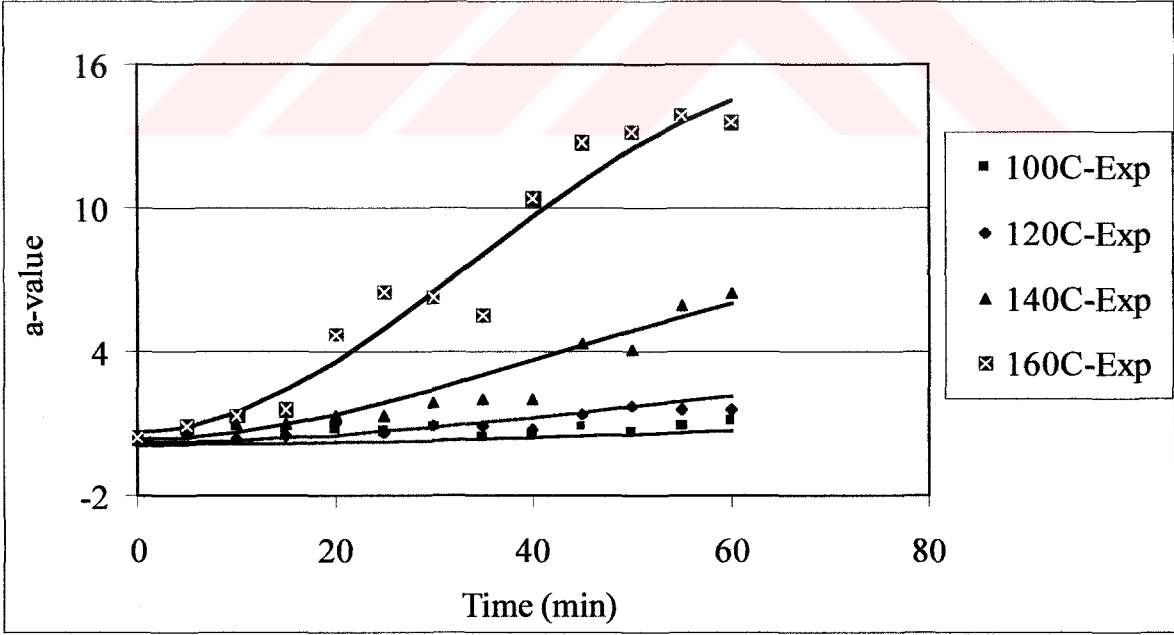


Figure 3.11. Predicted and experimental a -value for whole-kernel measurements (Exp: Experimental data; Continuous lines: Prediction data)

Figure 3.12. and Figure 3.13. show predicted curves for the experimental data of thin layer roasting of hazelnuts for the temperature range of 100-160°C for L - and a -value of ground-state measurements. Comparison of actual and predicted L -values and a -value of ground-state measurements were shown in Figure 3.14. and Figure 3.15. The experimental data generally banded around 45°C straight line which shows the suitability of the equation (E 22) and (E 24) in describing behavior color changes during hazelnut roasting.

Although L -value and a -value was successfully modeled over the temperature range of study, L -value, measuring relative lightness of a product, is analogous to the color observation made by operator in determining the degree of the roasted product (Moss & Otten, 1989). Therefore L -value can be preferred to monitor color formation during roasting of hazelnuts. L -value was also used to monitor non-enzymatic browning in garlic drying (Driscoll & Madamba, 1994), peanut roasting (Moss & Otten, 1989) and hazelnut roasting (Perren & Escher, 1996a,b,c).

Possibility of estimating L - and a -value of roasted ground hazelnut (ground-state-measurements) from the outside color of the roasted hazelnuts (whole-kernel-measurements) was also investigated. The results of the one-step regression procedure as the curve fitting criteria of r^2 , MSE and percent standard deviation were shown in Table 3.7. For L -value correlation coefficient, MSE and percent standard error coefficient were better than that of a -value. Curve fitting criteria results for L - and a -value were comparable to those given in Table 3.6. The estimation equations (E 25) and (E 26) satisfactorily estimated ground-state L -, and a -values, using the whole-kernel measurements as shown Figure 3.16. and Figure 3.17. However, a -value estimation for roasting at 160°C for more than 20 min should be used with caution because it under estimated during 20-35 min roasting and over during between 40min-55 min roasting.

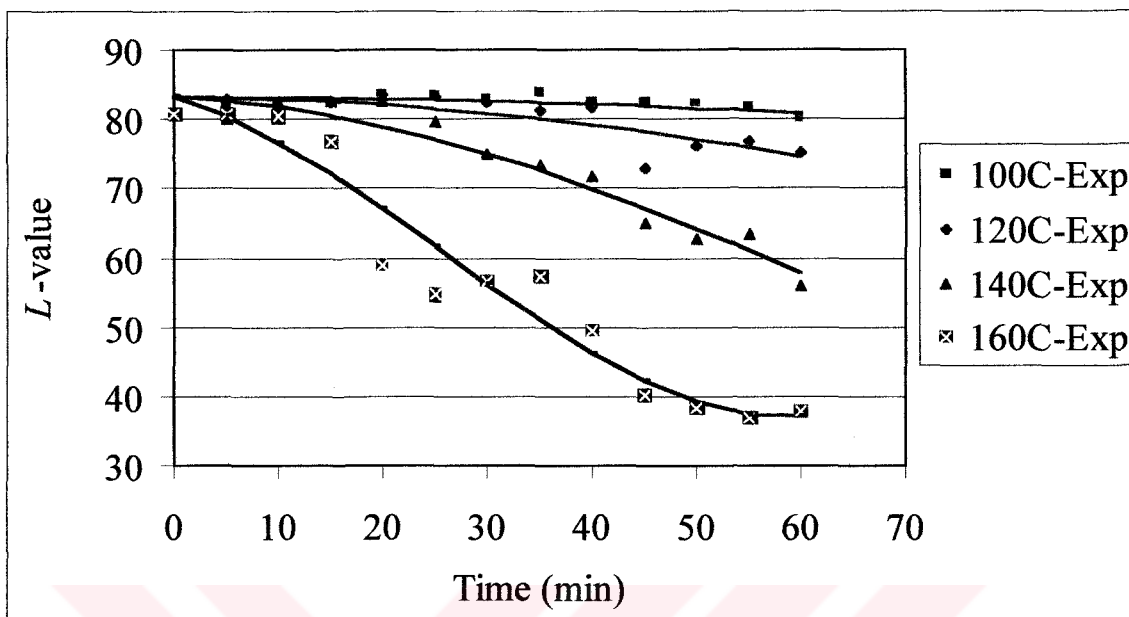


Figure 3.12. Predicted and experimental L -value for ground-state measurements (Exp: Experimental data; Continuous lines: Prediction data)

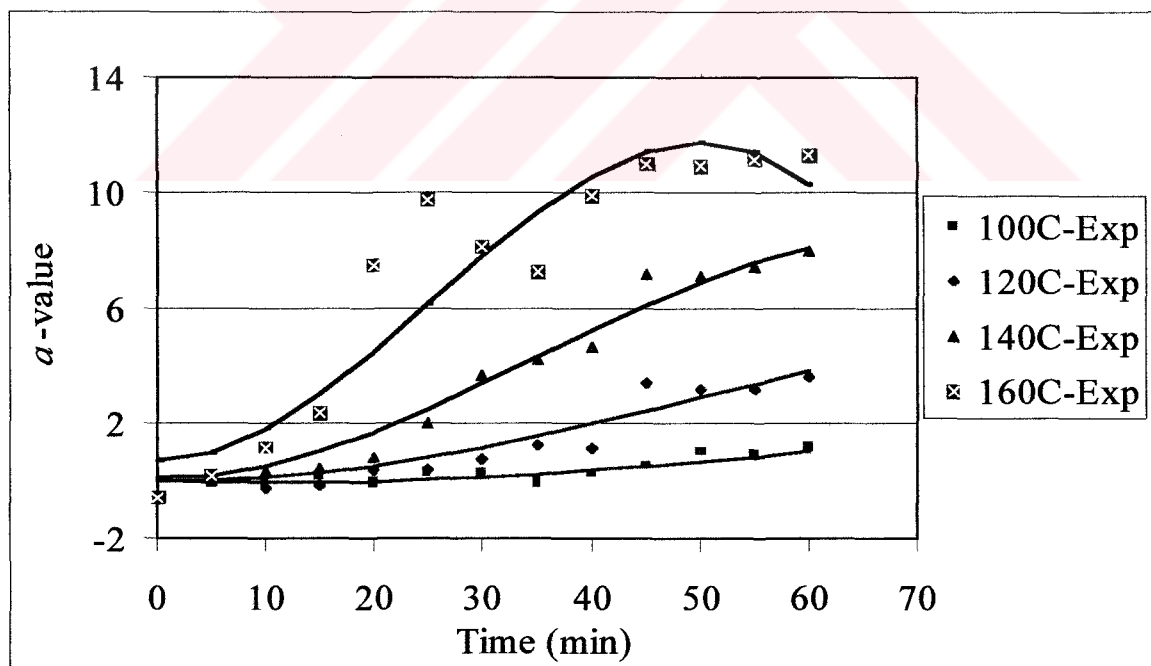


Figure 3.13. Predicted and experimental a -value for ground-state measurements (Exp: Experimental data; Continuous lines: Prediction data)

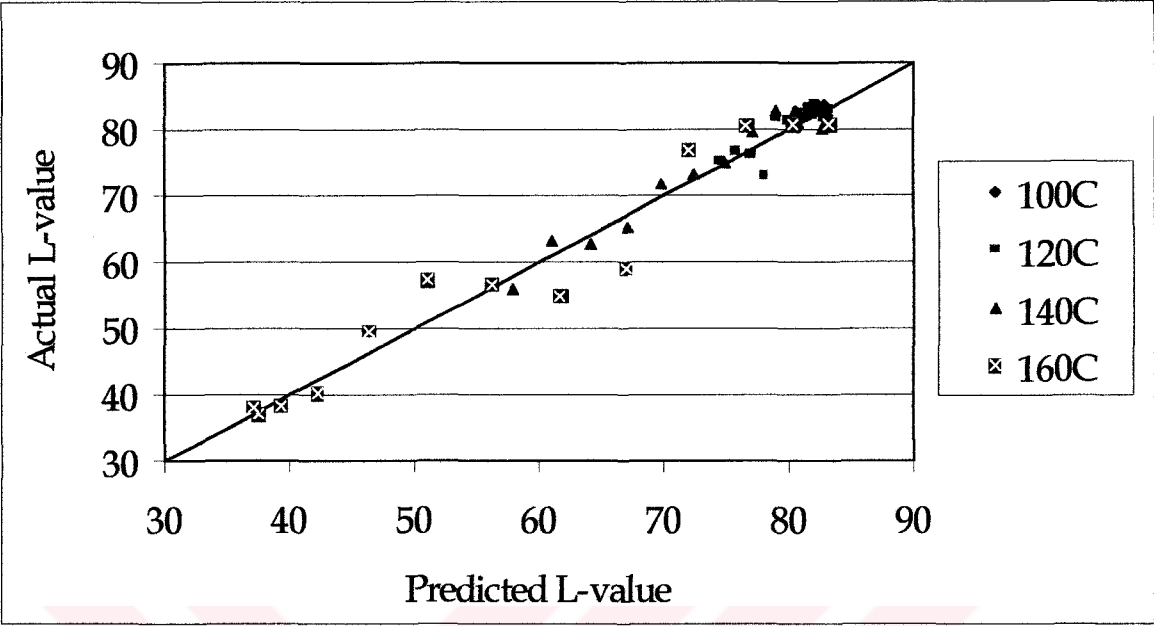


Figure 3.14. Comparison of predicted and actual L -values of ground-state measurements

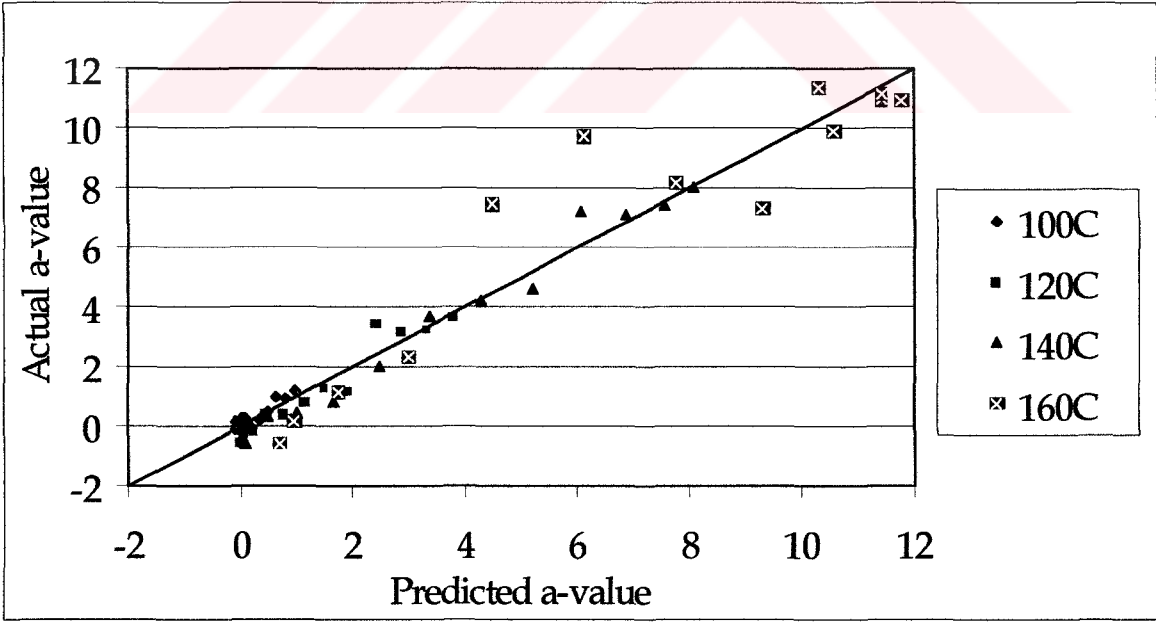


Figure 3.15. Comparison of predicted and actual a -values of ground-state measurements

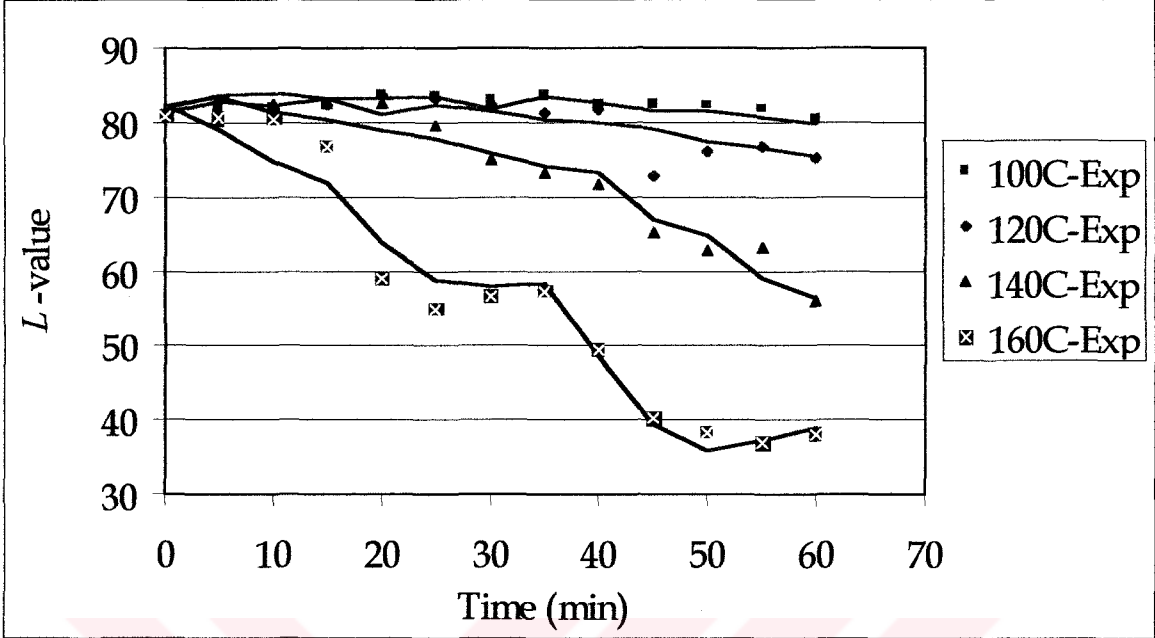


Figure 3.16. Predicted ground-state L -value from whole-kernel L -value (Exp: Experimental ground-state L -value; Continuous lines: Prediction data)

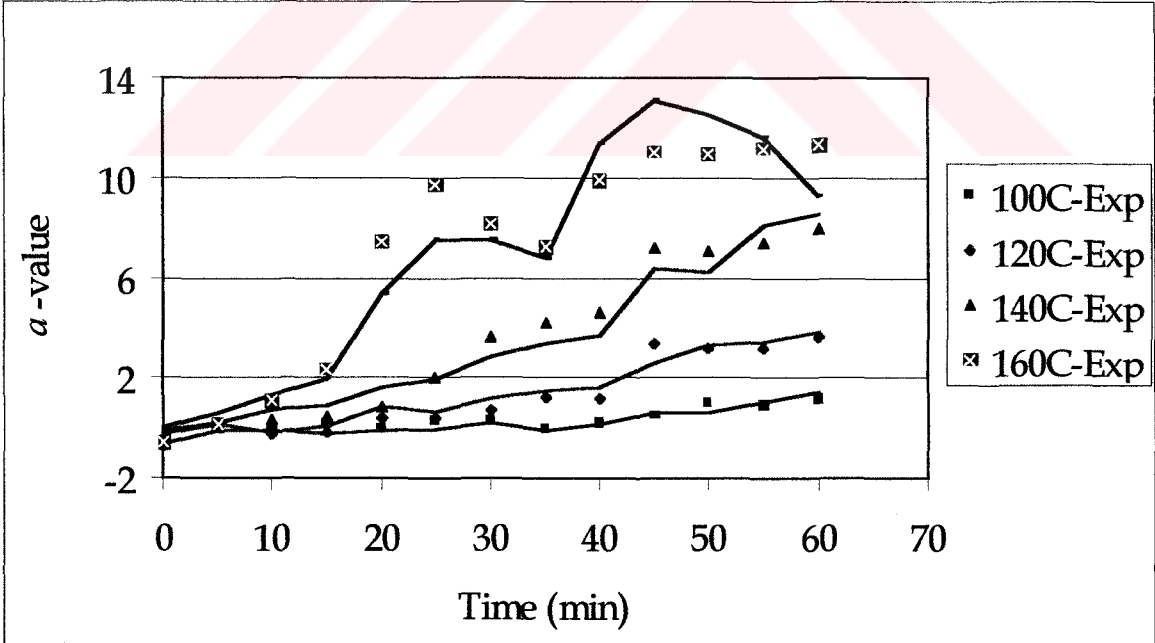


Figure 3.17. Predicted ground-state a -value from whole-kernel a -value (Exp: Experimental ground-state a -value; Continuous lines: Prediction data)

Table 3.7. One-step regression results for the third degree polynomial for ground state color estimation

Color-dimension	Estimated color	r^2 ^a	MSE ^b	σ (%) ^c
<i>L</i> -value	Ground-state	0.97	36127.5	2.95
<i>a</i> -value	Ground-state	0.96	145.9	26.34

^a Correlation coefficient; ^b Mean square error; ^c Percent standard deviation

$$L_{\text{ground}} = L_{\text{whole}} - 0.3049 \exp(184.4/T) - 7141.5 \exp(-1419.9/T) t + 7023 \exp(-2049.8/T) t^2 - 0.00103 \exp(-425.5/T) t^3 \quad (\text{E } 25)$$

$$a_{\text{ground}} = a_{\text{whole}} - 0.0779 \exp(256.56/T) + 0.0785 \exp(-3858.4/T) t + 0.0244 \exp(-632/T) t^2 - 0.201 \exp(-1222.7/T) t^3 \quad (\text{E } 26)$$

3.2.2 Calculation of activation energy

One step regression was used for the calculation of activation energies of *L*-value over the temperature range as recommended several authors (Haralumpu *et al.*, 1985; Saguy & Karel, 1987; Samaniego-Esguerra *et al.*, 1991; Driscoll & Madamba, 1994; Rapusas & Driscoll, 1995). Because two-step regression produces high standard deviation and confidence interval of E_a , caused by small degrees of freedom and the cumulative errors resulting from first and second regressions. Zero-order kinetic equation was assumed with Arrhenius type (E 12) temperature dependence so as to calculate activation energies for *L*-value of ground-state measurements.

$$L = L_o + k_o \exp\left(-\frac{E_a}{RT}\right) t \quad (\text{E } 27)$$

Activation energy of L -value for ground-type measurements were found to be 62.3 kJ/mole. The results are lower than typical E_a values for non-enzymatic browning in foods (105-209 kJ/mole). The lower activation energy can be attributed to the increased mobility of water and reaction rates at higher roasting temperatures employed in this study. Driscoll & Madamba (1994) and Aguerre & Suarez (1987) also reported a lower activation energy than the typical E_a range at comparatively higher drying temperatures. Activation energy for garlic drying at temperature range of 50-90°C was 75.8-92.9 kJ/mole (Driscoll & Madamba, 1994) and that of corn during drying at temperature of 57-100°C was 71.06 kJ/mole (Aguerre & Suarez, 1987). Activation energy of browning in onions was also reported to be higher at lower temperatures. It was 128-190 kJ/mole for storage at a temperature range 20-40°C (Samaniego-Esguerra *et al.*, 1991) and 121-139 kJ/mole for drying at a temperature range of 40-80°C (Rapusas & Driscoll, 1995).

3.3 Analysis of Color Development During Roasting of Hazelnuts Using Response Surface Methodology

Experimental values of color dimensions of L -, a -, and b -value for whole-kernel, ground-state and cut-kernel measurements were given in Table 3.8. The regression coefficients of the second degree polynomial were given in Table 3.9. The equations obtained for the color dimensions were tested for adequacy and fitness by analysis of variance and residual, and partial F-test (Guerrero *et al.*, 1996). Summary of linear, quadratic and cross-product terms for L -value, a -value, b -value of whole-kernel, ground-state and cut-kernel measurements were given in Table 3.10. Non-significant terms were eliminated by applying the backward selection procedure (Guerrero *et al.*, 1996). Except for the b -value of cut-kernel measurements, the proposed equations explained more than 85% of the variation of the L -, a - and b - values of the three methods of measurements. The relative importance of linear (X_1 , X_2) and quadratic terms (X_1^2 , X_2^2) were highly important for the three-type of measurements while cross-product terms (X_1X_2) were highly important for ground-state and cut-kernel measurements (Table 3.10.).

Table 3.8. Experimental data for whole-kernel measurements as L -value, a -value and b -value under different roasting conditions of temperature (X_1) and exposure time (X_2)

Treatment no	Measurement method										
	X ₁	X ₂	Whole-kernel			Ground-state			Cut-kernels		
			L-value	a-value	b-value	L-value	a-value	b-value	L-value	a-value	b-value
1	-1	-1	84.66	0.93	24.52	81.45	0.37	21.44	78.41	4.10	22.93
2	1	-1	77.28	4.44	25.62	67.15	6.27	24.42	63.49	10.10	24.25
3	-1	1	84.09	1.41	24.24	76.29	2.44	22.82	72.91	6.27	22.41
4	1	1	71.79	7.47	28.33	59.12	9.37	25.29	56.33	11.24	22.70
5	0	0	83.32	3.13	25.66	70.09	4.97	24.88	64.83	9.75	23.92
6	0	0	82.05	2.98	25.30	65.82	6.09	24.62	66.22	8.88	23.36
7	-1.4142	0	85.42	1.08	24.50	80.83	0.21	22.16	80.83	2.58	22.42
8	1.4142	0	72.32	7.25	27.69	54.52	9.89	23.98	55.21	10.97	22.24
9	0	-1.4142	82.39	2.26	23.83	77.81	2.23	22.45	74.68	5.52	22.79
10	0	1.4142	83.96	2.43	26.30	64.94	7.62	24.78	62.82	9.73	23.12
11	0	0	84.41	2.97	25.18	70.33	5.80	24.88	63.33	9.96	23.87
12	0	0	85.14	2.39	25.03	68.35	5.32	24.51	66.04	9.04	24.17
Mean			81.40	3.23	25.52	69.73	5.05	23.85	67.09	8.18	23.18
Standard deviation			4.87	2.16	1.36	8.31	3.19	1.28	8.08	2.84	0.72

Table 3.9. Values of second-order polynomial regression coefficients denoting relationship between roasting conditions and color changes in roasted hazelnuts

Coefficient	Measurement method									
	Whole-kernel			Ground-state			Cut-kernels			
	L-value	a-value	b-value	L-value	a-value	b-value	L-value	a-value	b-value	
B ₀	-35.043	31.561	48.687	152.56	-21.42	-22.263	202.169	-67.363	-11.998	
B ₁	1.812	-0.485	-0.344	-0.431	0.167	0.568	-1.279	0.8858	0.468	
B ₁₁	-0.007	0.002	0.001	NS	NS	-0.002	0.003	-0.0029	-0.002	
B ₁₂	-0.006	0.003	0.004	NS	NS	NS	NS	NS	-0.001	
B ₂	1.157	-0.367	-0.412	-1.470	0.161	0.381	-1.381	0.5413	0.344	
B ₂₂	-0.007	NS	NS	0.018	NS	-0.005	0.017	-0.0071	-0.003	

NS: Non-significant.

Table 3.10. Analysis of variance table showing the effect of treatment variables as a linear term, quadratic term and interactions (cross-product) on the *L*-value, *a*-value, *b*-value of roasted hazelnuts

Source	df	Sum of squares					
		Whole-Kernel Measurements			Ground-State Measurements		
		<i>L</i> -value	<i>a</i> -value	<i>b</i> -value	<i>L</i> -value	<i>a</i> -value	<i>b</i> -value
Model	5	241.92***	49.37***	19.75***	734.95***	110.08***	16.80***
Linear	2	184.40***	43.63***	16.14***	712.04***	108.30***	11.91***
Quadratic	2	196.95***	44.89***	16.31***	696.93***	105.55***	10.61**
Cross product	1	50.65	16.22	12.03**	411.37***	64.68***	8.58**
Residual	6	18.57	1.89	0.43	25.14	1.92	1.32
Lack of fit	3	17.70	1.55	0.04	24.25	1.74	1.06
Pure Error	3	0.87	0.34	0.47	0.89	0.18	0.26
R ²		86.93	93.25	97.86	93.94	96.86	86.68
						97.01	
							93.73
							36.10

df: Degree of freedom.
Significant at *5%/level, **1% level, ***0.1% level.
R²: % Variability explained.

The adequacy of the fitted models was verified by F-lack of fit statistic and sum of square which is an indicator of common variance (Table 3.10.). The results led to conclusion that there is no doubt about the adequacy of the proposed model for each color attributes of whole-kernel, ground-state and cut-kernel measurements.

Regression equations obtained were used to generate response surfaces (Figure 3.18. - Figure 3.20.) The shape of response surfaces differed between measurement methods. The response surface of L -value of whole kernel measurements vertically displaced to significantly lower L -value ($p < 0.0001$) in ground-state and cut-kernel measurements. In fact, L -value ranged from 85.42 to 71.79 for whole-kernel measurements, from 81.45 to 54.52 for ground-state measurement, from 80.83 to 55.21 for cut-kernel measurements over the experimental conditions. The mean L -value of whole-kernel measurements (81.40 ± 4.87) was higher than the ground-state measurements (69.73 ± 8.31) and cut-kernel measurements (67.09 ± 8.08) (Table 3.8.). L -value of whole-kernel measurements remained relatively constant before a significant color change was observed (Figure 3.18.). In fact, a slight lightening of the nuts at the beginning of the roast was also observed. The length of this time delay or induction period was inversely proportional to temperature as also stated above. During the induction period several precursor reactions such as Amadori rearrangements and concentration of substrates is likely to occur. The induction period was followed by the main browning period near the half way point of a full roast as also indicated in the mathematical modeling of drying section of the thesis. The induction period and main browning period during roasting were previously reported for peanuts by Moss & Otten (1989).

The response surface of a -value of whole-kernel measurements vertically displaced to significantly higher a -value ($p < 0.0001$) in ground-state and cut-kernel measurements. a -value ranged from 0.93 to 7.47 for whole-kernel measurements, from 0.37 to 9.89 for ground-state measurements, and from 2.58 to 11.24 for cut-kernel measurements over the experimental conditions. The mean a -value of whole-kernel measurements (3.23 ± 2.16) were lower than the ground-state measurements (5.05 ± 3.19) and cut-kernel measurements (8.18 ± 2.84) (Table 3.8.). The higher a -values in ground-state

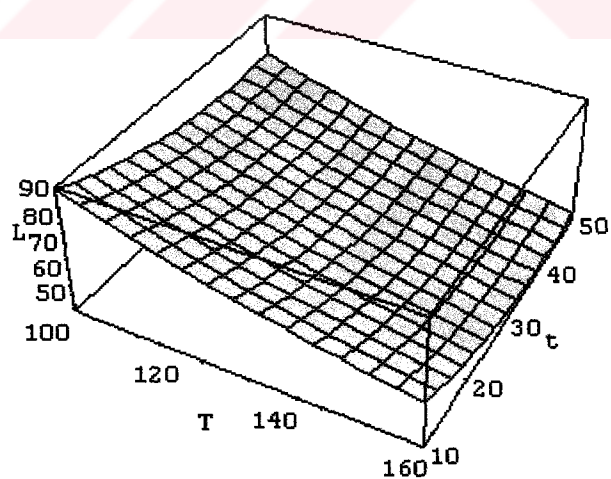
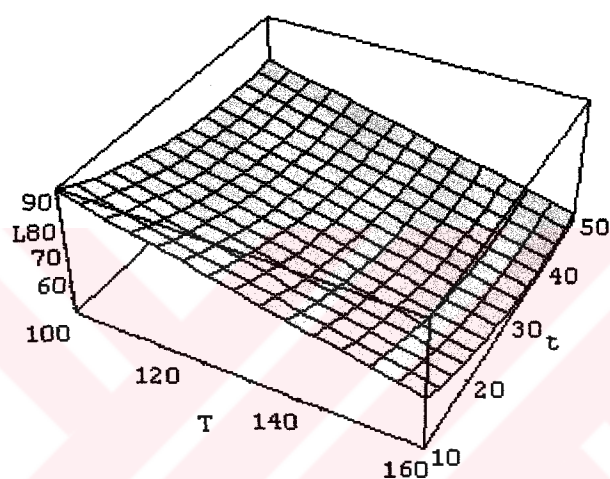
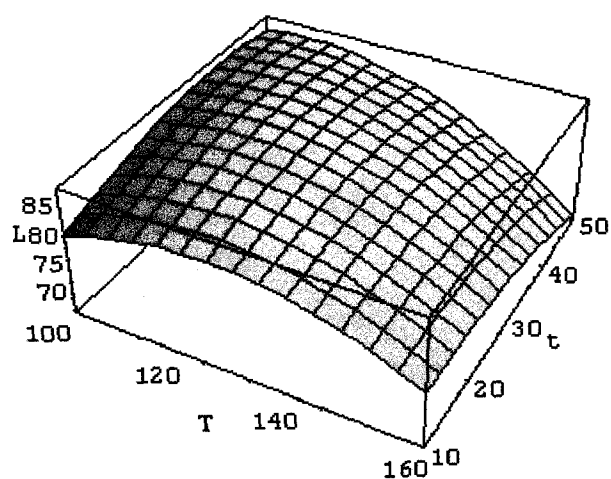


Figure 3.18. Response surface for L -value of (A) whole-kernel measurements, (B) ground-state measurements, (C) cut-kernel measurements

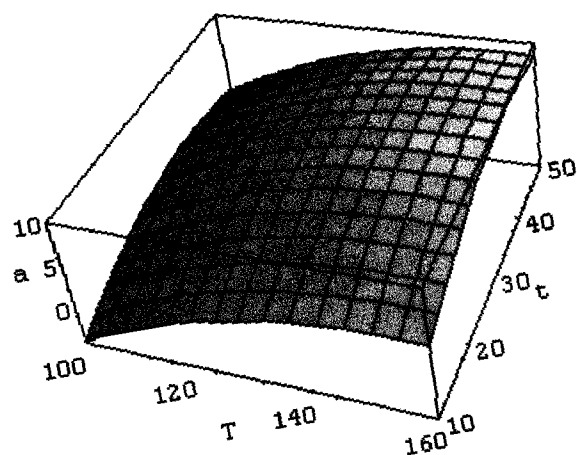
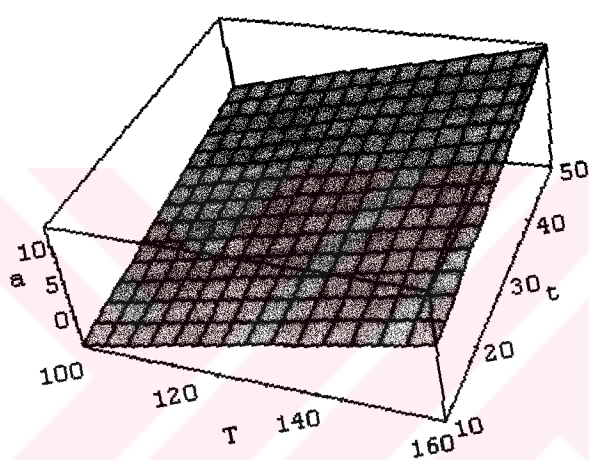
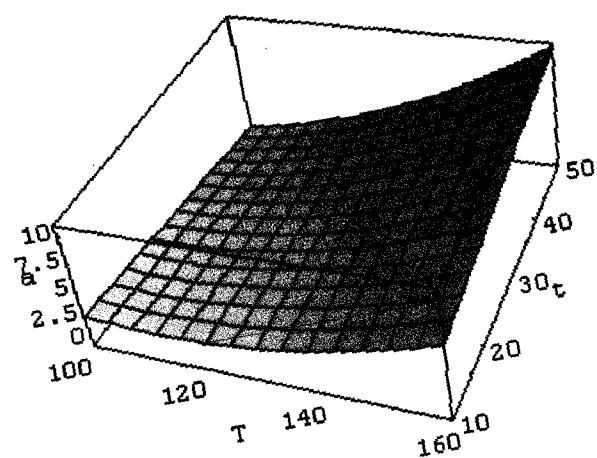


Figure 3.19. Response surface for a -value of: (A) whole-kernel measurements, (B) ground-state measurements, (C) cut-kernel measurements

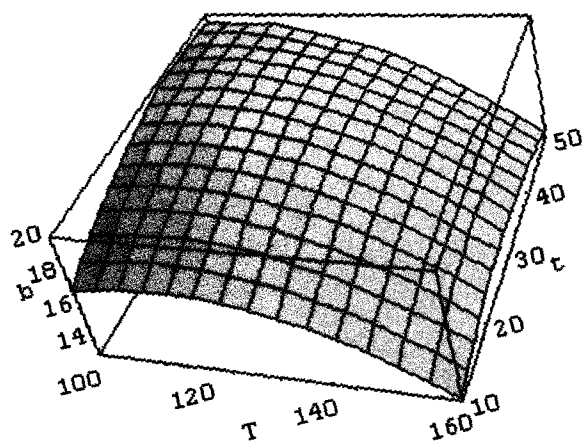
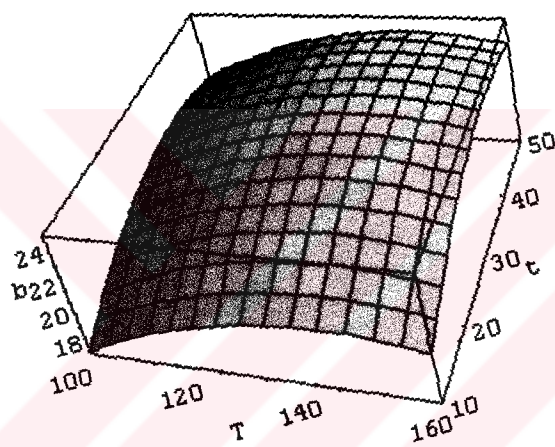
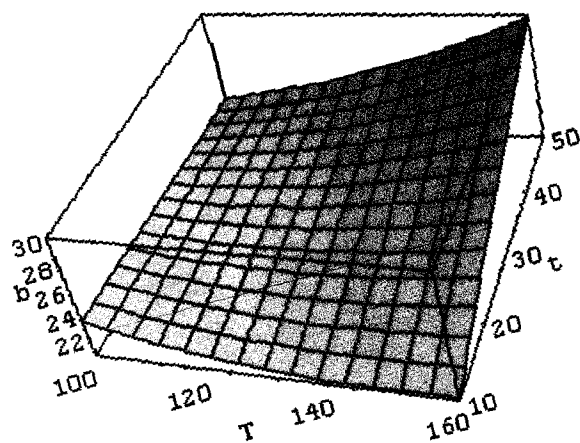


Figure 3.20. Response surface for b -value of: (A) whole-kernel measurements, (B) ground-state measurements, (C) cut-kernel measurements

measurements, related to an increase in redness, is indication of the internal browning (Table 3.8.). The a -value of whole-kernel measurements was greater than 5 for only two treatments: 150°C, 40 min and 158°C, 30 min. However, the a -value of ground-state measurements at roasting temperatures equal to or higher than 130°C and exposure times longer than 20 min was equal to or greater than 5. Cut-kernel measurements showed that the a -value were greater than 5 even at the roasting condition 110°C, 20 min. The higher roasting temperature and longer exposure time resulted in the greater a -value, and subsequently darker internal browning. The internal browning caused to increase a -value of ground-state and cut-kernel. The internal browning is especially a problem for the roasted product that are consumed as whole-kernels because the difference between outside color and inside color of roasted product makes the product unpleasant for the consumer. Similar internal browning was also reported by Özdemiş *et al.*, (2000a) in roasted hazelnuts, by King *et al.*, (1983) in roasted almond and pecans. The internal browning may be due to differences in the rate of nonenzymatic browning between the outside and inside of the kernel. Özdemiş *et al.*, (2000a) found that there was a significant difference between inner and outer layer of hazelnuts in terms of the protein and sugar contents. Protein content of outer layer (20.14%, db) were significantly higher than that of inner layer (14.36%, db). Total sugar (1.45%, db) and sucrose content (1.38%, db) of outer layer were significantly lower than total sugar (2.84%, db) and sucrose (2.69%, db) content of inner layer. These results indicated that sugar components concentrated in the inner layer (about 50% higher) of raw hazelnuts compared to outer layer. Therefore, non-enzymatic browning reaction may develop faster in the inner parts of the kernels (Özdemiş *et al.*, 2000a). Moreover, temperature and moisture distribution difference within the kernel occurring during roasting may also enhance localized development of Maillard reaction as stated by Göğüş *et al.*, (1998). This observation coincides with the pattern of internal browning which develops in the inner parts of the hazelnut while color of outer parts of the hazelnuts remain similar that of surface of roasted hazelnuts. Therefore, homogenous temperature and moisture distribution during roasting of hazelnuts is important, and should be taken into account in the design of hazelnut roasters.

The response surface of b -value of whole-kernel measurements also vertically displaced to significantly lower b -value ($p<0.0001$) in ground-state and cut-kernel measurements. The range of b -value was 23.83 to 28.33 in whole-kernel measurements, 21.44 to 25.29 in ground-state measurements, 22.24 to 24.25 in cut-kernel measurements over the experimental conditions. The mean b -value of whole-kernel measurements (25.52 ± 1.36) were higher than ground-state measurements (23.85 ± 1.28) and cut-kernel measurements (23.18 ± 0.72) (Table 3.8.).

The significance of the effect of each variable (roasting temperature and exposure time) on color attributes of roasted hazelnuts was shown in Table 3.11. Temperature affected L -value and a -value of whole-kernel, ground-state and cut-kernel measurements significantly but it did not affected significantly b -value of the measurement methods. Moreover, effect of exposure time was insignificant for the color attributes for the three measurement methods. The results are in aggrement with the finding in the mathematical modeling of color formation section of the thesis about roasting temperature (above 120°C) necessary for a significant color change in outside color.

Table 3.11. Analysis of variance table showing significance of the effect of the treatment variables on L -value, a -value and b -value of whole-kernel, ground-state and cut-kernels measurements

Measurements	df	Sum of squares		
		<i>L</i> -value	<i>a</i> -value	<i>b</i> -value
Roasting temperature (X ₁)				
Whole-kernel	11	260.49***	51.25**	20.18
Ground-state	11	760.09**	112.0*	18.12
Cut-kernel	11	717.62**	88.83*	5.68
Exposure time (X ₂)				
Whole-kernel	11	260.49	51.25	5.68
Ground-state	11	760.09	111.98	18.12
Cut-kernel	11	717.62	88.830	5.68

df: Degree of freedom

Significant at *5%level, **1% level, ***0.1% level.

As also stated in the mathematical modeling of color formation section of the thesis, analysis of color formation using RSM showed that whole-kernel measurements obtained significantly lighter color (higher *L*-value, higher *b*-value and lower *a*-value) compared to ground-state and cut-kernel measurements due to the internal browning of hazelnuts during roasting.

L-value should be preferred to monitor color development during hazelnut roasting because *L*-value (relative lightness of a product) is analogous to the color observation made by operator in determining the degree of the roasted product (Moss & Otten, 1989). However, *L*-value of whole-kernel measurements (outside color) underestimates *L*-value of ground state measurements (hazelnut meal) due to internal browning of hazelnuts during roasting. Therefore, *L*-value of ground state measurements should be preferred during monitoring of roasting process. *L*-value was also used to monitor nonenzymatic browning in garlic drying (Driscoll & Madamba, 1994), peanut roasting (Moss & Otten, 1989) and hazelnut roasting (Perren & Escher, 1996a,b,c).

3.4 Changes in Moisture, Protein, Total Sugar and Non-reducing Sugar Content of Hazelnuts During Roasting

Results of ANOVA and Duncan test for moisture, total sugar and non-reducing sugar were given in Table 3.12. - Table 3.14. for experimental data, effect of time and effect of temperature, respectively. Moreover experimental data also given as figures in Figure 3.21. - Figure 3.24. The results showed that there is a significant difference between treatments for moisture, protein, total sugar and non-reducing sugar content at $p < 0.0001$ (Table 3.12.). Duncan test between treatments indicated that moisture and protein content of control were significantly higher than that of roasted samples (Table 3.12.).

Roasting time and temperature significantly affected moisture at $p < 0.005$ level (Table 3.13., Table 3.14.). The higher roasting degree (higher roasting temperature and longer roasting time) resulted in the higher moisture loss in the roasted samples (Table 3.12.). Roasting even at 102°C for 30 min resulted in 58% moisture loss. At 150°C for 40 min roasting, 96% of the moisture was lost.

Table 3.12. Analysis of moisture, protein, total sugar and non-reducing sugar content of hazelnut samples roasted at different roasting conditions with ANOVA.

T (°C)	T (min)	Moisture (% db)		Protein (% db)		Total Sugar (% db)		Non-reducing sugar (% db)	
		AV	SD	AV	SD	AV	SD	AV	SD
Control		4.48	0.07g	16.17	0.03e	4.97	0.03d	4.72	0.03d
102	30	1.88	0.10f	14.50	0.47a	3.21	0.08a	3.05	0.08a
110	20	1.81	0.02f	15.52	0.02d	6.50	0.05g	6.17	0.04g
110	40	1.21	0.09e	15.24	0.01c	5.28	0.05e	5.02	0.05e
130	16	1.73	0.13f	15.06	0.01bc	5.64	0.03f	5.36	0.03f
130	30	0.72	0.12c	14.81	0.09b	4.95	0.11d	4.71	0.10d
130	44	1.03	0.12d	15.18	0.19c	4.95	0.01d	4.70	0.01d
150	20	0.64	0.14c	15.09	0.10c	4.64	0.02c	4.41	0.02c
150	40	0.15	0.04a	15.07	0.01c	4.31	0.03b	4.09	0.03b
158	30	0.34	0.01b	15.03	0.04bc	4.35	0.03b	4.14	0.02b
p		<0.0001		<0.0001		<0.0001		<0.0001	

Values in the same column with different lower-case letters (a-g) are significantly different at $p < 0.05$.

Table 3.13. Effect of roasting time on moisture, protein, total sugar and non-reducing sugar content of roasted hazelnuts at different roasting temperatures

T (°C)	t (min)	Moisture (% db)		Protein (% db)		Total Sugar (% db)		Non-reducing sugar (% db)	
		AV	SD	AV	SD	AV	SD	AV	SD
110	20	1.81	0.02	15.52	0.02	6.50	0.05	6.17	0.04
110	40	1.21	0.09	15.24	0.01	5.28	0.05	5.02	0.05
p		<0.0001		<0.0001		<0.0001		<0.0001	
130	16	1.73	0.13c	15.06	0.01b	5.64	0.03b	5.36	0.03b
130	30	0.72	0.12a	14.81	0.09a	4.95	0.11a	4.71	0.10a
130	44	1.03	0.12b	15.18	0.19b	4.95	0.01a	4.70	0.01a
p		<0.0001		<0.0001		<0.0001		<0.0001	
150	20	0.64	0.14	15.09	0.10	4.64	0.02	4.41	0.02
150	40	0.15	0.04	15.07	0.01	4.31	0.03	4.09	0.03
p		0.005		0.753		<0.0001		<0.0001	

Values in the same column with different lower-case letters (a-c) are significantly different at $p < 0.05$.

Table 3.14. Effect of roasting temperature on moisture, protein, total sugar and non-reducing sugar content of roasted hazelnuts at different roasting time

t (min)	T (°C)	Moisture (% db)		Protein (% db)		Total Sugar (% db)		Non-reducing sugar (% db)	
		AV	SD	AV	SD	AV	SD	AV	SD
20	110	1.81	0.02	15.52	0.02	6.50	0.05	6.17	0.04
20	150	0.64	0.14	15.09	0.10	4.64	0.02	4.41	0.02
	p	<0.0001		0.002		<0.0001		<0.0001	
40	110	1.21	0.09	15.24	0.01	5.28	0.05	5.02	0.05
40	150	0.15	0.04	15.07	0.01	4.31	0.03	4.09	0.03
	p	<0.0001		<0.0001		<0.0001		<0.0001	
30	102	1.88	0.10c	14.50	0.47a	3.21	0.08a	3.05	0.08a
30	130	0.72	0.12b	14.81	0.09b	4.95	0.11c	4.71	0.10c
30	158	0.34	0.01a	15.03	0.04b	4.35	0.03b	4.14	0.02b
	p	<0.0001		0.012		<0.0001		<0.0001	

Values in the same column with different lower-case letters (a-c) are significantly different at $p < 0.05$.

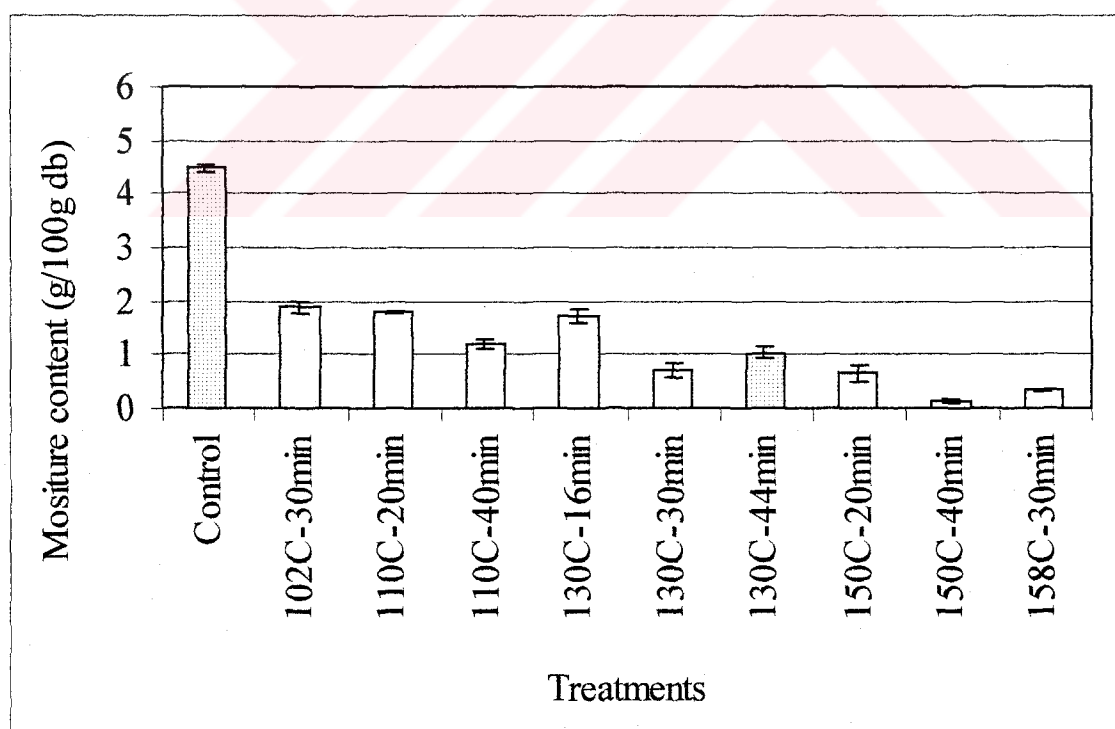


Figure 3.21. Changes in moisture content of hazelnuts during roasting

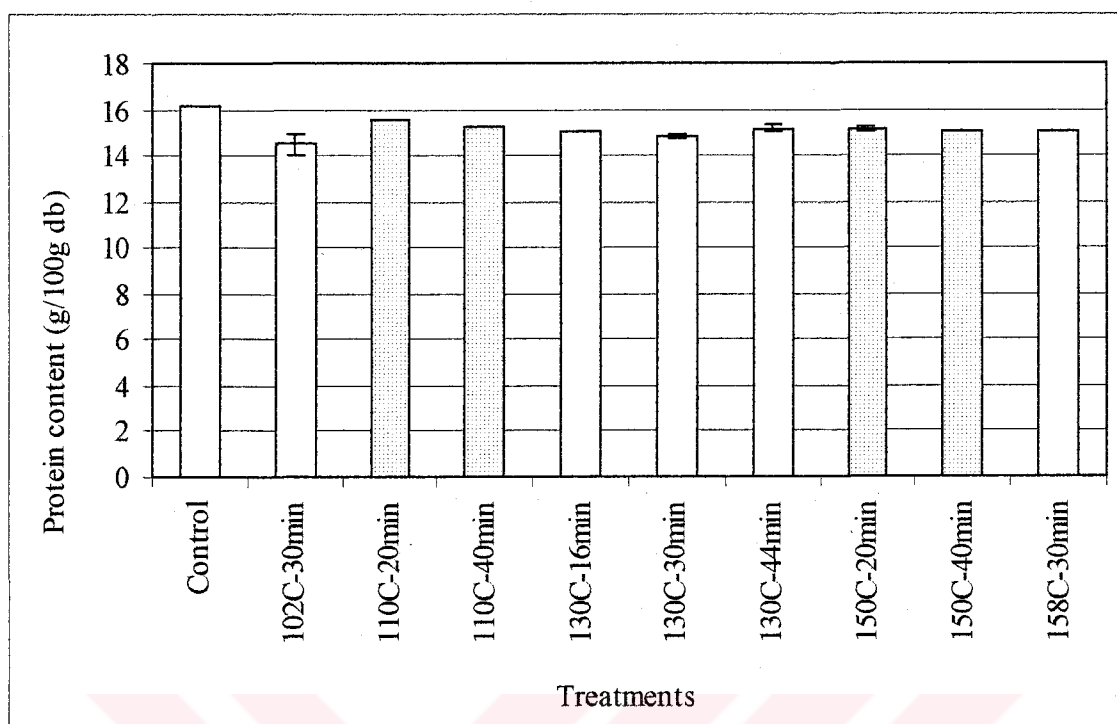


Figure 3.22. Changes in protein content of hazelnuts during roasting

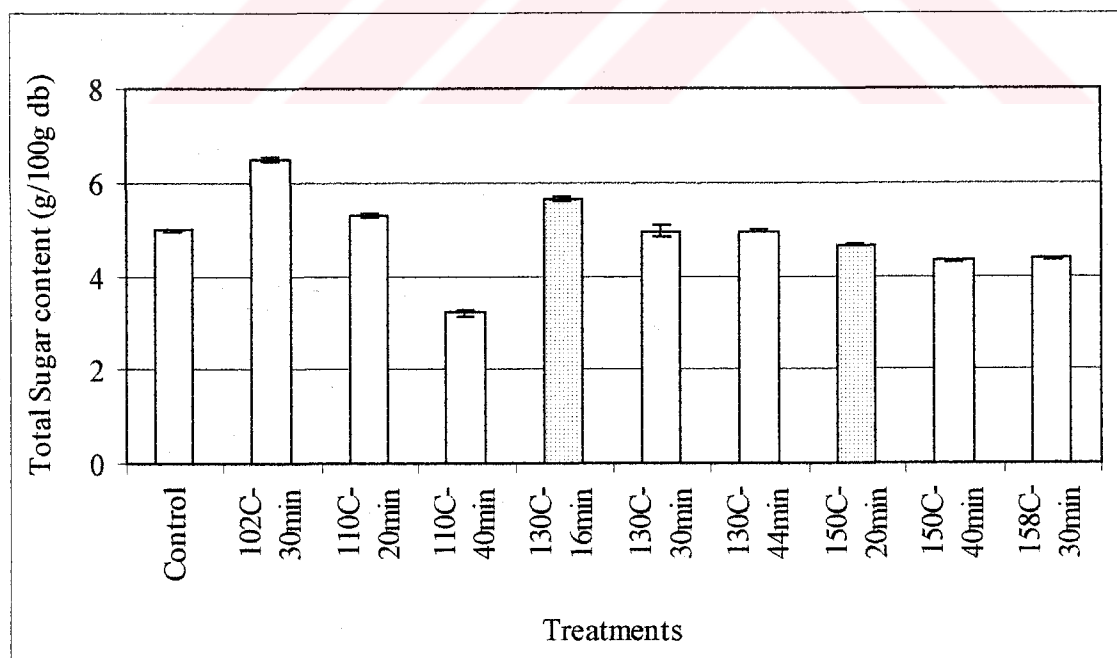


Figure 3.23. Changes in total sugar content of hazelnuts during roasting

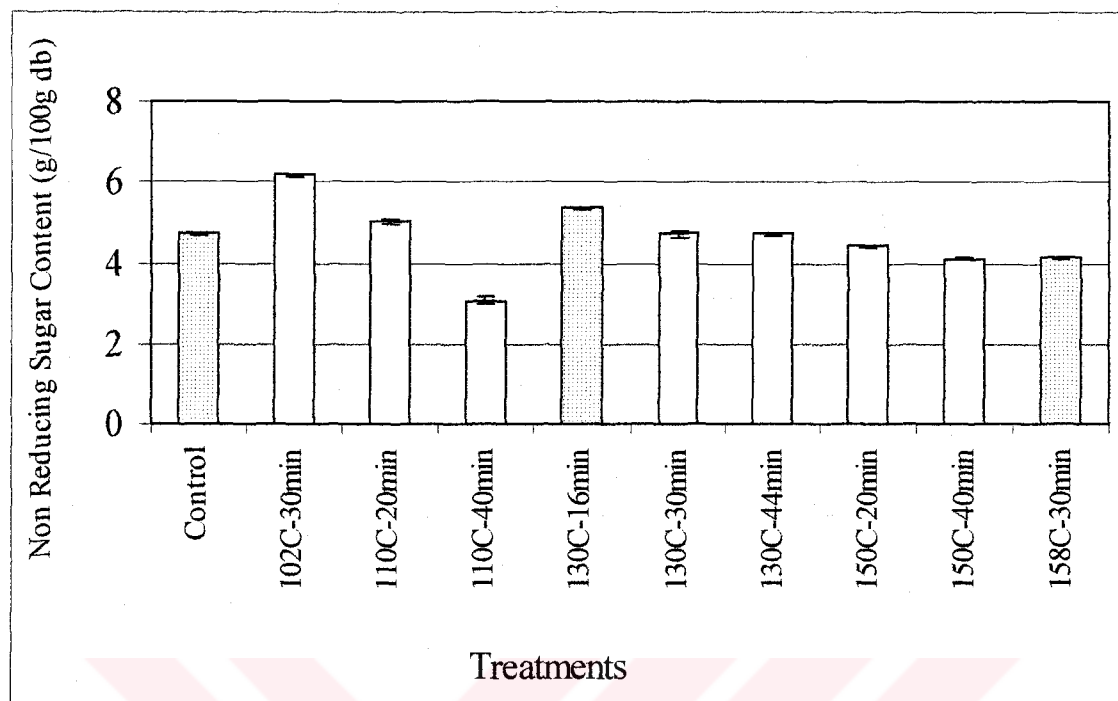


Figure 3.24. Changes in non-reducing sugar content of hazelnuts during roasting

The higher roasting temperature resulted in the higher moisture loss. Similarly the longer roasting time generally resulted in the higher moisture loss. The higher moisture content in the sample roasted at 130°C for 44 min compared to the samples roasted at 130°C for 16 and 30 min may be due to moisture generation as a result of nonenzymatic browning reaction, indicating a delay in the moisture loss (Perren & Escher, 1996c). Saklar *et al.*, (2001) stated consumer acceptable moisture content to be 0.26-1.81% for the roasted hazelnuts. Duncan test indicates that there is no significant difference between moisture content of the samples roasted at 102°C for 30 min, at 110°C for 20 min and at 130°C for 16 min and their moisture content are around 1.8% db. Moreover sample roasted at 150°C for 40 min had moisture content (0.15% db) lower than acceptable moisture content range. The other samples had moisture contents within in the acceptable moisture content range (Table 3.12.).

A loss of nitrogen was also observed in roasted samples (given as protein levels in Table 3.12., Figure 3.22.). The loss as protein was at most 10%. Some amine nitrogen and

rarely amide nitrogen loss may be expected during roasting which may also cause a slight increase in amino acid content per unit of total nitrogen (Ayatse *et al.*, 1983). Roasting time significantly affected protein content of roasted samples generally at $p < 0.0001$ level as shown (Table 3.13.). Protein content of samples roasted for 40 min at 110°C and 130°C was lower or equal to that of the samples roasted for 20 min. There was, however, no significant difference between 20 min and 40 min roasting at 150°C. Nevertheless the loss in protein content caused by longer roasting times at the same temperature was at most is 2.5%. Roasting temperature significantly affected protein content of roasted samples generally at $p < 0.0001$ level as shown (Table 3.14.). There was generally a significant protein loss between samples roasted for same roasting time at higher temperature. Nevertheless the loss in protein content caused by higher roasting temperatures for the same roasting time was at most is 3.5%.

No reducing sugar was found in all of the samples (Table 3.12.), having initial water activity of 0.7 (Read from adsorption isotherm raw hazelnut at 20°C given by Özdemir *et al.*, 2000a). Özdemir *et al.*, (2000a) also found reducing sugar in only raw samples with 0.83 and 0.80 water activity that were stored at 20 °C \pm 0.1°C for 4 months but not in the samples with lower water activity and in the roasted samples. Total sugar and non-reducing sugar content of control were significantly lower than that of the samples roasted at 110°C-20 min, 110°C-40 min and 130°C-16 min. Total sugar and non-reducing sugar content of control were not significantly different from that of the samples roasted at 130°C-30 min and 130°C-44 min. Total sugar and non-reducing sugar content were lower than the control in the samples roasted at 102°C-30 min and at 150°C or higher temperatures (Table 3.12.). Fluctuations in sugar content of roasted macadamia nut and peanut was also observed which was attributed to non-enzymatic browning reaction (Prichavudhi & Yamamoto, 1965; Qupadissakoon & Young, 1984). Decrease in starch, sucrose, fructose and glucose was attributed to hydrolysis of sucrose and starch into their monomers, and involvement of fructose and glucose in non-enzymatic browning reaction during coconut roasting which generally increased with increasing roasting temperature (Jayalekshmy & Mathew, 1990). Decrease in roasted pistachionuts and hazelnuts was related to hydrolysis of starch into its monomers during

roasting (Kashani & Valadon, 1984; Kırbaşlar, 1998). Moreover hydrolysis of non-reducing sugar into reducing sugars (fructose, glucose) in macadamia nuts, peanut and almond were reported (Prichavudhi & Yamamoto, 1965; King *et al.*, 1983; Qupadissakoon & Young, 1984). Reducing sugars are completely lost during cocoa roasting (Rohan & Shewart, 1966).

Roasting time significantly affected total sugar and non-reducing sugar of roasted samples generally at $p < 0.0001$ level as shown (Table 3.13.). Total sugar and non-reducing sugar contents were lower at longer roasting times at the same roasting temperatures. The loss for longer roasting times was in the range of 7-18% with the highest loss at 110°C (Table 3.13.). Roasting temperature significantly affected total sugar and non-reducing sugar of roasted samples generally at $p < 0.0001$ level as shown (Table 3.14.). Total sugar and non-reducing sugar contents were generally lower for the samples roasted at higher roasting temperatures at the same roasting times. The loss at higher roasting temperatures was in the range of 12-28% with the highest loss at 20 min roasting (Table 3.14.). The lower total sugar and non-reducing sugar content at higher temperature were also observed in roasted macadamia nuts by Prichavudhi & Yamamoto (1965) and in roasted coconuts by Jayalekshmy & Mathew (1990).

3.5 Changes in Amino Acid Composition of Hazelnuts During Roasting

Results of ANOVA and Duncan test for essential amino acids and non-essential amino acids were given in Table 3.15. - Table 3.21. for experimental data, effect of time and effect of temperature. Moreover experimental data also given as figures in Figure 3.25. - Figure 3.26. The results showed that there was a significant difference between treatments for non-essential and essential amino acids generally at $p < 0.0001$ (Table 3.15. - Table 3.16.). Non-essential and essential amino acid composition increased in the early stages of roasting, and decreased upon prolonged roasting. Moreover total typical, atypical, essential and non-essential amino acids and variation with respect to unroasted control hazelnut were investigated as shown in Table 3.17.

Table 3.15. Analysis of essential total amino acid (mg/100g, db) of the hazelnut samples roasted at different roasting conditions with ANOVA.

T (°C)	t (min)	Lysine		Leucine		Isoleucine		Threonine		Valine		Phenylalanine		Tyrosine		Methionine	
		AV	SD	AV	SD	AV	SD	AV	SD	AV	SD	AV	SD	AV	SD	AV	SD
Control		463.0	14.1cd	1027.0	7.1bc	508.0	12.7ab	485.0	5.7b	622.0	2.8a	670.5	4.9bc	428.5	3.5cd	145.0	4.2ab
102	30	361.5	0.7b	830.5	21.9a	449.5	19.1a	328.5	31.8a	581.5	46.0a	543.0	18.4a	281.0	67.9ab	95.0	5.7a
110	20	562.5	10.6ef	1330.0	67.9f	689.5	19.1e	647.0	36.8cd	813.5	30.4d	887.5	9.2e	523.0	21.2d	142.5	26.2ab
110	40	447.5	0.7c	1035.0	2.8c	557.0	1.4bc	458.5	4.9b	708.0	0.0b	682.5	3.5bc	425.0	2.8cd	99.5	0.7a
130	16	534.0	2.8e	1241.0	9.9e	651.0	5.7de	608.5	55.9c	780.0	9.9bcd	842.5	14.8de	500.0	2.8cd	170.5	3.5bc
130	30	489.3	23.0d	1158.6	44.2d	590.8	37.6cd	589.0	49.5c	717.6	38.5bc	800.9	49.6d	415.9	79.7cd	148.6	38.2ab
130	44	316.0	19.8a	949.0	76.4b	488.0	41.0a	455.5	55.9b	608.5	92.6a	623.0	55.2b	255.0	18.4a	177.5	13.4bcd
150	20	575.0	2.8f	1569.5	10.6g	647.5	0.7de	726.5	3.5d	803.0	1.4cd	1022.5	3.5f	441.5	2.1cd	232.0	1.4d
150	40	571.0	5.7f	1249.5	12.0ef	654.5	4.9e	599.0	42.4c	761.0	35.4bcd	862.0	7.1de	380.0	7.1bc	223.5	4.9cd
158	30	345.0	2.8ab	1059.5	2.1c	590.0	2.8cd	443.0	2.8b	746.5	2.1bcd	703.5	4.9c	404.0	1.4cd	165.0	1.4b
p		<0.0001		<0.0001		<0.0001		<0.0001		<0.0001		<0.0001		<0.004		0.001	

* Phenylalanine+tyrosine

** Methionine+Cystine

Values in the same column with different lower-case letters (a-f) are significantly different at p<0.05.

Table 3.16. Analysis of non-essential total amino acid (mg/100g, db) of the hazelnut samples roasted at different roasting conditions with ANOVA.

T (°C)	t (min)	Aspartic acid		Serine		Glutamic acid		Proline		Glycine		Alanine		Histidine		Arginine	
		AV	SD	AV	SD	AV	SD	AV	SD	AV	SD	AV	SD	AV	SD	AV	SD
Control																	
102	30	1578.5	48.8b	1002.0	25.5b	2679.5	40.3bcd	537.5	40.3a	657.0	41.0b	706.0	1.4d	346.5	36.1b	2138	41.0c
110	20	1214.0	60.8a	716.0	1.4a	1997.0	55.2a	690.5	150.6ab	521.0	73.5a	586.0	12.7b	281.5	2.1a	1521	203.6a
110	40	2119.5	82.7d	1177.0	48.1cd	3008.0	120.2e	1619.0	41.0c	970.5	99.7f	684.5	33.2cd	492.5	7.8e	2680	28.3e
130	16	1574.5	0.7b	955.0	11.3b	2478.0	17.0bc	759.0	188ab	705.5	2.1bc	517.5	7.8a	378.5	0.7bc	2126	4.2c
130	30	1923.5	72.8cd	1147.5	84.1cd	2915.0	91.9de	519.5	48.8a	916.0	58.0ef	638.0	7.1bc	482.0	28.3de	2586	19.8de
130	44	1833.5	110.5c	1099.5	43.8c	2728.4	186.8cde	735.5	131ab	799.9	54.2cd	610.4	36.7b	437.9	41.8cde	2399	122.8d
150	20	1445.0	173.9b	925.0	96.2b	1924.5	48.8a	558.0	2.8ab	617.5	43.1ab	467.0	25.5a	358.0	8.5b	1811	125.9b
150	40	2340.0	25.5e	1373.5	7.8e	3502.0	15.6f	800.5	21.9b	978.0	9.9f	793.5	2.1e	592.0	7.1f	3066	6.4f
158	30	1986.5	106.8cd	1223.0	41.0d	2630.5	71.4bcd	584.5	21.9ab	828.5	3.5de	634.5	0.7bc	425.0	14.1cd	2473	12.0de
		1540.5	14.8b	903.5	3.5b	2422.5	21.9b	678.5	20.5ab	710.5	9.2bc	511.0	2.8a	387.5	4.9bc	2079	14.1c
p		<0.0001		<0.0001		<0.0001		<0.0001		<0.0001		<0.0001		<0.0001		<0.0001	

Values in the same column with different lower-case letters (a-f) are significantly different at p<0.05.

Table 3.17. Changes in total typical, atypical, essential and non-essential amino acids

T (°C)	t (min)	Total typical amino acids (mg/100 g db)	Variation (%)	Total atypical amino acids (mg/100 g db)	Variation (%)	Total essential amino acid (mg/100 g db)	Variation (%)	Total Non- essential amino acid (mg/100 g db)	Variation (%)
Control		5275		4517		4349		9645	
102	30	4036	-23	3208	-29	3471	-20	7527	-22
110	20	6508	23	5590	24	5596	29	12751	32
110	40	5114	-3	4412	-2	4413	1	9494	-2
130	16	6163	17	5376	19	5328	22	11128	15
130	30	5801	10	4993	11	4911	13	10644	10
130	44	4351	-18	3763	-17	3873	-11	8106	-16
150	20	7457	41	6182	37	6018	38	13445	39
150	40	5904	12	5246	16	5301	22	10785	12
158	30	5054	-4	4175	-8	4457	2	9233	-4

Table 3.18. Effect of roasting time on essential amino acids (mg/100g, db) of roasted hazelnuts at different roasting temperatures

T (°C)	t (min)	Lysine		Leucine		Isoleucine		Threonine		Valine		Phenylalanine		Tyrosine		Methionine	
		AV	SD	AV	SD	AV	SD	AV	SD	AV	SD	AV	SD	AV	SD	AV	SD
110	20	562.5	10.6	1330.0	67.9	689.5	19.1	647.0	36.8	813.5	30.4	887.5	9.2	523.0	21.2	142.5	26.2
110	40	447.5	0.7	1035.0	2.8	557.0	1.4	458.5	4.9	708.0	0.0	682.5	3.5	425.0	2.8	99.5	0.7
	p	0.004		0.026		0.01		0.019		0.039		0.001		0.023		NS	
130	16	534.0	2.8c	1241.0	9.9b	651.0	5.7b	608.5	55.9b	780.0	9.9b	842.5	14.8b	500.0	2.8b	170.5	3.5
130	30	489.3	23.0b	1158.6	44.2b	590.8	37.6b	589.0	49.5b	717.6	38.5b	800.9	49.6b	415.9	79.7b	148.6	38.2
130	44	316.0	19.8a	949.0	76.4a	488.0	41.0a	455.5	55.9a	608.5	92.6a	623.0	55.2a	255.0	18.4a	177.5	13.4
	p	<0.0001		<0.0001		0.004		0.021		0.013		0.002		0.019		NS	
150	20	575.0	2.8	1569.5	10.6	647.5	0.7	726.5	3.5	803.0	1.4	1022.5	3.5	441.5	2.1	232.0	1.4
150	40	571.0	5.7	1249.5	12.0	654.5	4.9	599.0	42.4	761.0	35.4	862.0	7.1	380.0	7.1	223.5	4.9
	p	<0.0001		<0.0001		0.001		0.003		0.0138		<0.0001		0.002		<0.0001	

Values in the same column with different lower-case letters (a-c) are significantly different at p<0.05.

Table 3.19. Effect of roasting time on non-essential amino acids (mg/100g, db) of roasted hazelnuts at different roasting temperatures

T (°C)	t (min)	Aspartic acid		Serine		Glutamic acid		Proline		Glycine		Alanine		Histidine		Arginine	
		AV	SD	AV	SD	AV	SD	AV	SD	AV	SD	AV	SD	AV	SD	AV	SD
110	20	2119.5	82.7	1177.0	48.1	3008.0	120.2	1619.0	41.0	970.5	99.7	684.5	33.2	492.5	7.8	2680	28.3
110	40	1574.5	0.7	955.0	11.3	2478.0	17.0	759.0	188.1	705.5	2.1	517.5	7.8	378.5	0.7	2126	4.2
	p	0.011		0.024		0.025		0.024		NS		0.02		0.002		0.001	
130	16	1923.5	73.8b	1147.5	84.1b	2915.0	91.9b	519.5	48.8	916.0	58.0c	638.0	7.1b	482.0	28.3b	2586	19.8b
130	30	1833.5	110.5b	1099.5	43.8b	2728.4	186.8b	735.5	131.1	799.9	54.2b	610.4	36.7b	437.9	41.8b	2399	122.8b
130	44	1445.0	173.9a	925.0	96.2a	1924.5	48.8a	558.0	2.8	617.5	43.1a	467.0	25.5a	358.0	8.5a	1811	125.9a
	p	0.004		0.007		<0.0001		NS		0.001		0.001		0.027		<0.0001	
150	20	2340.0	25.5	1373.5	7.8	3502.0	15.6	800.5	21.9	978.0	9.9	793.5	2.1	592.0	7.1	3066	6.4
150	40	1986.5	106.8	1223.0	41.0	2630.5	71.4	584.5	21.9	828.5	3.5	634.5	0.7	425.0	14.1	2473	12.0
	p	0.003		0.001		<0.0001		0.005		<0.0001		<0.0001		<0.0001		<0.0001	

Values in the same column with different lower-case letters (a-c) are significantly different at p<0.05.

Table 3.20. Effect of roasting temperature on essential amino acids (mg/100g, db) of roasted hazelnuts at different roasting time

t (min)	T (°C)	Lysine		Leucine		Isoleucine		Threonine		Valine		Phenylalanine		Tyrosine		Methionine	
		AV	SD	AV	SD	AV	SD	AV	SD	AV	SD	AV	SD	AV	SD	AV	SD
20	110	562.5	10.6	1330.0	67.9	689.5	19.1	647.0	36.8	813.5	30.4	887.5	9.2	523.0	21.2	142.5	26.2
20	150	575.0	2.8	1569.5	10.6	647.5	0.7	726.5	3.5	803.0	1.4	1022.5	3.5	441.5	2.1	232.0	1.4
P		NS		0.026		NS		NS		NS		0.003		0.033		0.04	
30	102	361.5	0.7a	830.5	21.9a	449.5	19.1a	328.5	31.8a	581.5	46.0a	543.0	18.4a	281.0	67.9	95.0	5.7a
30	130	489.3	23.0b	1158.6	44.2c	590.8	37.6b	589.0	49.5c	717.6	38.5b	800.9	49.6c	415.9	79.7	148.6	38.2ab
30	158	345.0	2.8a	1059.5	2.1b	590.0	2.8b	443.0	2.8b	746.5	2.1b	703.5	4.9b	404.0	1.4	165.0	1.4b
P		<0.0001		<0.0001		0.002		<0.0001		0.002		<0.0001		NS		NS	
40	110	447.5	0.7	1035.0	2.8	557.0	1.4	458.5	4.9	708.0	0.0	682.5	3.5	425.0	2.8	99.5	0.7
40	150	571.0	5.7	1249.5	12.0	654.5	4.9	599.0	42.4	761.0	35.4	862.0	7.1	380.0	7.1	223.5	4.9
P		0.001		0.002		0.001		0.043		NS		0.001		0.014		0.001	

Values in the same column with different lower-case letters (a-c) are significantly different at p<0.05.

Table 3.21. Effect of roasting temperature on non-essential amino acids (mg/100g, db) of roasted hazelnuts at different roasting temperatures

t (min)	T (°C)	Aspartic acid		Serine		Glutamic acid		Proline		Glycine		Alanine		Histidine		Arginine	
		AV	SD	AV	SD	AV	SD	AV	SD	AV	SD	AV	SD	AV	SD	AV	SD
20	110	2119.5	82.7	1177.0	48.1	3008.0	120.2	1619.0	41.0	970.5	99.7	684.5	33.2	492.5	7.8	2680	28.3
20	150	2340.0	25.5	1373.5	7.8	3502.0	15.6	800.5	21.9	978.0	9.9	793.5	2.1	592.0	7.1	3066	6.4
p		NS		0.029		0.029		0.002		NS		0.044		0.006		0.003	
30	102	1214.0	60.8a	716.0	1.4a	1997.0	55.2a	690.5	150.6	521.0	73.5a	586.0	12.7b	281.5	2.1a	1521	203.6a
30	130	1833.5	110c	1099.5	43.8c	2728.4	186.8b	735.5	131.1	799.9	54.2b	610.4	36.7b	437.9	41.8b	2399	122.8c
30	158	1540.5	14.8b	903.5	3.5b	2422.5	21.9b	678.5	20.5	710.5	9.2b	511.0	2.8a	387.5	4.9b	2079	14.1b
p		<0.0001		0.001		<0.0001		NS		<0.0001		0.012		0.002		<0.0001	
40	110	1574.5	0.7	955.0	11.3	2478.0	17.0	759.0	188.1	705.5	2.1	517.5	7.8	378.5	0.7	2126	4.2
40	150	1986.5	106.8	1223.0	41.0	2630.5	71.4	584.5	21.9	828.5	3.5	634.5	0.7	425.0	14.1	2473	12.0
p		0.032		0.012		NS		NS		0.001		0.002		0.043		0.001	

Values in the same column with different lower-case letters (a-c) are significantly different at p<0.05.

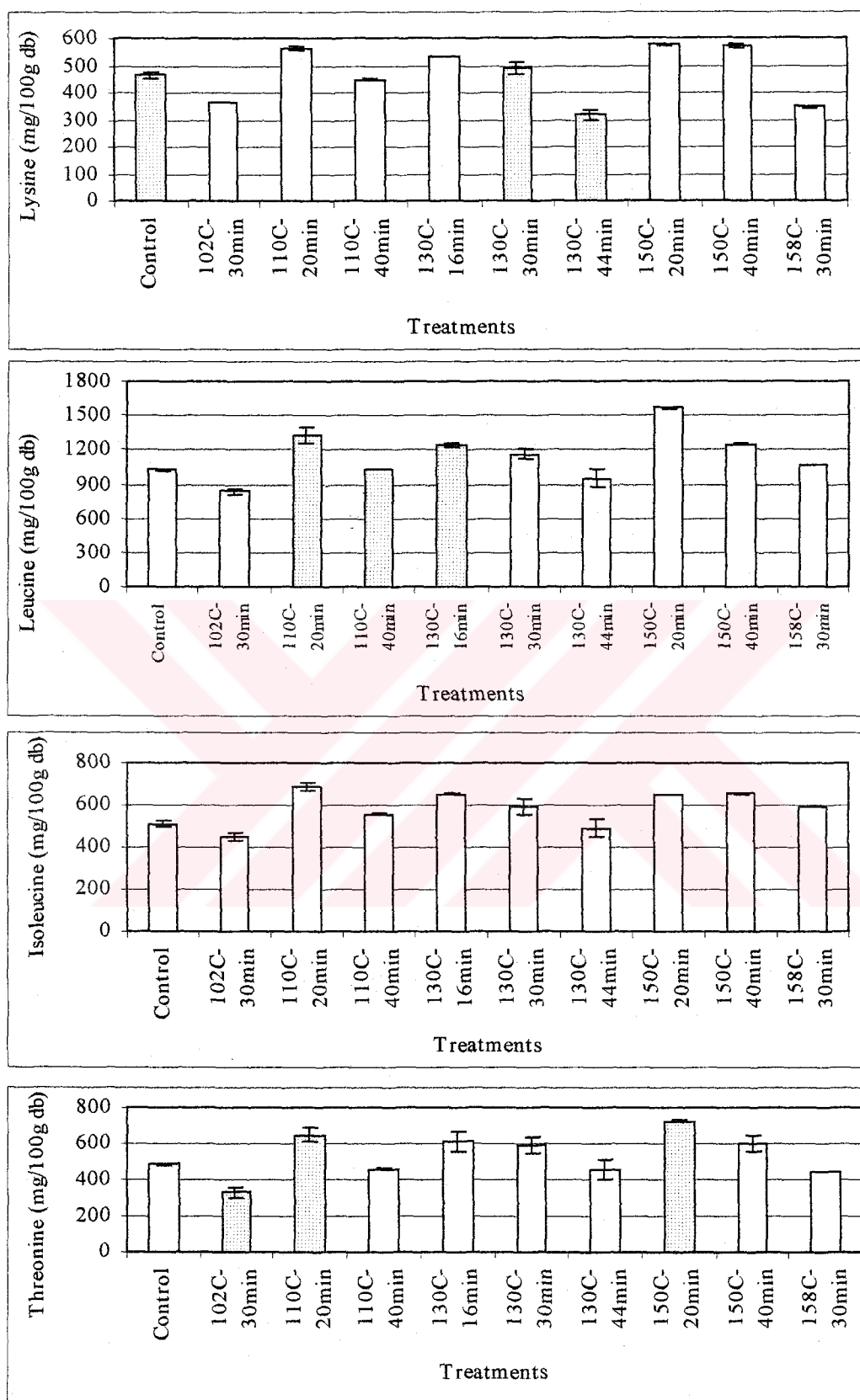


Figure 3.25. (a) Changes in essential amino acids of hazelnuts during roasting

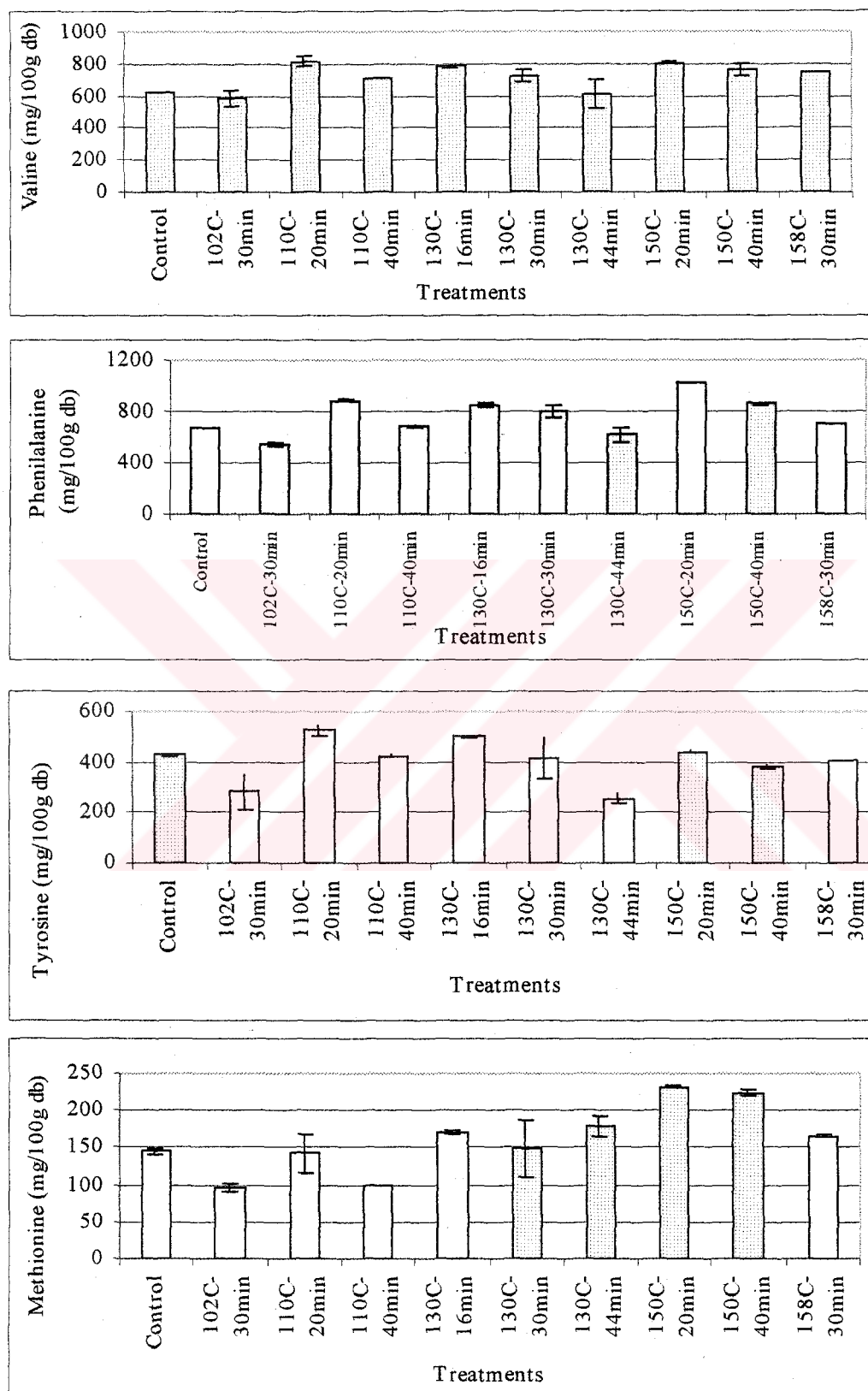


Figure 3.25. (b) Changes in essential amino acids of hazelnuts during roasting

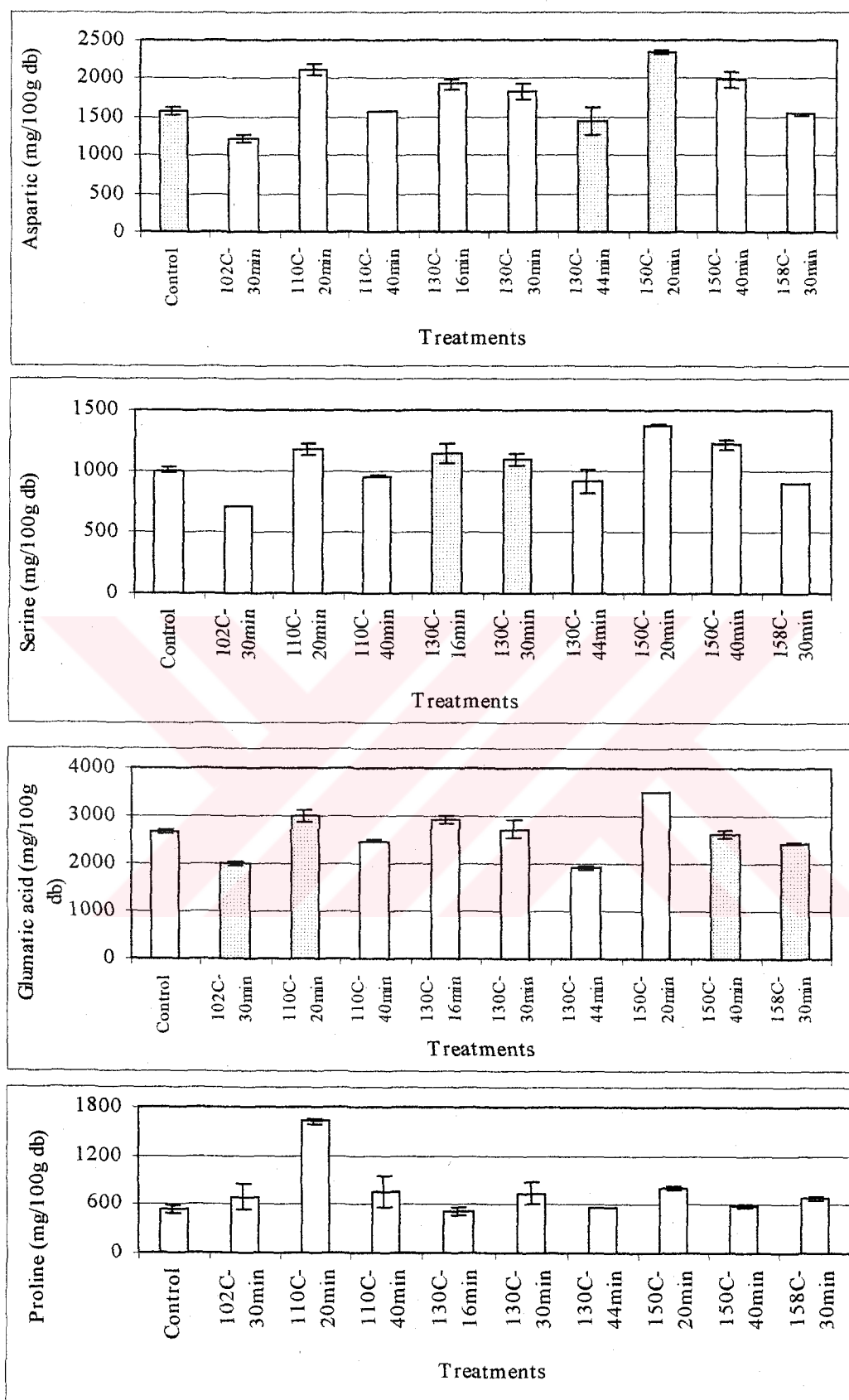


Figure 3.26. (a) Changes in non-essential amino acids of hazelnuts during roasting

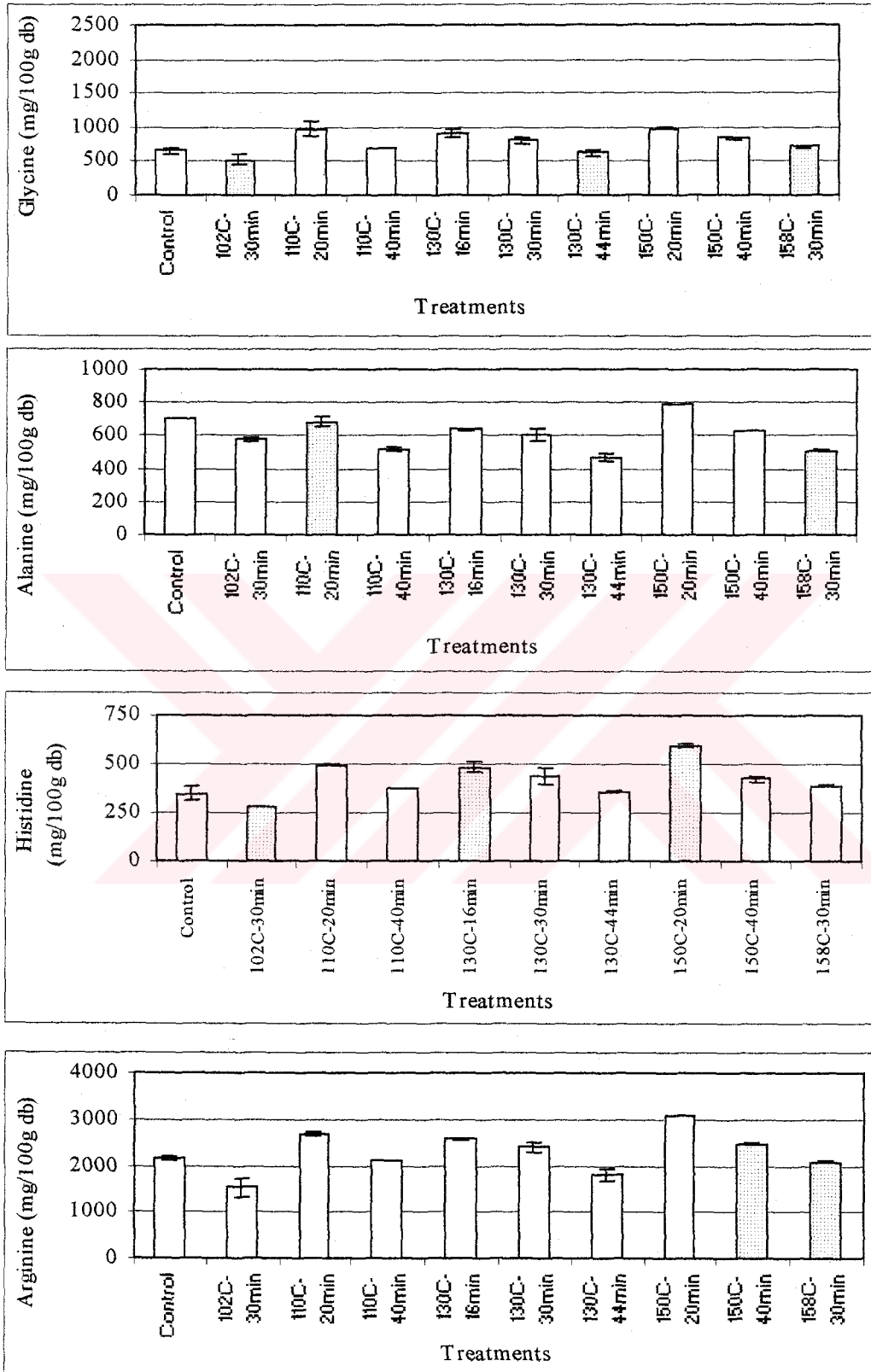


Figure 3.26. (b) Changes in non-essential amino acids of hazelnuts during roasting

Total typical (Aspartic acid, glutamic acid, phenylalanine and histidine), atypical (Threonine, tyrosine, lysine), essential and non-essential amino acids increased in the early stages of the roasting but decreased during prolonged roasting (Table 3.17.). Among the non-essential amino acids, glutamic acid, aspartic acid and arginine, accounting about 45% of the total amino acids, also increased in the early stages of the roasting, and then decreased at the later stages of roasting (Table 3.16.). Since most of the moisture is evaporated within the first 20 min of roasting, polypeptides are hydrolyzed to release amino acids in this period. The longer roasting time bring about decrease in amino nitrogen content through involvement in flavor development reactions (Chiou *et al.*, 1991a).

Roasting time significantly affected essential and non-essential amino acids generally at $p < 0.0001$ level (Table 3.18., Table 3.19.). The results indicated that the longer roasting at the same roasting temperature decreased amino acid more (Table 3.18., Table 3.19.). Among the essential amino acids lysine, tyrosine and methionine levels decreased more than 30% compared to control sample when roasted longer (Table 3.18.). Among the essential amino acids only methionine content did not significantly effect by the roasting time at 110°C and 130°C but longer roasting time also resulted in a lower methionine in the samples roasted at 150°C (Table 3.18.). Among the non-essential amino acids alanine, arginine and glutamic acid levels decreased more than 15% compared to control sample when roasted longer (Table 3.18.). Similarly among the non-essential amino acids glycine at 110°C and proline at 130°C did not significantly differ when roasted for a longer time (Table 3.19.). Kırbaşlar (1998) also reported a significant loss of total amino acids of hazelnuts roasted at 135°C for longer than 20 min. The losses were higher in essential amino acids compared to non-essential amino acids. Losses in essential amino acids were 10% and 61.7% in 20 min and 30 min roasting, respectively. Losses in non-essential amino acids were 5% and 22%, in 20 min and 30 min roasting, respectively (Kırbaşlar, 1998). Roasting time also reduced most of the free essential amino acids, namely lysine, methionine+cystine, isoleucine, valine, leucine, phenylalanine, tyrosine content of lupin seed during roasting at 80-90°C up to 40 min. Among the non-essential amino acids, only free arginine decreased significantly upon

roasting for a longer time (Yanez *et al.*, 1986). Lysine loss in the roasted maize (26.7%) and in the roasted sunflower (31.1%) was also reported by Ayatse *et al.*, (1983) and Madhusudhan *et al.*, (1986), respectively. The loss in lysine was attributed to Maillard reaction (Madhusudhan *et al.*, 1986). Moreover, large decreases in glutamic acid and a peptide were observed in roasted peanuts (Qupadissakoon & Young, 1984). Ayatse *et al.*, (1983) also reported a decrease in the levels of most amino acids, and an increase methionine (36%) and proline (15%) in the roasted maize. The losses in amino acids of roasted maize was previously related with thermal destruction (Ayatse *et al.*, 1983).

Roasting temperature significantly affected essential and non-essential amino acids generally at $p < 0.0001$ level as shown Table 3.20. and Table 3.21. Except for tyrosine, essential amino acids were significantly higher at the higher roasting temperature for the samples roasted for 20 min or 40 min (Table 3.20.). For 30 min roasting, samples roasted at 130°C contained equal to or more essential amino acids than the samples roasted at 158°C and 102°C. Similarly, except for proline, non-essential amino acids were higher at the higher roasting temperature for the samples roasted for 20 min or 40 min (Table 3.21.). Moreover, trend in non-essential amino acids of the roasted samples for 30 min was also the like that of essential amino acids: samples roasted at 130°C contained equal to or more non-essential amino acids than the samples roasted at 158°C and 102°C. Increase in methionine, histidine and phenylalanine during roasting of hazelnuts; and some free amino acids of cysteine, tyrosine and phenylalanine during coconut roasting were also observed by Özdemir *et al.*, (2000b), and Jayalekshmy & Mathew (1990), respectively. The reason of the increase in the some of total amino acids during early stages of roasting is, however, unexplained.

The changes in amino acids may be attributed to hydrolysis of polypeptides, resulting in an increase, and subsequently undergoing a series of chemical reactions that results in a decrease (Chiou *et al.*, 1991a). Lower amino acid and sucrose content at darker colored samples were also observed by Chiou (1992) and darker color was also related to higher anti-oxidant activity in the roasted peanuts (Chio *et al.*, 1991b; Chio, 1992).

3.6 Effect of Roasting Conditions on PV and FFA Content of Hazelnuts During Roasting

Results of ANOVA and Duncan test for free fatty acid content (FFA) and peroxide value (PV) content of roasted hazelnuts just after roasting were given in Table 3.22. , and Table 3.23. and Table 3.24. for experimental data, effect of time and effect of temperature, respectively. Moreover experimental data also given as figure in Figure 3.27. The results showed that there was a significant difference between treatments for FFA content at $p < 0.0001$ except for PV (Table 3.22.). PV was not found in the control sample and in the roasted samples just after roasting. Jung *et al.*, (1997) also reported zero PV in the roasted soybean oils. Moreover, Perren & Escher (1996b) stated that radicals or peroxides formed prior to roasting are either destroyed or continue to reaction during roasting.

Duncan test between treatments indicated that FFA content of control was significantly higher than that of roasted samples. The lower FFA in the roasted samples compared to that of control may be attributed to oxidation of formed free fatty acids through oxidation reactions to peroxidized free fatty acids (Seyhan & Özdemir, 1999). Roasting time and temperature significantly affected FFA content of roasted samples at $p < 0.01$ or higher levels as shown Table 3.23.

The longer roasting time and temperature produced higher FFA (Table 3.23., Table 3.24.). But higher FFA in the samples roasted at higher temperature and/or longer time could be due to presence of more anti-oxidative non-enzymatic browning reaction products, lowering rate of oxidation of free fatty acids to peroxidized free fatty acids through oxidation reactions (Nicoli *et al.*, 1997). Lopez *et al.*, (1997c) also observed higher FFA at higher temperatures (above 50°C) during drying of hazelnuts. FFA of the samples were lower than 0.5-0.7% which was indication of onset of rancidity (Radtke & Heiss, 1971; Harris *et al.*, 1972; Hadorn *et al.*, 1977; Keme *et al.*, 1983a; Lopez *et al.*, 1997c) and lower than limit (1-1.3%) given in the Turkish Standards (TS-1917, 1993).

Table 3.22. Analysis of changes in FFA and PV content of roasted hazelnuts with ANOVA

T (°C)	t (min)	PV (meq/kg)		FFA (% of oleic acid)	
		AV	SD	AV	SD
Control		0.0	0.0	0.093	0.001e
102	30	0.0	0.0	0.042	0.001a
110	20	0.0	0.0	0.044	0.001a
110	40	0.0	0.0	0.051	0.000b
130	16	0.0	0.0	0.042	0.001a
130	30	0.0	0.0	0.043	0.00a
130	44	0.0	0.0	0.053	0.000bc
150	20	0.0	0.0	0.060	0.001cd
150	40	0.0	0.0	0.067	0.001d
158	30	0.0	0.0	0.057	0.003c
p		NS		<0.0001	

Values in the same column with different lower-case letters (a-f) are significantly different at $p < 0.05$.

Table 3.23. Effect of roasting time on FFA content of roasted hazelnuts

T (°C)	t (min)	FFA (% of oleic acid)	
		AV	SD
110	20	0.044	0.001
110	40	0.051	0.0001
	P		0.002
130	16	0.042	0.001a
130	30	0.043	0.001a
130	44	0.053	0.0001b
	P		0.004
150	20	0.060	0.001
150	40	0.067	0.001
	P		0.023

Values in the same column with different lower-case letters (a-c) are significantly different at $p < 0.05$.

Table 3.24. Effect of roasting temperature on FFA content of roasted hazelnuts

t (min)	T (°C)	FFA (% of oleic acid)	
		AV	SD
20	110	0.044	0.001
20	150	0.060	0.001
	P		0.0023
30	102	0.042	0.001a
30	130	0.043	0.00a
30	158	0.057	0.003b
	P		<0.0001
40	110	0.051	0.0001
40	150	0.067	0.001
	p		0.001

Values in the same column with different lower-case letters (a-c) are significantly different at $p<0.05$.

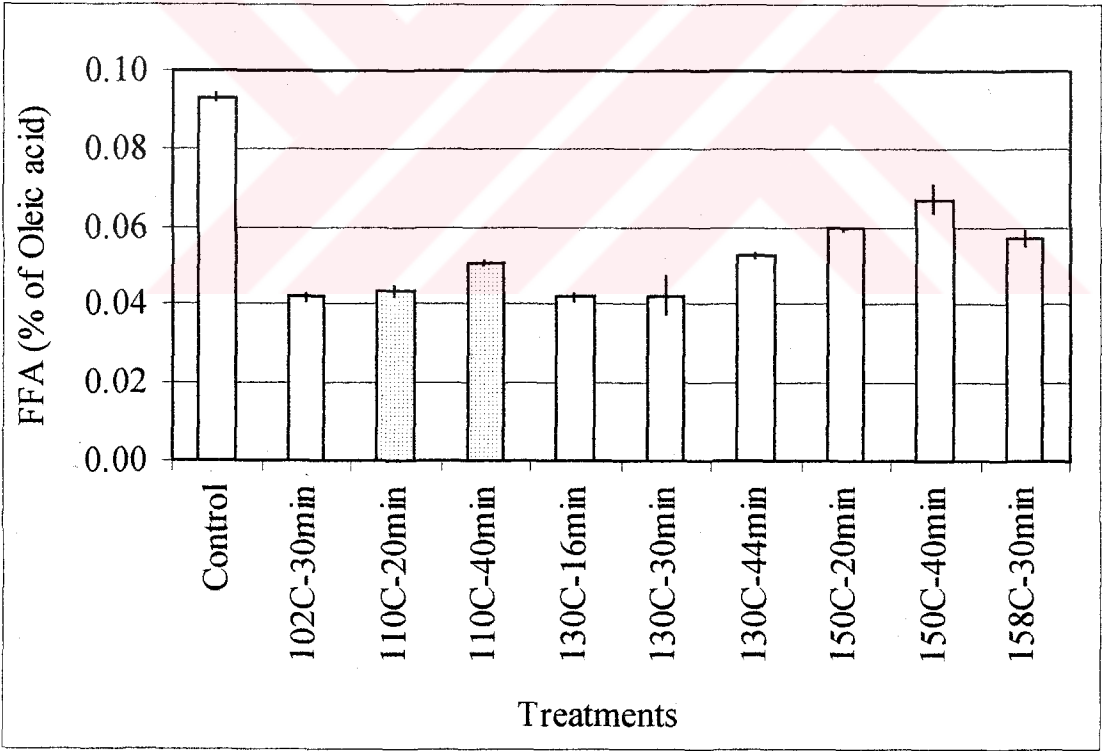


Figure 3.27. FFA content of roasted hazelnuts

3.7 Effect of Storage at 37°C for 1 Month on the Stability of Roasted Hazelnuts

Roasted samples were also stored at 37°C for 1 month and fatty acid composition, PV and FFA of the stored samples were determined at the end of storage as shown in Table 3.25. and in Figure 3.28. - Figure 3.31. PV of the roasted samples was higher than that of control and raw sample at the end of storage. The roasted samples obtained higher PV with increasing roasting degree at the end of storage (Table 3.25.) which was also observed in the study of Mostafa (1987) for peanuts. The increase in PV of samples was attributed to the formation and accumulation of hydroperoxides (Fourie & Basson, 1989). PV was above 2 meq/kg only in the samples roasted at 158°C for 30 min at the end of the storage. Above PV of 2 meq/kg rancid flavors were determined in the roasted hazelnuts (Richardson & Ebrahim, 1996). PV in the samples was, nevertheless, considerably lower than flavor quality endpoint (8 meq/kg) (Braddock *et al.*, 1995), and lower than limit (7-8 meq/kg) given in the Turkish Standards (TS-1917, 1993).

Roasting time significantly affected PV of stored samples, roasted at 110°C and 130°C at $p < 0.01$ or higher levels as shown in Table 3.26. The longer roasting time generally resulted in the higher PV content at the end of storage for the samples, roasted at 110°C and 130°C. There was no significant difference between roasting time at 150°C for PV at the end of storage. Roasting temperature significantly affected PV content at the end of the storage at $p < 0.01$ or higher levels as shown in Table 3.27. The higher roasting temperature produced the higher PV at the end of the storage (Table 3.27.). Roasting at 158°C for 30 min obtained the highest PV (4.94 meq/kg) at the end of storage. Roasting at 102°C for at 30 min resulted in the lowest PV at the end of the storage (0.17 meq/kg) (Table 3.27.). The results are in agreement with that of Richardson & Ebrahim (1996) who investigated PV of the roasted hazelnuts in the samples just after three days after roasting and after 2 months of storage in which storage conditions and PV of unroasted hazelnut was not indicated. The roasting temperature and roasting times were in the range of 93.3°C – 176.7°C and 10 min - 40 min, respectively. The PV was in the range of 0.72 and 3.37 meq/kg in the samples stored for three days. The range was 1.15 to 19.9 meq/kg in the stored for 2 months.

Table 3.25. Analysis of changes in PV, FFA and fatty acid composition of roasted hazelnuts stored at 37°C for 1 month with ANOVA

ANOVA		Fatty acids (% of total oil)													
T (°C)	t (min)	PV (meq/kg)	FFA		Palmitic		Palmitoleic		Stearic		Oleic		Linoleic		
			(% of oleic acid)		Palmitic		Palmitoleic		Stearic		Oleic		Linoleic		
			AV	SD	AV	SD	AV	SD	AV	SD	AV	SD	AV	SD	
Control*		0.0	0.0a	0.093	0.001c	5.08	0.01a	0.15	0.01ab	1.30	0.06a	81.11	0.39a	12.43	0.40f
Raw		0.31	0.003c	0.207	0.01d	5.13	0.08a	0.15	0.01ab	1.94	0.08b	84.42	0.42e	8.37	0.43e
102	30	0.17	0.001b	0.069	0.05bc	6.40	0.05f	0.177	0.02d	2.79	0.01c	84.09	0.07cde	6.55	0.02a
110	20	0.82	0.028f	0.010	0.001a	6.03	0.17de	0.155	0.01bc	1.99	0.04b	84.47	0.04e	7.36	0.18c
110	40	0.87	0.050f	0.066	0.001bc	5.48	0.01bc	0.147	0.01ab	2.87	0.02c	83.81	0.02c	7.70	0.01d
130	16	0.42	0.009d	0.070	0.001bc	6.30	0.27ef	0.157	0.01bc	2.69	0.04c	83.38	0.22b	7.47	0.02cd
130	30	0.44	0.08d	0.065	0.01bc	5.58	0.11bc	0.14	0.01a	2.85	0.21c	84.50	0.22e	6.93	0.12b
130	44	0.56	0.008e	0.050	0.001b	5.30	0.10ab	0.155	0.01bc	1.89	0.07b	84.36	0.08de	8.30	0.10e
150	20	1.83	0.029h	0.057	0.01b	6.36	0.49ef	0.173	0.02cd	2.65	0.05c	83.93	0.47cd	6.89	0.01b
150	40	1.72	0.121g	0.087	0.01c	6.36	0.33ef	0.167	0.01bcd	2.71	0.04c	83.86	0.31c	6.91	0.07b
158	30	4.95	0.03i	0.066	0.01bc	5.73	0.01cd	0.15	0.01ab	2.88	0.12c	84.20	0.16cde	7.04	0.01b
p		0.0001		0.0001		<0.0001		0.001		<0.0001		<0.0001		<0.0001	

*Prior to roasting experiments.
Values in the same column with different lower-case letters (a-f) are significantly different at p<0.05.

Table 3.26. Effect of roasting time on PV, FFA and fatty acid composition of roasted hazelnuts stored at 37°C for 1 month

T (°C)	t (min)	PV (meq/kg)		FFA (% of oleic acid)		Fatty acids (% of total oil)							
		AV SD		AV SD		Palmitic		Palmitoleic		Stearic		Oleic	
						AV	SD	AV	SD	AV	SD	AV	SD
110	20	0.82	0.028	0.01	0.001	6.03	0.17	0.16	0.01	1.99	0.04	84.47	0.04
110	40	0.87	0.050	0.07	0.001	5.48	0.01	0.15	0.01	2.87	0.02	83.81	0.02
	p	0.019		<0.0001		0.005		0.1		<0.0001		<0.0001	
130	16	0.42	0.009a	0.07	0.001b	6.30	0.27c	0.16	0.01	2.69	0.04b	83.38	0.22a
130	30	0.44	0.08a	0.065	0.01ab	5.58	0.11b	0.14	0.01	2.85	0.21b	84.50	0.22b
130	44	0.56	0.008b	0.05	0.001a	5.30	0.10a	0.16	0.01	1.89	0.07a	84.36	0.08b
	p	0.03		0.107		<0.0001		0.024		<0.0001		<0.0001	
150	20	1.83	0.029	0.06	0.01	6.36	0.49	0.17	0.02	2.65	0.05	83.93	0.47
150	40	1.72	0.121	0.09	0.01	6.36	0.33	0.17	0.01	2.71	0.04	83.86	0.31
	p	0.187		0.006		1		0.579		0.143		0.847	

Values in the same column with different lower-case letters (a-c) are significantly different at $p < 0.05$.

Table 3.27. Effect of roasting temperature on PV, FFA and fatty acid composition of roasted hazelnuts stored at 37°C for 1 month

T (°C)	t (min)	PV		FFA		Fatty acids (% of total oil)											
		(meq/kg)		(% of oleic acid)		Palmitic		Palmitoleic		Stearic		Oleic		Linoleic			
		AV	SD	AV	SD	AV	SD	AV	SD	AV	SD	AV	SD	AV	SD		
20	110	0.82	0.028	0.01	0.001	6.03	0.17	0.16	0.01	1.99	0.04	84.47	0.04	7.36	0.18		
20	150	1.83	0.029	0.06	0.01	6.36	0.49	0.17	0.02	2.65	0.05	83.93	0.47	6.89	0.01b		
	p	<0.0001		<0.0001		0.339		0.152		<0.0001		0.119		0.011			
30	102	0.17	0.001b	0.07	0.05	6.40	0.05c	0.18	0.02b	2.79	0.01d	84.09	0.07a	6.55	0.02a		
30	130	0.44	0.08a	0.065	0.01	5.58	0.11a	0.14	0.01a	2.85	0.21	84.50	0.22b	6.93	0.12b		
30	158	4.94	0.024c	0.07	0.01	5.78	0.01b	0.15	0.01a	2.92	0.14e	84.12	0.11a	7.04	0.01b		
	p	<0.0001		0.964		<0.0001		0.001		0.807		0.009		<0.0001			
40	110	0.87	0.050	0.07	0.001	5.48	0.01	0.15	0.01	2.87	0.02	83.81	0.02	7.70	0.01		
40	150	1.72	0.121	0.09	0.01	6.36	0.33	0.17	0.01	2.71	0.04	83.86	0.31	6.91	0.07		
	p	<0.0001		0.011		0.010		0.055		0.002		0.765		<0.0001			

Values in the same column with different lower-case letters (a-c) are significantly different at p<0.05.

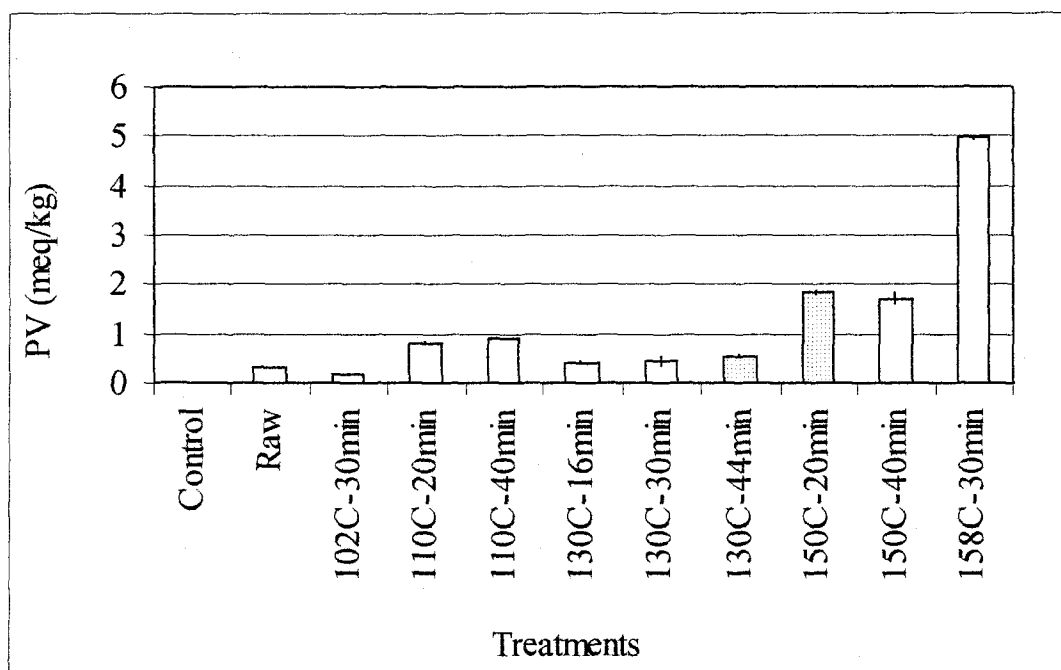


Figure 3.28. Changes in PV content of the samples after 1 month storage at 37°C

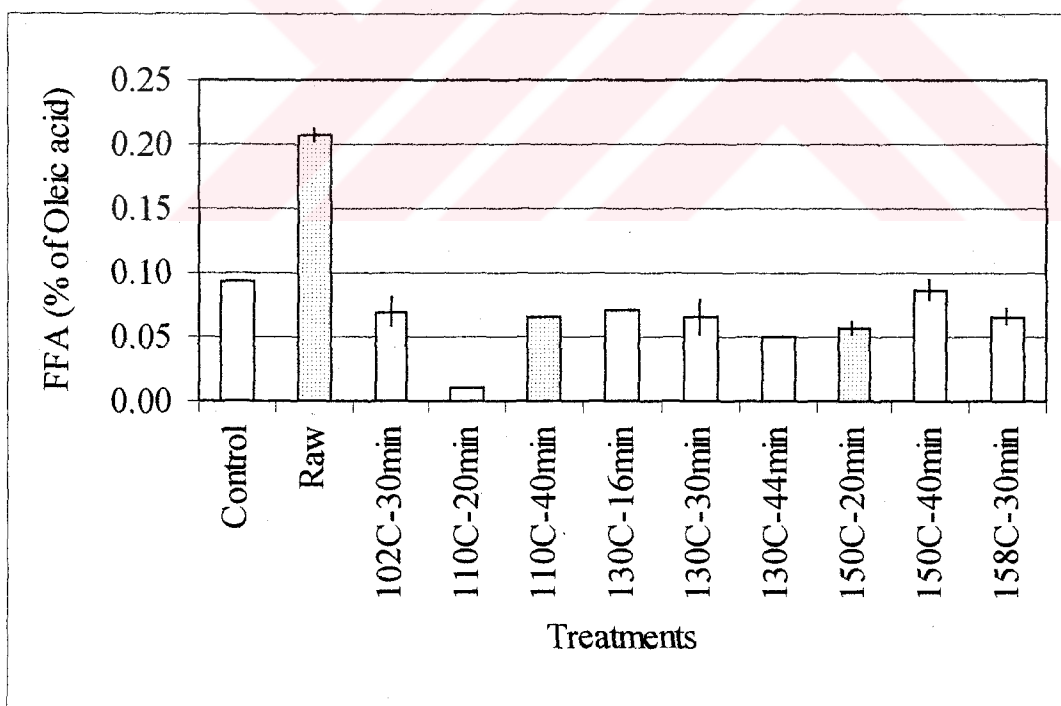


Figure 3.29. Changes in FFA content of the samples after 1 month storage at 37°C

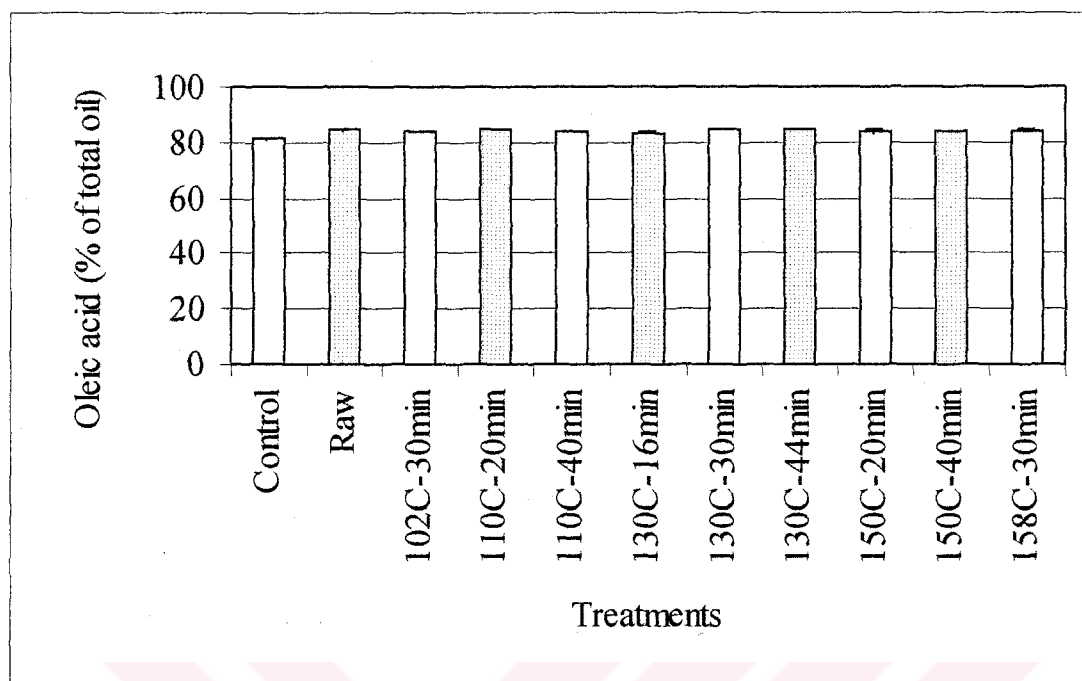


Figure 3.30. Changes in oleic acid content of the samples after 1 month storage at 37°C

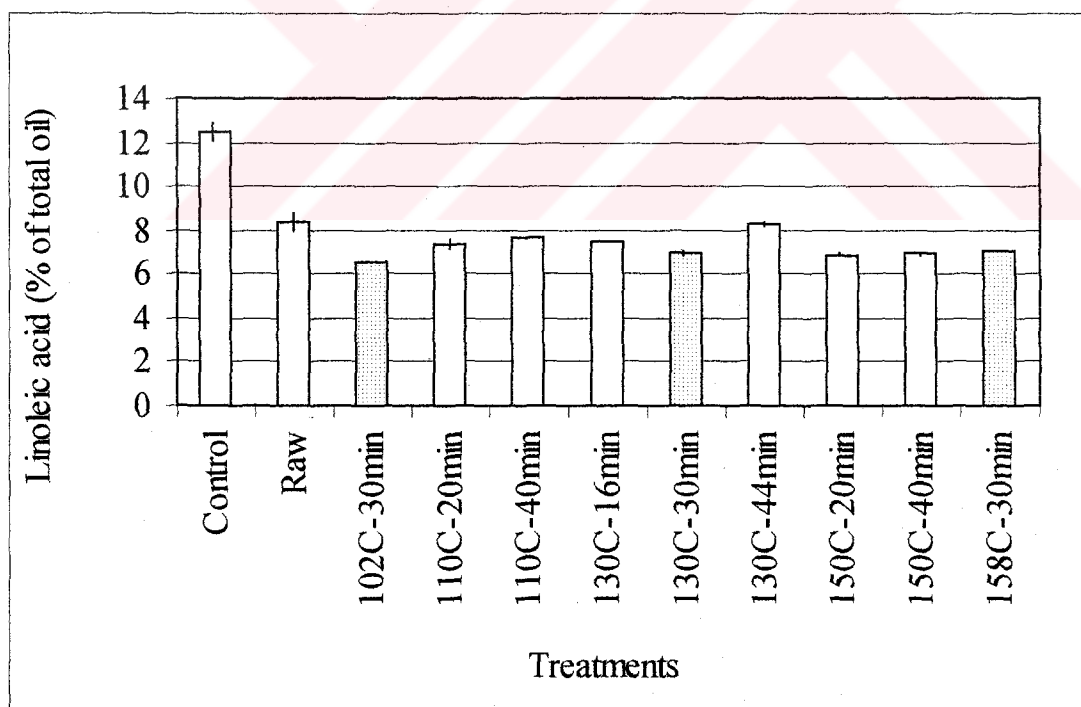


Figure 3.31. Changes in linoleic acid content of the samples after 1 month storage at 37°C

The higher roasting temperature and the longer time generally produced the higher PV values for the both sets of the samples (Richardson & Ebrahim, 1996). Similar results were reported for the roasted peanut oil (Mostafa, 1987). Moreover, it was reported that roasting temperature influences stability of roasted hazelnuts more compared to roasting time which may be attributed to destruction of micro-structure of the hazelnut cells and increased oxygen diffusion into to the hazelnut kernels (Perren & Escher, 1996c; Perren *et al.*, 1996a). However, non-enzymatic browning reaction products with their anti-oxidative properties may extend stability of roasted/dried hazelnuts (Perren & Escher, 1996c; Lopez *et al.*, 1997c). Moreover Chiou *et al.*, (1991b), Chiou (1992) and Lopez *et al.*, (1997c) stated that enhance of color formation renders kernels of peanut and hazelnuts with high oxidative stability, respectively. Similarly oxidative stability of soybean oils and sesame oils was significantly higher with increasing roasting temperature due to non-enzymatic browning reactions (Jung *et al.*, 1997; Yen & Shyu, 1989).

Roasting time significantly affected of FFA content of stored samples, roasted at 110°C and 150°C at $p < 0.001$ or higher levels (Table 3.26.). Roasting temperature significantly affected FFA content at the end of the storage at $p < 0.01$ or higher levels as shown in Table 3.27. The longer roasting time or the higher roasting temperature produced generally higher FFA at the end of the storage at all roasting temperature (Table 3.26.). The roasted samples obtained lower FFA than the raw and control sample at the end of storage (Table 3.25.). This may be due to reduced activity of lipase, peroxidase and esterase after roasting through enzyme-catalyzed lipid oxidation reactions (hydrolytic rancidity) (Grosch *et al.*, 1983; Keme *et al.*, 1983b; Perren & Escher, 1996b). The lower FFA in the roasted samples compared to that of control may also be attributed to oxidation of formed free fatty acids through oxidation reactions to peroxidized free fatty acids (Seyhan & Özdemir, 1999). But higher FFA in the samples roasted at higher temperature and/or longer time could be due to presence of more anti-oxidative non-enzymatic browning reaction products, lowering rate of oxidation of free fatty acids to peroxidized free fatty acids through oxidation reactions (Nicoli *et al.*, 1997). As

indicated above, Lopez *et al.*, (1997c) also observed higher FFA at higher temperatures (above 50°C) during drying of hazelnuts. Fluctuation in FFA was also observed in peanut oil during oil roasting of macadamia nut (Harris *et al.*, 1972). FFA in the samples were lower than 0.5-0.7% which was indication of onset of rancidity (Radtke & Heiss, 1971; Harris *et al.*, 1972; Hadorn *et al.*, 1977; Keme *et al.*, 1983a; Lopez *et al.*, 1997c), and lower than limit (1-1.3%) given in the Turkish Standards (TS-1917, 1993).

Changes in fatty acid composition were reported to be indirect measurement of lipid oxidation (Melton, 1983; Chiou, 1992; Maskan & Karataş, 1998). The stearic acid known to contribute to the stability of hazelnuts but oleic acid decreases stability of the hazelnuts. Oleic acid was stated to oxidize 10 times faster than stearic acid (O'Keefe *et al.*, 1993). The rates of oxidation of fatty acids for stearic acid (C_{18:0}), oleic acid (C_{18:1}), linoleic acid (C_{18:2}) and linolenic acid (C_{18:3}) was reported to be approximately 1:10:100:200, respectively (O'Keefe *et al.*, 1993). Previously, oleic acid and linoleic acid auto-oxidation was stated to main sources of the rancid substances in hazelnuts (Bergner *et al.*, 1974; Grosch *et al.*, 1983; Keme *et al.*, 1983b; Kinderlerer & Johnson, 1992). Therefore fatty acid composition of the roasted hazelnuts were also studied in the samples stored at 37°C for 1 month. ANOVA indicated that there was a significant difference between palmitic, palmitoleic, stearic, oleic and linoleic acid contents of samples at the end of storage (Table 3.25.). Relative proportion of linoleic acid of control was significantly higher than that of the raw and roasted at the end of storage. As expected relative proportion of the other fatty acids were affected accordingly (Table 3.25.). Linoleic acid decreased less as roasting degree increased which may be due to anti-oxidative effect of nonenzymatic browning reaction products. Chiou (1992) reported that linoleic acid content of the untreated unroasted peanut decreased from 39.42% total fatty acids to below 0.5% total fatty acids at the end of storage at 62°C for 40 days. Subsequently, relative proportion of other fatty acids, i.e., palmitic, stearic, eicosenoic acids, increased. But linoleic acid content of treated roasted peanuts remained unchanged at the end of the storage due to anti-oxidative factors produced

during roasting. Özdemir *et al.*, (2000b) also reported about changes in palmitic, stearic and oleic acid proportions and around 13% decrease in linoleic acid content of roasted hazelnuts stored at room temperature for 12 weeks. Similar findings were also reported for storage of raw hazelnut, raw pistachio nuts and roasted soybean oil by Kinderlerer & Johnson, (1992), Maskan & Karataş, (1998) and Jung *et al.*, (1997), respectively.

3.8 Consumer acceptance test

Results of the consumer acceptance test were summarized in Table 3.28. Analysis of the results using ANOVA indicated that there was a significant difference at $p < 0.005$ between samples in terms of color, flavor, texture and overall evaluation (Table 3.28.). Samples very light roasted (102°C for 30 min) and very dark (150°C for 40 min, 158°C for 30 min) roasted samples obtained significantly lower color, flavor, texture and overall scores than the others. In addition sample roasted at 110°C for 20 min obtained significantly lower color, texture and overall scores than the others.

Table 3.28. Analysis of consumer acceptance test with ANOVA.

T (°C)	t (min)	Color		Flavor		Texture		Overall Evaluation	
		AV	SD	AV	SD	AV	SD	AV	SD
102	30	5.86	1.53abc	5.61	1.93abc	5.71	1.94ab	5.64	1.68bc
110	20	6.11	1.55bc	5.61	1.66abc	5.64	1.50a	5.75	1.55bc
110	40	6.43	1.77c	6.57	1.71c	7.11	1.03c	6.68	1.28d
130	16	6.39	1.50bc	6.71	1.49c	6.54	1.43bc	6.46	1.53cd
130	30	6.57	1.03c	6.64	1.66c	6.79	1.17c	6.86	1.01d
130	44	6.57	1.67c	6.39	1.93bc	6.82	1.70c	6.79	1.69d
150	20	6.14	1.63bc	6.43	1.81bc	6.75	1.65c	6.54	1.64cd
150	40	5.50	2.06ab	5.46	2.15ab	6.82	1.59c	5.39	2.13ab
158	30	5.07	1.86a	4.61	1.93a	5.75	1.67ab	4.61	1.93a
p		0.006		<0.0001		<0.0001		<0.0001	

Values in the same column with different lower-case letters (a-f) are significantly different at $p < 0.05$

Samples having a mean score of 6.05 was evaluated as acceptable (Saklar, 1999). Color, flavor, texture and overall evaluation scores of samples roasted at 102°C for 30 min, at 110°C for 20 min (excluding color) at 150°C for 40 min (excluding texture) and at 158°C for 30 min was lower than acceptance criteria of 6.05 (See Table 3.28.). Texture of the sample roasted at 150°C for 40 min was among the highest scores, indicating very liked texture. But texture of the sample roasted at 110°C for 20 min was among the lowest scores, indicating a disliked texture. Therefore consumers preferred samples roasted at 110°C for 40 min, at 130°C for 16 min; at 130°C for 30 min; at 130°C for 44 min and at 150°C for 20 min during the overall evaluations.

Samples roasted at 102°C for 30 min, at 110°C for 20 min (excluding color), at 150°C for 40 (excluding texture), at 158°C for 30 (excluding flavor and overall evaluation) were in the category of neither liked nor dislike, having a mean score of 5.05-5.99 (Table 3.28.). Flavor and overall evaluation scores of samples roasted at 158°C for 30 were below 5 which indicates a dislike category. The reasons of not liking the sample roasted at 102°C for 30 min and 110°C for 20 min were stated to be its pale color, low aroma and hard texture. The reasons of not liking the sample roasted at 150°C for 40 min and at 158°C for 30 min were stated to be its burnt and/or rancid flavor and dark color. Saklar (1999) also stated that very light roasted (125°C, 1 m/s, 15 min) and very dark roasted (165 °C, 3 m/s, 25 min) obtained the lowest scores and were in the dislike category. Light roasted hazelnuts (125°C, 3 m/s, 15 min; 145°C, 2 m/s, 12 min; 111°C, 2 m/s, 20 min; 125 °C, 1 m/s, 25 min) were in the category of neither liked nor dislike (Saklar, 1999). Medium roasted (145°C, 2 m/s, 28 min; 165°C, 1 m/s, 25 min; 145°C, 3.7 m/s, 20 min) hazelnuts obtained the highest scores (Saklar, 1999)

Scores given by the consumer for color, flavor, texture and overall of each samples were also summed so as to find out total score of each attribute of each sample, as shown in the Figure 3.32 - Figure 3.35.

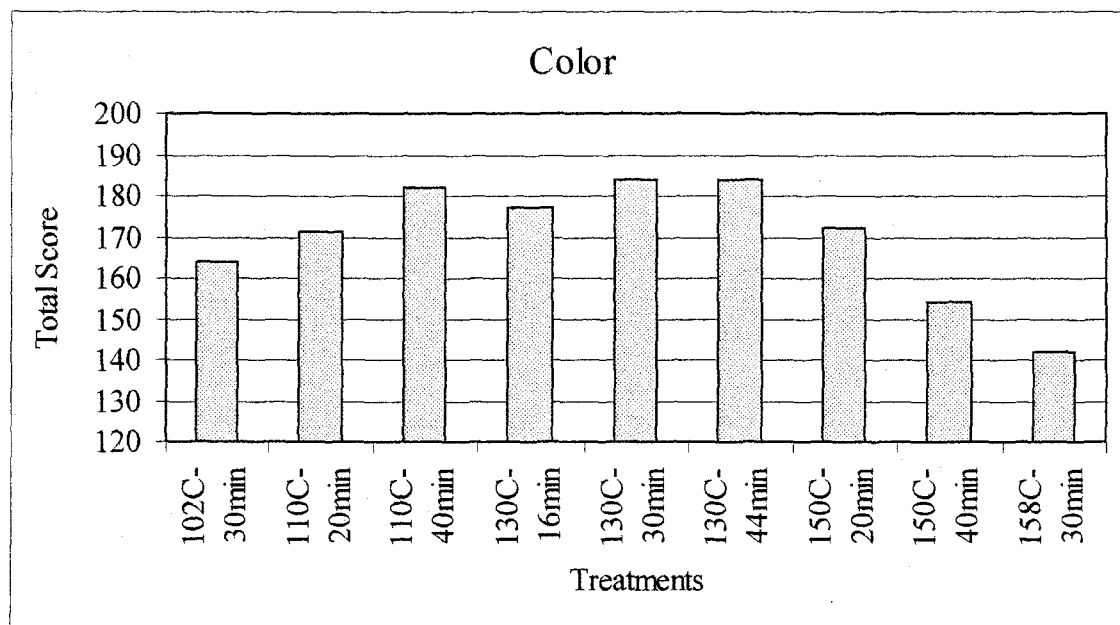


Figure 3.32. Total score of color of the samples in the consumer acceptance test

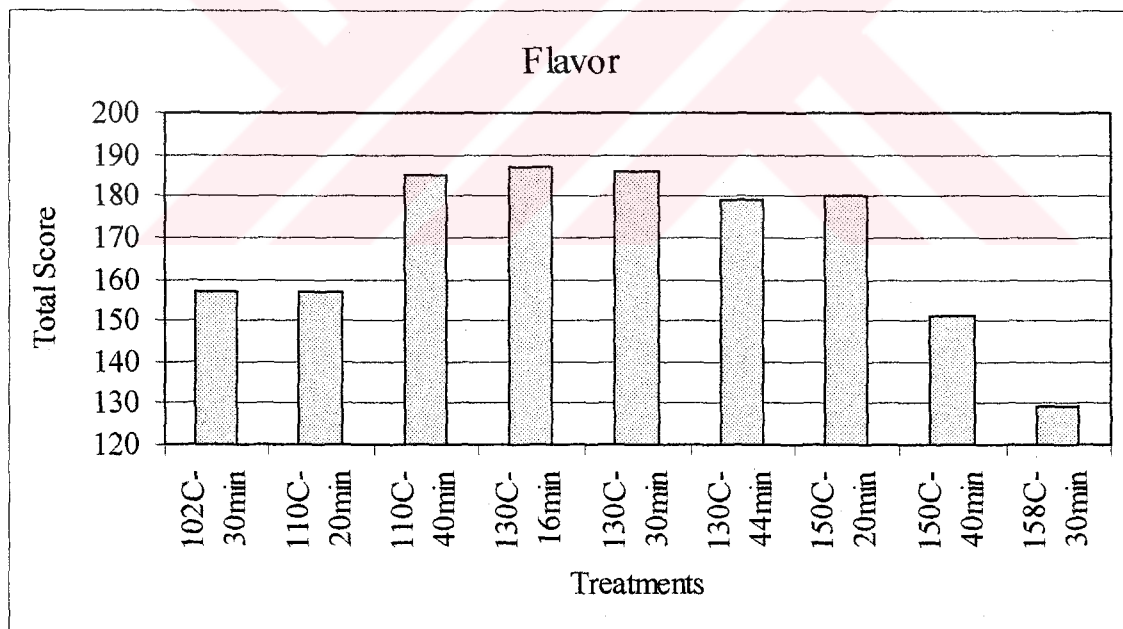


Figure 3.33. Total score of flavor of the samples in the consumer acceptance test

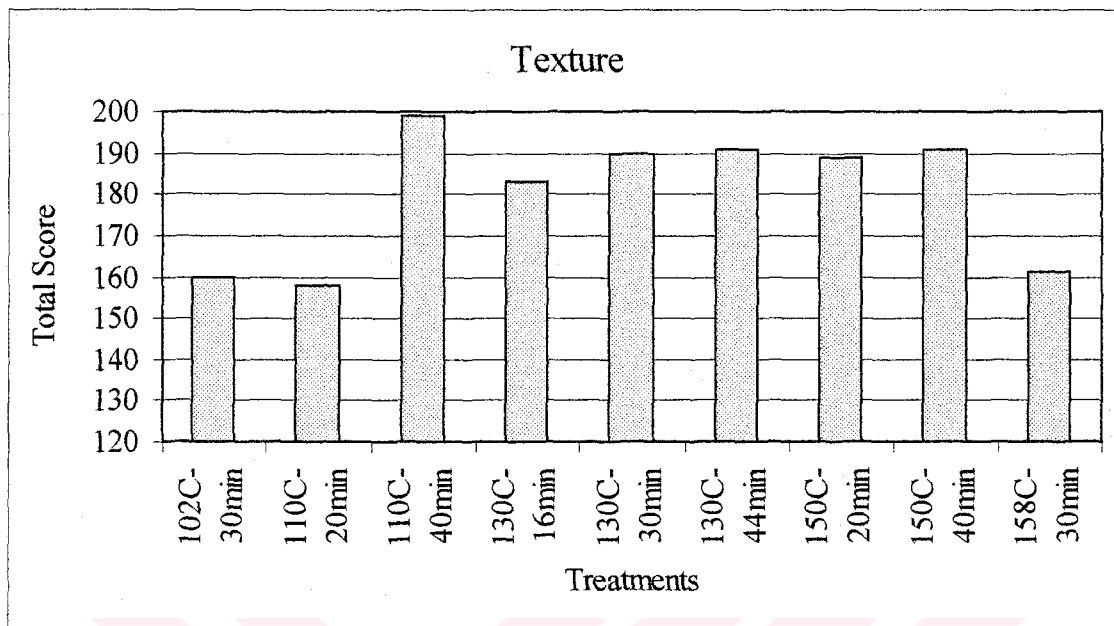


Figure 3.34. Total score of texture of the samples in the consumer acceptance test

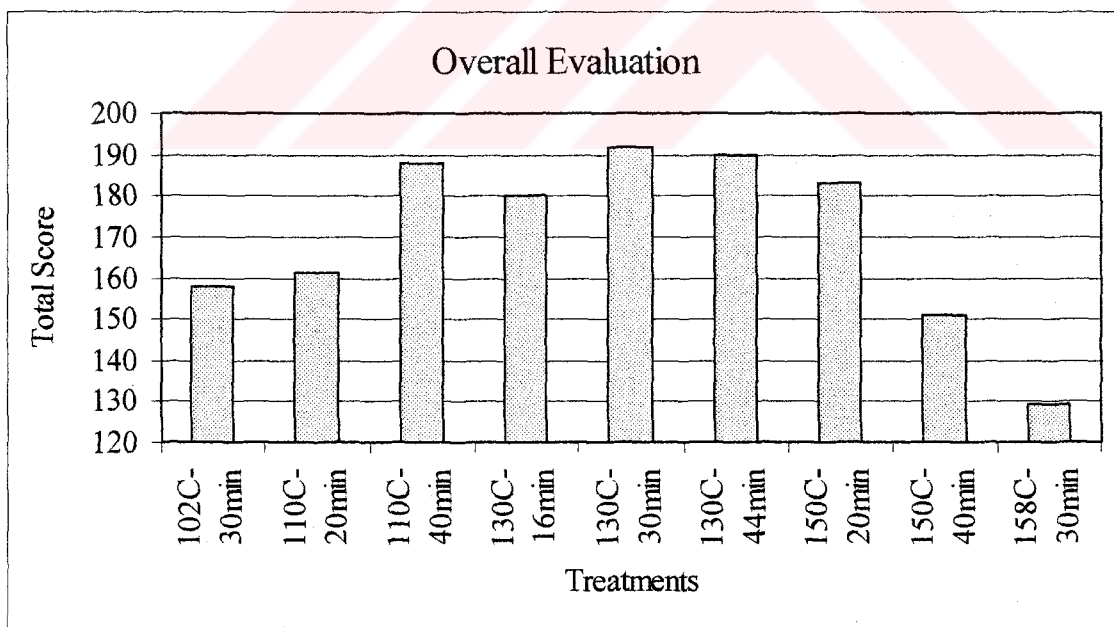


Figure 3.35. Total score of overall evaluation of the samples in the consumer acceptance test

Scores above 168 (2/3 of the maximum score, 252) was evaluated as acceptable. As also stated above, color, flavor, texture and overall evaluation scores of samples roasted at 102°C for 30 min, at 110°C for 20 min (excluding color), at 150°C for 40 min (excluding texture) and at 158°C for 30 min were lower than acceptance criteria of 168 (Figure 3.32 - Figure 3.35). Therefore consumers preferred samples roasted at 110°C for 40 min, at 130°C for 16 min; at 130°C for 30 min; at 130°C for 44 min and at 150°C for 20 min. The range of the total scores in the preferred samples were 171-184 for the color, 179-187 for the flavor, 183-199 for the texture, 180-192 for the overall evaluation.



4 CONCLUSION

Roasting is one of the most important step of the nut processing and drying is among the important changes occurring during roasting of nuts. In this study, drying during thin layer roasting of hazelnuts was characterized. Hazelnut drying during roasting occurred in the falling rate period. Temperature dependence of the diffusivity coefficients was described by Arrhenius-type relationship. The effective diffusivity varied from 2.301×10^{-7} to $11.759 \times 10^{-7} \text{ m}^2/\text{s}$ over the temperature range 100-160°C. The activation energy for moisture diffusion was found to be 1891.6 kJ/kg. Thin layer drying characteristics of hazelnut roasting was satisfactorily described by empirical Thompson model with the linear temperature dependence.

The kinetics of color changes during hazelnut roasting was satisfactorily described by a third degree polynomial with Arrhenius type temperature dependence of the model coefficients. A generalized model as a function of temperature and time, which can be used to predict color changes during roasting of hazelnuts, was developed.

Response surface methodology was employed to analyze effect of process variables on color development. The results showed that roasting temperature is the main factor, affecting color development during roasting of hazelnuts. Prediction models, derived from second degree polynomial, were satisfactorily described *L*-value, *a*-value and *b*-value of whole-kernel, ground-state and cut-kernel measurements as a function of roasting temperature and exposure time.

Both RSM and mathematical modeling studies about color formation during roasting indicated that whole-kernel measurements produced significantly lighter color (higher *L*-value, higher *b*-value and lower *a*-value) compared to ground-state and cut-kernel measurements due internal browning of hazelnuts during roasting. Internal browning was observed even at 110°C and 20 min of roasting. Therefore, *L*-value of ground state measurements, taking into account internal browning during roasting, should be used to monitor roasting of hazelnuts.

Roasting conditions significantly affected protein, total sugar, non-reducing sugar and amino acid composition of the roasted hazelnuts. The longer roasting times resulted in the lower moisture, protein, sugar and amino acid contents at any roasting temperature. Similarly the higher roasting temperature resulted in the lower moisture, protein and sugar content at any roasting time. Sugar and amino acid composition fluctuated over the experimental range of the study. This may be due to complex nature of the reactions during roasting such as hydrolysis of the constituents and non-enzymatic browning reactions.

The roasting conditions also significantly affected PV, FFA fatty acid composition of hazelnuts. Samples roasted at higher temperature obtained higher PV after 1 month storage at 37°C. Sample roasted at 102°C obtained and the lowest PV after the storage period. Sample roasted at 158°C for 30 min obtained the highest PV (4.94 meq/kg) at the end of storage. The results also indicated that roasting as much as at lower temperature result in the higher stability.

Consumer acceptance test showed that samples roasted at 110°C for 40 min, at 130°C for 16 min; at 130°C for 30 min; at 130°C for 44 min and at 150°C for 20 min were preferred by the consumer. Very light roasted (samples at 102°C for 30 min, at 110°C for 20 min) and very dark roasted (samples at 150°C for 40 min, at 158°C for 30 min) hazelnuts was not preferred by the consumer.

Further research about effect of initial moisture content, air velocity, air relative humidity and layer thickness on drying characteristics and quality of roasted hazelnuts is necessary for optimization of hazelnut roasting and development of hazelnut roasters.



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APPENDIX A: DATA

Table A.1. Moisture content data for mathematical modeling of drying (% db) during roasting of hazelnuts at 100 °C, 120 °C, 140 °C and 160 °C

Time	100°C		120°C		140°C		160°C	
	AV	SD	AV	SD	AV	SD	AV	SD
0	5.21	0.10	5.21	0.10	5.21	0.10	5.24	0.33
5	4.37	0.00	4.51	0.06	3.90	0.01	3.62	0.04
10	3.95	0.01	4.20	0.05	3.12	0.11	1.80	0.01
15	3.64	0.19	3.63	0.17	2.18	0.03	0.84	0.07
20	2.90	0.05	3.16	0.14	1.91	0.05	0.52	0.09
25	2.91	0.01	2.57	0.05	1.39	0.06	0.23	0.02
30	2.88	0.06	2.63	0.14	1.07	0.04	0.34	0.10
35	2.40	0.03	1.97	0.17	0.83	0.02	0.23	0.00
40	2.24	0.05	1.64	0.04	0.56	0.04	0.07	0.03
45	1.75	0.00	0.77	0.05	0.32	0.00	0.01	0.00
50	1.60	0.06	0.48	0.00	0.27	0.00	0.01	0.00
55	1.33	0.05	0.41	0.04	0.23	0.00	0.01	0.00
60	1.33	0.01	0.32	0.00	0.19	0.01	0.01	0.00

Table A.2. Whole-kernel measurements data for kinetics of color changes at roasting air temperature of 100°C

time	L		a		b	
	AV	SD	AV	SD	AV	SD
0	83.28	1.03	0.38	0.29	25.23	1.51
5	84.78	2.66	0.86	0.86	24.22	2.53
10	84.13	2.64	0.82	0.66	24.05	1.92
15	85.34	2.26	0.68	0.55	23.20	1.62
20	85.28	1.87	0.76	0.38	23.83	2.11
25	85.72	2.32	0.71	0.73	23.25	2.15
30	84.13	2.58	0.86	0.53	24.23	1.89
35	86.18	2.87	0.43	0.90	23.52	2.25
40	85.70	2.21	0.53	0.45	23.55	1.79
45	84.87	1.94	0.80	0.74	24.23	2.01
50	85.57	2.07	0.65	0.57	23.97	2.11
55	85.22	2.33	0.91	0.62	23.25	1.43
60	85.09	2.72	1.10	0.94	23.58	2.11

Table A.3. Whole-kernel measurements data for kinetics of color changes at roasting air temperature of 120°C

time	L		a		b	
	AV	SD	AV	SD	AV	SD
0	83.28	1.03	0.38	0.29	25.23	1.51
5	85.39	2.13	0.76	0.32	23.88	2.02
10	85.82	2.06	0.33	0.54	23.64	1.42
15	85.53	1.80	0.45	0.28	24.03	2.47
20	83.55	2.34	1.06	0.79	24.51	1.71
25	85.28	2.55	0.65	0.54	24.05	1.77
30	84.93	2.29	0.91	0.69	24.43	1.94
35	84.68	2.24	0.92	0.66	24.28	1.79
40	85.00	2.56	0.74	0.68	23.77	1.53
45	85.07	2.64	1.38	0.63	23.71	1.27
50	84.34	2.55	1.74	0.99	24.29	1.92
55	84.81	2.43	1.56	0.76	23.87	1.56
60	85.33	2.18	1.58	0.73	24.33	1.22

Table A.4. Whole-kernel measurements data for kinetics of color changes at roasting air temperature of 140°C

time	L		a		b	
	AV	SD	AV	SD	AV	SD
0	83.28	1.03	0.38	0.29	25.23	1.51
5	85.97	1.73	0.64	0.50	23.34	1.72
10	84.88	2.85	0.96	0.60	24.17	2.14
15	85.24	2.19	0.94	0.58	23.98	2.12
20	84.91	1.47	1.30	0.54	23.91	1.39
25	84.74	1.74	1.28	0.88	24.37	1.80
30	83.86	2.40	1.84	0.79	23.89	1.27
35	83.31	2.97	1.98	0.89	24.13	1.56
40	83.93	2.86	1.97	1.03	24.55	1.84
45	78.90	3.48	4.37	1.92	27.48	1.41
50	78.32	3.48	4.09	1.27	26.73	0.95
55	74.44	3.11	5.91	1.74	28.18	1.36
60	73.92	3.00	6.43	1.24	28.79	1.16

Table A.5. Whole-kernel measurements data for kinetics of color changes at roasting air temperature of 160°C

time	L		a		b	
	AV	SD	AV	SD	AV	SD
0	83.28	1.03	0.38	0.29	25.23	1.51
5	84.51	1.47	0.90	0.54	23.54	1.46
10	83.83	1.88	1.33	0.60	23.81	1.63
15	83.82	2.73	1.58	0.97	22.93	1.68
20	77.67	4.67	4.66	2.34	26.67	1.70
25	73.85	2.44	6.48	0.78	28.06	1.14
30	73.55	3.18	6.30	1.29	27.90	1.57
35	73.95	4.23	5.55	2.14	27.40	1.64
40	63.36	4.94	10.41	1.50	27.09	1.68
45	53.06	2.95	12.76	0.74	23.63	1.70
50	48.03	4.26	13.19	0.86	20.85	2.66
55	47.06	4.05	13.85	0.89	20.30	2.50
60	46.55	2.09	13.57	0.69	19.98	1.27

Table A.6. Ground-state measurements data for kinetics of color changes at roasting air temperature of 100°C

Time	L		a		b	
	AV	SD	AV	SD	AV	SD
0	80.84	1.20	-0.58	0.27	21.86	1.05
5	81.89	1.31	-0.10	0.29	21.61	0.61
10	82.03	1.12	-0.12	0.10	21.37	0.27
15	82.10	1.14	0.14	0.29	20.57	0.33
20	83.60	1.33	-0.04	0.24	20.85	0.73
25	83.39	1.34	0.25	0.25	20.42	0.60
30	82.91	1.05	0.26	0.22	20.56	0.63
35	83.73	1.23	-0.08	0.29	20.84	0.71
40	82.33	1.24	0.22	0.35	21.27	1.15
45	82.44	1.23	0.46	0.20	21.49	0.58
50	82.15	1.03	0.97	0.32	21.11	0.78
55	81.61	1.00	0.90	0.36	20.81	0.55
60	80.34	1.22	1.19	0.41	21.20	0.62

Table A.7. Ground-state measurements data for kinetics of color changes at roasting air temperature of 140°C

Time	L		a		b	
	AV	SD	AV	SD	AV	SD
0	80.84	1.20	-0.58	0.27	21.86	1.05
5	80.12	1.22	0.01	0.26	21.62	0.50
10	82.37	1.40	0.30	0.15	21.06	0.54
15	82.58	0.97	0.45	0.29	21.63	0.57
20	82.60	1.61	0.82	0.29	20.87	0.58
25	79.56	1.46	1.99	0.34	22.93	0.54
30	74.84	1.33	3.66	0.31	23.79	0.60
35	73.23	1.04	4.22	0.41	24.12	0.52
40	71.63	2.11	4.61	0.40	24.45	0.81
45	65.06	1.51	7.18	0.46	25.87	0.51
50	62.73	2.07	7.09	0.72	24.49	1.07
55	63.25	1.15	7.42	0.40	25.81	0.59
60	55.86	1.95	7.98	0.61	23.28	1.15

Table A.8. Ground-state measurements data for kinetics of color changes at roasting air temperature of 160°C

Time	L		a		b	
	AV	SD	AV	SD	AV	SD
0	80.84	1.20	-0.58	0.27	21.86	1.05
5	80.65	1.42	0.14	0.24	21.42	0.36
10	80.42	1.02	1.13	0.28	21.54	0.38
15	76.72	1.17	2.34	0.50	21.84	0.41
20	58.95	1.98	7.48	0.67	23.42	0.76
25	54.81	1.18	9.72	0.26	24.24	0.43
30	56.66	1.13	8.15	0.74	23.67	0.86
35	57.38	2.69	7.28	0.45	23.20	1.13
40	49.40	1.38	9.91	0.33	22.41	0.65
45	40.16	1.74	11.00	0.44	18.83	0.84
50	38.34	2.10	10.93	0.43	17.55	1.20
55	37.06	1.59	11.14	0.45	16.90	0.71
60	37.99	1.29	11.33	0.47	17.36	0.57

Table A.9. A balanced incomplete block design for consumer acceptance test

Block (Consumer number)	Replicates		Sample no	
1	1	1	2	3
2	1	4	5	6
3	1	7	8	9
4	2	1	4	7
5	2	2	5	8
6	2	3	6	9
7	3	1	5	9
8	3	7	2	6
9	3	4	8	3
10	4	1	8	6
11	4	4	2	9
12	4	7	5	3

İsim Soyadı:					Yaş:				
Cinsiyet <input type="checkbox"/> Kadın					<input type="checkbox"/> Erkek				
Örnek No:									
Fındık örneklerini dış görünüşü ve lezzeti açısından değerlendirerek ne kadar beğendiğinizi aşağıdaki ölçütlere belirtiniz.									
DIŞ GÖRÜNÜŞ									
<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
Son derece beğendim (Harika)	Çok beğendim	Oldukça beğendim	Biraz beğendim	Ne beğendim ne de beğenmedim	Biraz beğenmedim	Oldukça beğenmedim	Hiç beğenmedim	Hiç mi hiç beğenmedim (Çok kötü)	
Beğenmediyseniz nedeni? <input type="checkbox"/> Rengi koyu <input type="checkbox"/> Rengi açık <input type="checkbox"/> Dışı yağlı <input type="checkbox"/> Diğer									
Lezzet (Koku + Tad)									
<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
Son derece beğendim (Harika)	Çok beğendim	Oldukça beğendim	Biraz beğendim	Ne beğendim ne de beğenmedim	Biraz beğenmedim	Oldukça beğenmedim	Hiç beğenmedim	Hiç mi hiç beğenmedim (Çok kötü)	
Beğenmediyseniz nedeni? <input type="checkbox"/> Acı <input type="checkbox"/> Yanık <input type="checkbox"/> Ekşi <input type="checkbox"/> Tatlı <input type="checkbox"/> Aroması az <input type="checkbox"/> Diğer									
DOKUSU (Gevreklik + Kırılganlık)									
<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
Son derece beğendim (Harika)	Çok beğendim	Oldukça beğendim	Biraz beğendim	Ne beğendim ne de beğenmedim	Biraz beğenmedim	Oldukça beğenmedim	Hiç beğenmedim	Hiç mi hiç beğenmedim (Çok kötü)	
Beğenmediyseniz nedeni? <input type="checkbox"/> Yumuşak <input type="checkbox"/> Sert <input type="checkbox"/> Diğer									
GENEL DEĞERLENDİRME									
Fındık örneğinin bütün özelliklerini değerlendirdiğimde:									
<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
Son derece beğendim (Harika)	Çok beğendim	Oldukça beğendim	Biraz beğendim	Ne beğendim ne de beğenmedim	Biraz beğenmedim	Oldukça beğenmedim	Hiç beğenmedim	Hiç mi hiç beğenmedim (Çok kötü)	
Görüş:									

Figure A.1. Consumer acceptance evaluation sheet

CURRICULUM VITAE

Murat Özdemir was born in 08.06.1971, Edirne, Turkiye. He had B.Sc. degree (1994) from Food Engineering Department of Middle East Technical University, (Ankara) and M.Sc. degree (1996) from Food Engineering Department of School of Science of Middle East Technical University (Ankara). He has been enrolled Ph.D. program of Food Engineering Department of School of Science of Istanbul Technical University (Istanbul) since 1996. He worked for GTZ-DLG (Germany) as a short-term expert to improve hazelnut-cracking system (1996) and to develop a small capacity hazelnut dryer (1997). He has been working as a researcher in Food Science and Technology Research Institute of TÜBİTAK-Marmara Research Center (Kocaeli) since 1996. He has published 13 international articles, 7 national articles and one book. His current interests are drying and processing of grains, nuts, fruit and vegetables, and quality management systems.