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M.Sc. Thesis in Food Engineering

June 2012

**UNIVERSITY OF GAZİANTEP
GRADUATE SCHOOL OF
NATURAL & APPLIED SCIENCES**

**PHYSICOCHEMICAL AND RHEOLOGICAL PROPERTIES OF
RED COLORED FRUIT JUICE CONCENTRATES AND THEIR
SAUCES**

**M.Sc. THESIS
IN
FOOD ENGINEERING**

**BY
ŞELALE KARA
JUNE 2012**

**Physicochemical and Rheological Properties of Red Colored Fruit
Juice Concentrates and Their Sauces**

**M.Sc. Thesis
in
Food Engineering
University of Gaziantep**

**Supervisor
Assist. Prof. Dr. Emine ERÇELEBİ**

**by
Şelale KARA
June 2012**

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UNIVERSITY OF GAZIANTEP
GRADUATE SCHOOL OF NATURAL & APPLIED SCIENCES
FOOD ENGINEERING DEPARTMENT

Name of the thesis: Physicochemical and rheological properties of red colored fruit juice concentrates and their sauces

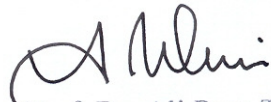
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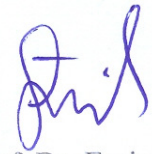
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I certify that this thesis satisfies all the requirements as a thesis for the degree of Master of Science.


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A handwritten signature in black ink, appearing to read 'Şelale KARA', with a long horizontal stroke extending to the right.

Şelale KARA

ABSTRACT

PHYSICOCHEMICAL AND RHEOLOGICAL PROPERTIES OF RED FRUIT JUICE CONCENTRATES AND THEIR SAUCES

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M.Sc. in Food Eng.

Supervisor: Assist. Prof. Dr. Emine ERÇELEBİ

June 2012, 102 pages

Red colored fruits of strawberry, blackberry, Cornelian cherry, Urmu mulberry, sour cherry, sweet cherry and pomegranate juices were concentrated via rotary vacuum evaporator at 40 °C. The objectives of this study were to determine physicochemical properties of prepared concentrates, to investigate the thermal degradation kinetics of anthocyanins and total color difference in these concentrates and, to prepare sauces with these concentrates with and without gum at three different gum concentrations (0.15, 0.30 and 0.60 % (w/v)) via three different gums (locust bean gum, xanthan gum, *ι*-carrageenan) and, to analyze rheological properties of these sauces by power law model.

All concentrates except sweet cherry concentrate had high phenolic content, total monomeric anthocyanins and exhibited high antioxidant activity. Monomeric anthocyanin degradation showed first order reaction kinetics. The zero order, first order and a combined kinetic model were applied to the total color change and, combined kinetic model was selected as the best fit.

Sauces prepared without gum has exhibited Newtonian flow characteristics, while sauces prepared with gums has exhibited non-Newtonian pseudoplastic flow characteristics. Pseudoplasticity has increased as gum concentration increased. Sauces prepared with xanthan gum at 0.30 % (w/v) gum concentration were selected as the best sauces.

This study shows that red fruits are rich in phenolics; mainly they are anthocyanins-rich fruits; and they are natural antioxidants. Consumption of these fruits as fresh or as carefully prepared sauce with maintaining their attractive red color and nutritional benefits, may offer enjoyable and health promoting food stuff.

Key words: Red fruits, physicochemical properties, kinetic, rheology, sauce

ÖZ

KIRMIZI RENKLİ MEYVE SUYU KONSANTRELERİNİN FİZİKOKİMYASAL VE REOLOJİK ÖZELLİKLERİ VE BUNLARIN SOSLARI

KARA, Şelale

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Tez Yöneticisi: Yrd. Doç. Dr. Emine ERÇELEBİ
Haziran 2012, 102 sayfa

Kırmızı renkli meyvelerden çilek böğürtlen, kıızılcık, Urmu dut, vişne, kiraz ve nar suları döner buharlaştırıcı vakum evaporatörde 40 °C’de konsantre edildi. Bu çalışmanın amaçları; hazırlanan konsantrelerin fizikokimyasal özelliklerinin belirlenmesi, konsantrelerin antosiyanin ve toplam renk değişiminin bozunma kinetiğinin araştırılması, konsantrelerden üç farklı hidrokolloid aracılığıyla (keçiboynuzu zamkı, ksantan zamkı, *ı*-karragenan) hidrokolloidli ya da hidrokolloidsiz üç farklı hidrokolloid konsantrasyonunda (% 0.15, 0.30 ve 0.60) sos yapılması ve bu sosların reolojik özelliklerinin güç kanunu modeliyle analiz edilmesi.

Kiraz konsantresi hariç bütün konsantreler yüksek fenolik madde içeriğine, yüksek toplam monomerik antosiyaninlere sahiplerdi ve yüksek antioksidan aktivite gösterdiler. Monomerik antosiyaninlerin bozunma kinetiği birinci derecede reaksiyon kinetiği gösterdi. Toplam renk değişimi, sıfırıncı derece, birinci derece ve birleştirilmiş kinetik model uygulandı ve birleştirilmiş kinetik model en uygun model olarak seçildi.

Hidrokolloid kullanılmadan hazırlanan soslar Newtonsu akış karakteristiği gösterirken, hidrokolloid kullanılarak hazırlanan soslar Newtonsu olmayan psödoplastik akış karakteristiği göstermişlerdir. Psödoplastiklik hidrokolloid konsantrasyonu artıkça artmıştır. % 0.30’luk ksantan zamkıyla hazırlanan soslar en iyi sos olarak seçilmiştir.

Bu çalışma kırmızı renkli meyvelerin, fenoliklerce zengin olduklarını, temel olarak antosiyaninlerce zengin olduklarını ve doğal antioksidan olduklarını göstermiştir. Bu meyvelerin taze olarak ya da çekici kırmızı renklerinin ve besinsel değerlerinin muhafaza edilerek hazırlanmış soslarının tüketilmesi hem zevkli hem de sağlığı destekleyen bir gıda maddesi olabilir.

Anahtar kelimeler: Kırmızı meyveler, fizikokimyasal özellikler, kinetik, reoloji, sos

To my beloved family...

Sincerely yours...

ACKNOWLEDGEMENTS

I wish to express my sincere thanks to my supervisor, Assist. Prof. Dr. Emine ERÇELEBİ for her patient supervision, continuous guidance, invaluable suggestions and assistance throughout this study. I am indebted to her.

I would like to thank to my committee members, Prof. Dr. Esra İBANOĞLU and Assist. Prof. Dr. Oya ÖZBAYRAM ÖZKANLI, for their enlightening suggestions throughout the study.

I would like to acknowledge the financial and technical support of University of Gaziantep, Scientific Research Projects Governing Unit, Turkey.

I would like to thank specially to my roommate Chemical Engineer Sevgi KUYUCU, for her motherly support and encouragement.

I appreciate to the all staffs of the Food Engineering Department of Gaziantep University for sharing their experiences sincerely, especially, Nazan ÇAĞLAR, Hatice ÇATAL, Aykut Ö. BARAZI and Fatih BALCI.

Most importantly, thanks ever so much to my beloved family; for always finding a way to lift the life's burden from my shoulders. I am granted to know that I am never alone and I will never be in desperate straits whenever they are. My patient mother, my worthy father and my sweet sweet brother, I am deeply grateful to have such a special family.

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LIST OF SYMBOLS/ABBREVIATIONS

A	Absorbance
<i>a</i>*	Redness/greenness
<i>A_C</i>	Absorbance of a control (t = 0 min)
<i>A_o</i>	Frequency factor (min ⁻¹)
<i>A_S</i>	Absorbance of a tested sample at the end of the reaction (t = 30 min)
<i>b</i>*	Yellowness/blueness
°Brix	Total soluble solids
<i>C</i>	Concentrations of color parameters at time t
<i>C</i>	Anthocyanin contents after time <i>t</i> (min)
CIE	Commission Internationale de l'éclairage
<i>C_o</i>	Concentrations of color parameters at time t=0
<i>C_o</i>	Initial anthocyanin contents
DF	Dilution factor
DPPH	2,2-dipheynl-1-picrylhydrazyl
<i>E_a</i>	Activation energy (kJ/mol)
Eq.	Equation
GAE	Gallic acid equivalents
h	Hour
<i>ι</i>-CARR	<i>ι</i> -carrageenan
<i>K</i>	Consistency index (Pas ⁿ)
<i>k</i>	Rate constants (min ⁻¹)
<i>k₀</i>	Zero-order kinetics constant
<i>k₁</i>	First order rate constant
<i>l</i>	Pathlength in cm
<i>L</i>*	Lightness
LBG	Locust bean gum
MW	Molecular weight

<i>n</i>	Flow behavior index
R	Universal gas constant (8.314 J/mol/ K)
<i>R</i>²	Correlation coefficient
<i>SE</i>	Standard error
<i>t</i>	Time (min)
T	Absolute temperature (Kelvin, K).
<i>t</i>_{1/2}	Half-lives
TCD*	Total color difference
TMA	Total monomeric anthocyanins
TSS	Total soluble solids
w/v	Weight per volume
XA	Xanthan gum
γ	Shear rate (s ⁻¹)
ϵ	Molar extinction coefficient in L/mol/cm
η_{app}	Apparent viscosity (Pas)
σ	Shear stress (Pa)
%	Percent

CHAPTER I

INTRODUCTION

In recent years, concerns increased over diet and human health due to the increased interest in nutrition, fitness and beauty. Besides their potential nutritional benefits, foods have now assumed the status of “functional” foods as a result of their additional physiological benefits. Recently, studies have been focused on examining foods for their protective and disease preventing potential instead of negative attributes such as adulteration, micro-organism count and etc. (Kaur and Kapoor, 2001). Local people have already traditionally believed that deep-coloured fruits are healthier for the human body (Ercisli and Orhan, 2007). Many epidemiological studies have consistently showed that a diet rich in fruits and vegetables offers protection against various diseases and, accordingly, approximately 20 % or more of all cancers may be prevented by the inclusion of five daily servings of fruit and vegetables (Kao, 2006). So, phytochemicals in fruits and vegetables, mainly phenolics including anthocyanins (Jakobek et al., 2007), have taken a great deal of attention due to their possible health promoting functions (Kaur and Kapoor, 2001).

In this respect, red colored fruits which are the main sources of anthocyanins (Pascual-Teresa and Sanchez-Ballesta, 2008) and whose juice concentrates have ever been regarded as antioxidant functional juices (Pilzac-Žeđerac et al., 2009) have taken part in many studies (Chaovanalikit and Wrolstad, 2004; Jakobek et al., 2007; Karlidag et al., 2009; Özgen et al., 2009; Pilzac-Žeđerac et al., 2009; Ferretti et al., 2010; Fazaeli et al., 2011). Studies have shown that antioxidant capacities of red fruits are relatively much higher than those of other fruits (Kao, 2006). Since these fruits have a brief harvest season in many cases further processing is required to extend shelf life. In Turkey, red-coloured fruits are eaten fresh and are also used in marmalades, juices, liquors, wines, natural dyes and in the cosmetics industry. However, their uses as fruit sauce are not common and, it has been supplied from abroad if required.

At the light of given facts, in this study, red colored fruits of strawberry, blackberry, Cornelian cherry, Urmu mulberry, sour cherry, sweet cherry and pomegranate juices were concentrated via rotary vacuum evaporator at 40 °C to maintain nutritional benefits and, following goals were targeted:

- To determine physicochemical properties such as titratable acidity, total soluble solid content, antioxidant activity, color, total monomeric anthocyanins and total phenolic matter in prepared concentrates. Since these properties are specific to related concentrate and, gives clues about their nutritional benefits.
- To investigate the thermal degradation kinetics of anthocyanins and total color difference in these concentrates. Since determination of the kinetic parameters is essential to predict the quality changes that occur during thermal processing.
- To prepare sauces with these concentrates with and without gum at three different gum concentrations (0.15, 0.30 and 0.60 % (w/v)) via three different gums (locust bean gum, xanthan gum, *l*-carrageenan) and to analyze rheological properties of these sauces by most common power law model.
- To select the best sauce with most appropriate gum type and gum concentration. Since adding different gums with different concentrations is done to improve stability and to produce more acceptable sauce.

As a result, it is planned to highlight the health promoting phytochemicals of red fruits, mainly phenolics and anthocyanins and, to widespread the production and use of sauces that will prepared with natural antioxidant red fruits and, lastly, to lead the production of the sauces in our country instead of the supplement from abroad.

CHAPTER II

LITERATURE SURVEY

2.1. Red fruits

Red fruits are popular fruits with high visual appeal and desirable flavor, but are highly perishable, being susceptible to mechanical injury, decay and physiological deterioration. Figure 2.1 shows the photographs of the some red fruits. In this study, only Urmu mulberry was studied as a mulberry genotype, the photograph of common black mulberry is given to differentiate Urmu mulberry from common well known black mulberry genotypes.

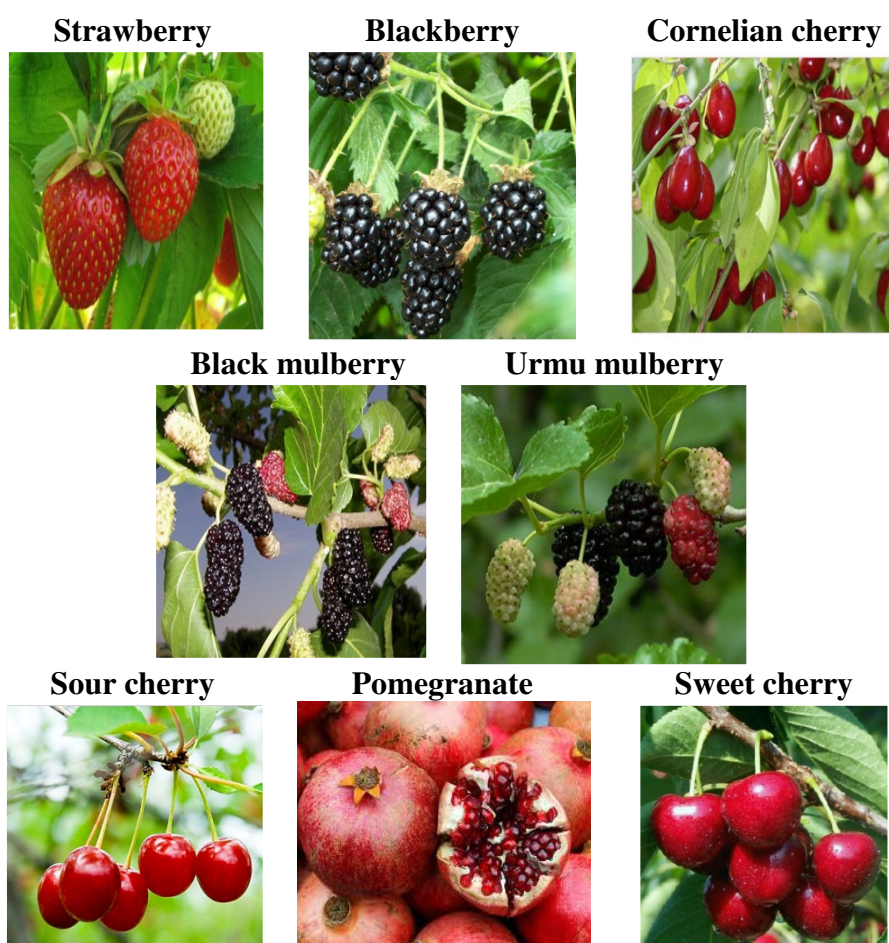


Figure 2.1. Photographs of some red fruits.

Recently, popularity and consumption of red fruits have been increased as a result of consumer awareness concerning nutritional value of these fruits, since consumer aware the facts that red fruits are the main sources of anthocyanins (Pascual-Teresa and Sanchez-Ballesta, 2008) and they have many health promoting antioxidant functions (Pilzac-Žegerac et al., 2009).

2.1.1. Strawberry

Strawberry (*Fragaria x ananassa* Duch.), is a very popular berry with high visual appeal, highly desirable taste, desirable flavor, is also considered a good source of antioxidants, mainly given to its high vitamin C and phenolic contents. Phenolic classes commonly found in strawberries are hydroxybenzoic acids (gallic and ellagic acids), hydroxycinnamic acids (p-cumaric), hydrolysable tannins (ellagitannins) which are present only in a few other berries and nuts (Aaby et al., 2012), condensed tannins, i.e., proanthocyanidin, flavonols (quercetin, kaempferol and myricetin), flavan-3-ols (catequins, epicatechins), and anthocyanins (Pineli et al., 2011). However, consumers seem to be primarily attracted by the bright red color and typical strawberry aroma of the fresh fruits, strawberry serve a wide diversity of health promoting compounds for many people. Beneficial health effects of strawberries include increased plasma antioxidant capacity in humans, antioxidant activity for low-density lipoproteins, and anticarcinogenic activity against human and mouse cancer cells; in addition, high ascorbic acid concentrations have protective roles against reactive oxygen species (Shin et al., 2007).

2.1.2. Blackberry

Several species of *Rubus* (*Rubus fruticosus* sp.) are called blackberries. Blackberries are one of the easiest to grow and are extremely tolerant of site and soil conditions. Some species of blackberries are upright and require no support but others are trailing and require a trellis (Kafkas et al., 2006). Blackberries are widely distributed around the world; it is believed that as many as 300 species of blackberries exist throughout the world (Cabral et al., 2007). Turkey is one of the origins of blackberries; blackberry cultivation started in the Marmara region several decades ago and now has been introduced as a new crop in the Mediterranean region. Besides, blackberry growing can be done in all parts of Turkey until irrigation is supplied. The blackberry fruits can be used in various food products such as ice

cream, juice, jam, marmalade, cake, etc (Kafkas et al., 2006). Blackberries have relatively high nutritional value due to being rich in vitamins, dietary fiber, phenolics (such as anthocyanins, flavonols, flavanols, ellagitannins, gallotannins, proanthocyanidins, and phenolic acids). The latter ones have many beneficial biological functions such as antioxidant, anticancer, anti-neurodegenerative, and anti-inflammatory activities (Du et al., 2010). Besides, flavonols, phenolic acids, ellagic acid, vitamins C and E, folic acid and b-sitosterol are the natural chemopreventative phytochemicals of blackberries (Bowen-Forbes et al., 2010).

2.1.3. Cornelian cherry

Cornelian cherry (*Cornus mas* L.) fruits are widely grown in different regions of Turkey, especially in eastern and northern Anatolia. *Cornus mas* varieties range from a shrub to a small tree of about 7-8 m in height (Yaltirik, 1981). Cornelian cherries are typically olive shaped, single-seeded fruits, 10–20 mm long, originating from an inferior ovary. They are typically red, but can also be found in pink and yellow. The fruits have a sweet-sour taste. They contain high amount of vitamin C and are rich in sugar, anthocyanins, organic acids and tannins (Seeram et al., 2002). In Turkey, approximately 12,800 tons of cornelian cherry fruit is produced annually. The fruit is either consumed directly or processed into various products such as jam, marmalade, pestil (a dried form of marmalade produced in the eastern part of Turkey), paste, and sherbet or is dried. Cornelian cherry fruits have also been used for the medical treatment of gastrointestinal disorder and diarrhea among people in Turkey (Tural and Koca, 2008).

2.1.4. Urmu Mulberry

Urmu mulberry (*Morus Nigra* L.), special Turkish name in Southeast part of Turkey, is a delicious fruit with extraordinary color and a unique, sour taste and refreshing flavor due to its aroma components. Urmu mulberry only grown in the province of Gaziantep, Urfa and Kahramanmaraş and, it has been defined as “sour black mulberry” in this region. Urmu mulberry is one of the three common mulberry species along with white mulberry (*Morus alba*) and red mulberry (*Morus rubra*) (Özgen et al., 2009). The studies on genetic relationships between Urmu mulberry and other black mulberry genotypes are lacking. Figure 2.1 shows the photographs of Urmu and common black mulberries, at which it is clear that Urmu mulberries are

smaller and fleshy fruits as compared to common black mulberry fruits (Figure 2.1). Besides, Urmu mulberry has sour acidic taste while common black mulberries are sweet in taste. Orhan and Ercisli (2010) have been reported that, previously, mulberry genotypes have been characterized with respect to morphological characters which are strongly dependent on environmental factors. He has also reported that, more recently, molecular markers gained more importance than morphological characters for describing mulberry genotypes; as a consequence, mulberry genotypes are characterized throughout mulberry growing countries.

Mulberries are rich in phenolics; mainly they are anthocyanins-rich fruits (Ercisli and Orhan, 2007; Du et al., 2008). Urmu mulberry sherbet is sold on the street benches in Gaziantep. In Gaziantep region, people traditionally believe that black and red mulberries are healthier for human body. So especially in this region, Urmu mulberry is known not only its nutritional qualities and its flavor, but also for its traditional use in natural medicine, where it is used as folk medicine in mouth lesions, strengthen the teeth, diabetes, hypertension and etc.

2.1.5. Cherries (Sour and sweet cherry)

Cherries (*Prunus* spp.) are the smallest members of the stone fruit family of Rosaceae. *Prunus avium* L., is known as "sweet cherry", and *Prunus cerasus* L., is known as "sour cherry or tart cherry" (Ferretti et al., 2010). Generally sweet cherries are consumed as fresh fruit whereas sour cherries are consumed as processed cherry products such as dry fruits, powders from individually quick frozen cherry, frozen cherry, juices and juice concentrates (Kirakosyan et al., 2009; Ferretti et al., 2010).

Sweetness in the cherry fruit is mainly due to glucose and fructose, while sourness is primarily due to the presence of organic acid (malic acid). Sweet cherries are characterized by a higher content of simple sugar with respect to sour cherries (Ferretti et al., 2010). Intrinsic sweet taste of sweet cherry juice related to its sugar composition, sweet cherries contains highest amounts of glucose, followed by fructose, sorbitol and sucrose (Kelebek and Selli, 2011).

Cherries contain vitamins (C, B, A, E, K), minerals (such as calcium, magnesium, phosphorous and potassium), and some carotenoids, in particular beta-carotene, and

to a lower extent lutein and zeaxanthine. Sour cherries are characterized by a higher content of vitamin A and beta-carotene (Ferretti et al., 2010). Cherry phenolics are flavonoids (anthocyanins), non-flavonoids, flavan-3-ols and flavanols (Kelebek and Selli, 2011). Anthocyanins include cyanidin 3-glucoside, cyanidin 3-rutinoside, cyanidin 3-sophoroside, pelargonidin 3-glucoside, pelargonidin 3-rutinoside, 3-glucoside, and peonidin 3-rutinoside; non-flavonoids include phenolic acids (hydroxycinnamic and hydroxybenzoic acids) flavonols and flavan-3-ols include catechin, epicatechin, quercetin 3-glucoside, quercetin 3-rutinoside, kaempferol 3-rutinoside. In general, sour cherries contain a higher level of total phenolics than sweet cherries due to having higher amount of anthocyanins and hydroxycinnamic acids. Antioxidants and phenolics of cherry fruits (both sweet and sour cherries) also have antioxidant, anticancer and anti-inflammation properties (Ferretti et al., 2010).

2.1.6. Pomegranate

Pomegranate (*Punica granatum* L.) is one of the oldest edible fruits widely grown in many tropical and subtropical countries. Over 1000 cultivars of *Punica granatum* exist, originating from the Middle East, extending throughout the Mediterranean, eastward to China and India, and on to the American Southwest, California and Mexico in the New World (Çam et al., 2009). The edible parts of the pomegranate fruits can be consumed fresh or used for the preparation of fresh juice, canned beverages, jelly, jam and paste and also for flavouring and colouring agents for beverages (Mousavinejad et al., 2009). Pomegranate juice is known to be a major source of phenolic compounds comparison with other fruit juices. They contain anthocyanins, ellagic acid, phytoestrogenic flavonoids, tannins, and organic acids (Fazaeli et al., 2011). Alighourchi et al. (2008) reported that among the polyphenols, anthocyanins have utmost interest. Besides their various health benefits (Pascual-Teresa and Sanchez-Ballesta, 2008), anthocyanins are responsible for the appealing bright red color of juice and other products of pomegranate fruit (Jaiswal et al., 2010). In addition, pomegranate juice contains high levels of antioxidants - higher than most other fruit juices and beverages (Tezcan et al., 2009). Moreover, valuable compounds in different parts of the fruit have functional and medicinal effects (Mousavinejad et al., 2009) and, pomegranate juice has been proposed as chemopreventive, chemotherapeutic, anti-atherosclerotic and anti-inflammatory

agent (Çam et al., 2009). Some clinical research studies suggest that pomegranate juice changes the blood parameters such as LDL, HDL, and cholesterol; increase the prostate specific antigen (PSA) and may be helpful against heart disease, Alzheimer's disease, cancer, improvement of sperm quality and erectile dysfunction in male patients (Tezcan et al., 2009).

2.2. Phenolic content

Phenolic compounds (polyphenols) constitute one of the most numerous and widely distributed groups of plant kingdom with more than 8000 phenolic structures (Paixão et al., 2007). They are almost ubiquitous in plant foods (vegetables, cereals, legumes, fruits, nuts, etc.) and beverages (wine, cider, beer, tea, cocoa, etc.). Most of the polyphenols in plant kingdom are phenolic acids and flavonoids (including anthocyanins, procyanidins, flavanones, flavanols, etc.); fewer are tannins. For example, in legumes and cereals, the main polyphenols are flavonoids, phenolic acids, and tannins. Berries are characterized by their high anthocyanin content, whereas fruits such as apples and citrus fruits are rich in phenolic acids and flavonoids, respectively (Bravo, 1998).

Phenolics divided basically into two main classes, i.e., flavonoids and nonflavonoids (Cheynier, 2005). The former accounting for over half of the eight thousand naturally occurring phenolic compounds (Balasundram et al., 2006). Nonflavonoids are mostly rather simple molecules, such as phenolic acids and stilbenes, but also include complex molecules derived from them (eg, stilbene oligomers, gallotannins, ellagitannins, and lignins) (Cheynier, 2005). Phenolic acids consist of two subgroups, i.e., the hydroxybenzoic and hydroxycinnamic acids. Hydroxybenzoic acids include gallic, p-hydroxybenzoic, protocatechuic, vanillic and syringic acids, which in common have the C_6-C_1 structure. Hydroxycinnamic acids, on the other hand, are aromatic compounds with a three-carbon side chain (C_6-C_3), with caffeic, ferulic, p-coumaric and sinapic acids being the most common (Balasundram et al., 2006).

Flavonoids are low molecular weight compounds, consisting of fifteen carbon atoms, arranged in a $C_6-C_3-C_6$ configuration (Balasundram et al., 2006). They are widespread in the plant kingdom, with the exception of algae and fungi (Bravo, 1998). Flavonoids classified at least 10 chemical classes, of which flavanones,

flavones, isoflavonoids, flavans (flavanols), anthocyanins, and flavonols are particularly common in the diet (Yao et al., 2004).

As known flavonoids are plant pigments which are found in all plant foods and generally display marvelous colors in the flowering parts of plants. Moreover, flavonoids in foods are generally responsible for color, taste, prevention of fat oxidation, and protection of vitamins and enzymes. Table 2.1 summarizes main type, functions and food source of flavonoids as plant pigments. Table 2.1 shows that flavanones occur predominantly in citrus fruits, isoflavonoids in legumes, and flavones mainly in herbs, while anthocyanins and catechins (flavanols) are found in teas, fruits, and vegetables as coloring agents (Yao et al., 2004). However in general, basic polyphenol pigments in plants are anthocyanins, which exhibit red, purple, or blue color, and, to a lesser extent, the yellow flavonols and flavones (Cheynier, 2005).

Finally it is clear that food phenolics are important due to their various beneficial functions depending on their particular structures:

- They include yellow, orange, red, and blue pigments as coloring agents, as well as various compounds involved in food flavor.
- Some volatile polyphenols, such as vanillin and eugenol (which is responsible for the characteristic odor of cloves), are extremely potent odorants, but the major flavors associated with polyphenols are bitterness and astringency.
- They have antioxidant properties
- They are able to interact with proteins which results in astringency perception (resulting from interactions of tannins with salivary proteins), formation of haze and precipitates in beverages, and inhibition of enzymes and reduced digestibility of dietary proteins (Cheynier, 2005).

2.3. Antioxidant activity

Oxidation is one of the most important free radical producing systems in food, chemicals and even in living systems (Pisoschi et al., 2009). Free radicals are unstable, highly

Table 2.1. Main subgroups of flavonoids, the individual compounds, and food sources (Yao et al., 2004).

Subgroup	Color	Representative flavonoids	Food sources	Comment
Anthocyanins	Blue, red, violet	Cyanidin	Fruits and flowers	Natural dyes
Flavanols	Colorless	Catechins, gallocatechin, epicatechin, epigallocatechin gallate,	Apples, hops, tea, beer	Astringent taste
	Yellow	Procyanidin	Wine, fruit juice	
		Theaflavins	Black tea	
Flavanones	Colorless	Hesperidin	Citrus fruits	Bitter taste
	Pale	Naringenin, eriodictyol	Cumin, oranges, grapefruits, peppermint	
	Yellow	Neohesperidin		
Flavones	Pale yellow	Apigenin, chrysin, luteolin	Herbs, cereals, fruits, parsley, thyme	Bitter taste
		Diosmetin, luteolin	Vegetables, flowers	
Flavonols	Pale yellow	Isorhamnetin, kaempferol, quercetin, myricetin, rutin	Onions, cherries, apples, broccoli, kale, tomatoes, berries, tea, red wine, tartary buckwheat	
Flavanonols		Taxifolin	Limon, Aurantium	
Isoflavones	Colorless	Daizein, genistein, glycitein, formononetin	Legumes (e.g. soybeans)	

reactive and energized molecules having unpaired electrons and they react quickly with other compounds by stealing their electrons to gain stability. Examples of oxygen derived free radicals include super oxide (O_2^-), hydroxyl (OH^-), hydroperoxyl (HOO^-), peroxy (ROO^-) and alkoxy (RO^-) radicals and nitric oxide (NO^-) and the peroxynitrite anion ($ONOO^-$). The latter two are the reactive oxygen species produced by body. The possible mechanisms are free radicals attack the nearest stable molecules, 'stealing' its electrons. When the molecule that has been attacked and lost its electron becomes a free radical itself, starting a chain reaction, initiating lipid peroxidation resulting in destabilization and disintegration of the cell membranes or oxidation of other cellular components like proteins and DNA, finally resulting in the disruption of cells. This mechanism reduces capabilities to combat ageing and serious illness, including cancer, kidney damage, atherosclerosis and heart diseases (Kaur and Kapoor, 2001).

Antioxidants are the substances that are capable of quenching or stabilizing free radicals via neutralizing them by donating one of their own electrons, ending the electron-stealing reaction. The antioxidants do not themselves become free radicals by donating electrons because they are stable in either form. In recent years, some synthetic antioxidants have been restricted due to their potential carcinogenic and toxic effects. In this respect, natural antioxidants particularly in fruits and vegetables have attracted increasing interest among consumers and the scientific community due to their presumed safety, potential nutritional and therapeutic effects (Kaur and Kapoor, 2001).

The protective effects of natural antioxidants in fruits and vegetables are related to their dietary components acting as antioxidants: fiber, polyphenols, flavonoids, conjugated isomers of linoleic acid, D-limonene, epigallocatechin, gallate, soya protein, isoflavanones, vitamins (A, B, C, E), tocopherols, calcium, selenium, chlorophyllin, alipharin, sulphides, catechin, tetrahydrocurecumin, sesaminol, glutathione, uric acid, indoles, thiocyanates and protease inhibitors (Karakaya and Kavas, 1999). These components may act independently or in combination and defensive effects of these natural antioxidants might be additive and/or synergistic, so total antioxidant measurements will possibly give a better estimation of the overall contributors of antioxidant components (Shin et al., 2008).

Among various antioxidants present in fruits and vegetables, polyphenols (including anthocyanins) have taken much attention since being reported to have a positive influence on human health (Jakobek et al., 2007).

2.4. Color and anthocyanins

Color is an important quality indicator because it is usually the first property for the consumer observes (Ahmed and Shivhare, 2001). Color plays an important role in our enjoyment of foodstuff; it is appreciated both for its aesthetic role and as a basis for assessment of quality. Color gives visual cues to flavor identification and taste thresholds, influencing food preference, food acceptability and ultimately food choice (Bridle and Timberlake, 1996).

Anthocyanins (in Greek *anthos* means flower, and *kyanos* means blue) are the plant pigments responsible for colors of most plants ranging from salmon pink through red and violet to dark blue (Cavalcanti et al., 2011).

The anthocyanidins are the basic structures of the anthocyanins, the aglycon form of anthocyanins (the flavylium cation), which contains conjugated double bonds responsible for absorption of light around 500 nm causing the pigments to appear red to human eye (Rein, 2005). When anthocyanidins bonded to sugar moiety becoming in their glycoside form they are called as anthocyanins. Until now, more than 500 anthocyanins and 23 anthocyanidins are reported being in nature differing due to the number of hydroxylated groups, the nature and the number of bonded sugars to their structure, the aliphatic or aromatic carboxylates bonded to the sugar in the molecule and the position of these bonds (Castañeda-Ovando et al., 2009). The most common ones of these 23 anthocyanidins in fruits and vegetables are pelargonidin, cyanidin, peonidin, delphinidin, malvidin, and petunidin (Pascual-Teresa and Sanchez-Ballesta, 2008; Castañeda-Ovando et al., 2009). Table 2.2 indicates the eye perception of these most common anthocyanidins. Figure 2.2 shows the structure of anthocyanins most commonly found in foods.

Table 2.2. Color of most common anthocyanidins found in nature (Cavalcanti et al., 2011).

Anthocyanidin	Color
Pelargonidin	Orange or salmon
Cyanidin	Magenta or crimson
Delphinidin	Purple, mauve, or blue
Peonidin	Magenta
Petunidin	Purple
Malvidin	Purple

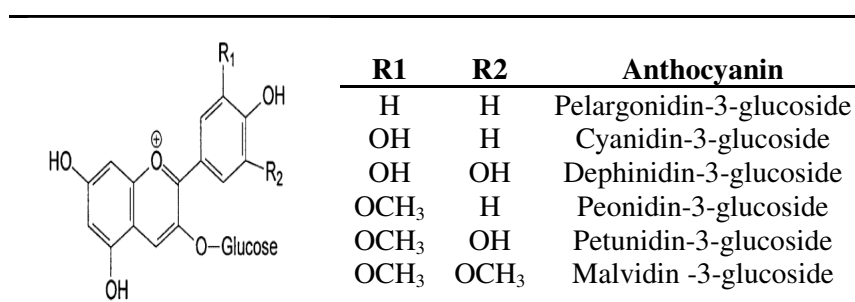


Figure 2.2. Structure of anthocyanins most commonly found in foods (Clifford, 2000).

Besides their being natural food colorant, anthocyanins takes great attention due to their antioxidant properties and their possible health benefits. They have many beneficial activity which secure human health: defensive impact on prevention of cardiovascular disease; their anticancer, antitumor and antimutagenic activity; useful effects in diabetes; protective effect against hepatic damage; protective effect on gastric; defensive ocular effects; and protective effects on neurodegenerative processes (Pascual-Teresa and Sanchez-Ballesta, 2008).

The main sources of anthocyanin are red fruits, mainly berries and red grapes, cereals, principally purple maize, vegetables and red wine among drinks. (Pascual-Teresa and Sanchez-Ballesta, 2008). In scope of this study, main red fruits and their anthocyanin composition is given in Table 2.3.

Table 2.3. Possible major anthocyanins of some red fruits.

Fruit	Major anthocyanins	Reference
Strawberry	Pelargonidin-3-glucoside	Patras et al, 2010.
Blackberry	Cyanidin- 3-glucoside	Wang and Xu, 2007.
Cornelian cherry	Pelargonidin 3-O-glucoside Cyanidin 3-O-glucoside Cyanidin 3-O-rutinoside	Tural and Koca, 2008.
Mulberry	Cyanidin-3-glucoside Cyanidin-3-rutinoside	Fazaeli et al., 2011.
Sour cherry	Cyanidin-3-glucosylrutinoside Cyanidin-3-rutinoside	Wang and Xu, 2007
Sweet cherry	Cyanidin-3-rutinoside	Patras et al, 2010.
Pomegranate	Delphinidin, Cyanidin, and Pelargonidin 3-glucosides and 3,5- diglucosides	Alighourchi et al., 2008.

2.4.1. Factors effecting stability of anthocyanins

Anthocyanins take great attention due to their possible health benefits, moreover, anthocyanins give their characteristic color to our red fruits and sauces prepared from these fruits on account of being a major quality parameter that effect consumer sensory acceptance.

Since anthocyanins are highly unstable and vulnerable to degradation, the following factors which affect both their stability -as a nutrient- and their color stability -as a natural food colorant- are mainly; chemical structure, pH, concentration, oxygen, light, enzymes, other additional substances (ascorbic acid, sugars, sulfites, copigments, metallic ions and etc.) and temperature should be take into consideration during processing and storage of anthocyanin containing foods.

2.4.1.1. Chemical structure

Chemical structure of anthocyanin have significant effects on their stability and reactivity i.e., the glycosyl units and acyl groups attached to the aglycone, and the site of their bonding of the anthocyanin molecule, the substitution pattern of the anthocyanidin, the number and placement of the hydroxyl and methoxyl groups in the aglycone are all important factors which effect their stability (Rein, 2005).

2.4.1.2. pH

Anthocyanins can be found in different chemical forms resulting in different colors and hues in the pH range of 1-14 (Rein, 2005). At pH 1, the flavylium cation (red color) is the predominant species and contributes to purple and red colours. At pH values between 2 and 4, the quinoidal blue species are predominant. At pH values between 5 and 6 only two colourless species can be observed, which are a carbinol pseudobase and a chalcone, respectively. pH values between 4 and 6, four structural forms of the anthocyanins coexist: flavylium cation, anhydrous quinoidal base, colourless carbinol base and the pale yellow chalcone. Flavylium cation supplies the balance between the quinoidal bases and carbinol. As pH increases, amount anhydrous base increases, in the same manner, as pH decreases, amount of red flavylium ion becomes dominant. At pH values higher than 7, the anthocyanins are degraded depending on their substituent groups (Castañeda-Ovando et al., 2009).

2.4.1.3. Concentration

As anthocyanin concentration increases the anthocyanin color stability increases independent of the type of individual anthocyanins (Giusti and Wrolstad, 2003; Cavalcanti et al., 2011). Increased stability achieved by self-association of anthocyanins (Rein, 2005).

2.4.1.4. Oxygen

Oxygen affects anthocyanin degradation processes. For example, removal of oxygen defends against thermal degradation. It is reported that the presence of oxygen together with elevated temperature, was the most detrimental combinations of many factors tested against color deterioration of different berry juices and isolated anthocyanins (Cavalcanti et al., 2011). Destructive reaction between anthocyanins and oxygen can be direct or indirect, the latter case, further reaction occurs between the oxidized systems components resulting in increased colorless or brown products (Rein, 2005).

2.4.1.5. Light

Light is essential for the biosynthesis of anthocyanins, but it also fastens anthocyanin degradation (Markakis, 1982). It was reported that anthocyanins preserve their color

much better in the darkness; the difference was seen already after 24 h when anthocyanins were stored in light and for comparison in the dark at room temperature (Cavalcanti et al., 2011). Moreover, it was reported that the end products of light caused degradation of anthocyanins found to be the same as in thermal degradation, nevertheless, just differing in the kinetic pathway of the degradation including the excitation of the flavylum cation (Rein, 2005).

2.4.1.6. Enzymes

Enzymes such as polyphenoloxidase, peroxidase and glycosidase have destructive effect on anthocyanins (Wrolstad et al., 2005). The latter has direct effect on stability of anthocyanin via breaking down the covalent bonds between glycosyl residue and aglycone resulting in unstable aglycones. It is reported that peroxidases and phenolases, such as phenol oxidases and polyphenol oxidases, which both are found naturally in fruits and berries themselves, are known as common anthocyanin degrading enzymes (Rein, 2005).

2.4.1.7. Other additional substances

Presence of ascorbic acid will fasten anthocyanin degradation (Wrolstad et al., 2005). Also, it is reported that ascorbic acid increases the polymer pigment formation and bleaches anthocyanin pigments. Sugars and the end products of their degradation are known to decrease anthocyanin stability. Moreover, reactions of anthocyanins with both degradation products of sugars and ascorbic acid results in brown pigment polymers (Rein, 2005). However, it is also reported that slightly increasing the concentration of sugar (such as 20 %) possessed protective effects on anthocyanins stability and color quality of different refrigerated berries extracts, but in higher concentration this affect was reduced (Cavalcanti et al., 2011).

Stability of anthocyanin and its color can be supported by copigmentation via intramolecular and intermolecular copigmentation, self-association, metal complexing and presence of inorganic salts be increased via copigmentation (Giusti and Wrolstad, 2003).

Sulfites and sulfates used in food storage combines anthocyanins of fruits resulting in discoloration via formation of colorless sulfur derivatives (Cavalcanti et al., 2011).

2.4.1.8. Temperature

Thermal processing of foods as a unit operation involves heating temperatures from 50 to 150 °C varying the pH and desired shelf-life of the foodstuff (Patras et al., 2010). It is reported that low temperatures have long been considered to promote, and high temperatures to reduce, anthocyanin synthesis (Pascual-Teresa and Sanchez-Ballesta, 2008).

In some cases temperature supposed to have positive impact on anthocyanin stability. It was claimed that enzymatic degradation of anthocyanins by polyphenoloxidase can be prevented by blanching (heating nearly 50°C) (Patras et al., 2010). They reported that, in one study, it was observed that addition of a blanched blueberry-pulp extract to blueberry juice resulted in no degradation of anthocyanins, whereas addition of an unblanched extract caused a 50 % loss of anthocyanins, which was suggested an enzyme role in anthocyanin degradation. Pascual-Teresa and Sanchez-Ballesta (2008) reported that, habitats with cool weather were associated with a rapid anthocyanin accumulation in the skin of 'Starkrimson' and 'Golden Delicious' apple, whereas the warm weather was associated with slower anthocyanin accumulation. Rein (2005) reported, in one study, it was observed that the anthocyanin content of different cranberry varieties increased during three months storage at 15°C. Also, he reported that, in another study, it was observed that the anthocyanin content in strawberries and raspberries stored fresh for eight days was increased in storage temperatures over 0°C. In addition, Pascual-Teresa and Sanchez-Ballesta (2008) reported that in one study on the effect of processing and storage on strawberry anthocyanins, it was observed that freezing strawberries (-37°C followed by 1 month storage at -23°C) produced a slight increase in the anthocyanin content. He concluded that, this result was in accordance with another study at which an increase of total anthocyanins in raspberries after frozen storage at -24°C for one year was observed.

It has been reported that the rate of anthocyanin degradation fastens during processing and storage as temperature increases (Patras et al, 2010). Many studies on heat treatments revealed the destructive effects of high temperature heat treatments on anthocyanins and, first order degradation kinetics was reported for anthocyanin

degradation (Garzón and Wrolstad, 2002; Cemeroglu et al., 2004; Wang and Xu, 2007; Shao-qian et al., 2011).

Since thermal degradation of anthocyanins leads to decrease in nutritional and visual quality of foodstuff which impact consumer acceptance, understanding degradation mechanism becomes prerequisite during heat treatment of foodstuff. Thermal degradation of anthocyanins can result in huge amounts of chemical species with respect to the severity and nature of heating (Patras et al, 2010). Figure 2.3 shows the degradation of anthocyanins and formation of various intermediate compounds.

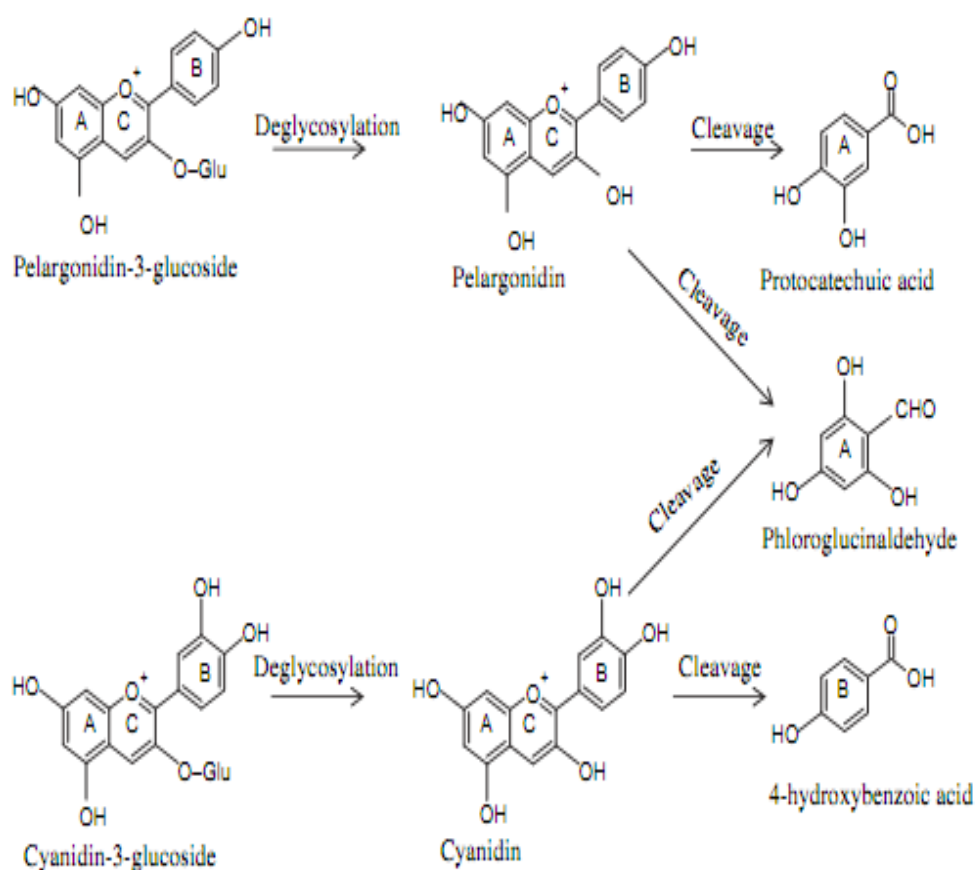


Figure 2.3. Potential thermal degradation mechanism of two common anthocyanins (Patras et al, 2010).

Although, still relatively little known about precise degradation mechanism, the outcomes of thermal degradation known to be color loss and introduction of brown compounds. It is reported that possible mechanism have to be chalcone formation being first step, loss of glycosyl moieties and α -diketone formation. Besides,

coumarin derivatives, benzoic acid derivatives and trihydrobenzaldehyde have been reported as end products of thermal degradation (Reyes and Cisneros-Zevallos, 2007).

2.5. Kinetic studies

The related fruits in this study are popular fruits with high visual appeal and desirable flavor, but are highly perishable, being susceptible to mechanical injury, decay and physiological deterioration. In fact, in addition to their nutritional and sensory properties, red fruits have recently been recognized as acting as protective agents as well. Dietary recommendations for healthy eating include the consumption of red fruits due to their various health benefits (Erçelebi and Kara, 2011). As mentioned before, these fruits rich in phenolics and anthocyanins and, they show high antioxidant activity. Unfortunately, these fruits have brief harvest season; therefore further processing is needed to extend shelf-life. So, these fruits were concentrated via rotary vacuum evaporator under low temperature (40°C) to maintain nutritional benefits. One of the important factors to be considered in food processing is the loss of nutrients. So, it was necessary to judge the change in quality of fruits during processing.

Quality means satisfying expectations of consumer. Quality is multidimensional, it contains both subjective and objective elements, and it is situation specific and dynamic in time. Food quality attributes are all those product attributes that are relevant in determining quality (shape, color, flavor, texture, flavor, nutritional value, food safety, convenience, brand name, price and etc.). When a consumer evaluates a product, a first impression arises from so-called quality cues: attributes that can be perceived prior to consumption and that are believed to be indicative of quality. An example can be strawberry fruit with bright red color and high visual appeal with nice shape. When a consumer starts eating, he is confronted with the physical product properties and this leads to a quality experience. If the quality expectation and the quality experience, integrated in each other, exceed a certain quality experience, the consumer will accept it, if not he will reject it. A consumer however does not analyze all elements of food quality consciously but gives an integrated response based on complex judgments made in mind (Van Boekel, 2009). Since idea of quality is somewhat elusive, it will be helpful to express desired quality in terms

of manageable quality indicators and model these, which is to state change in quality quantitatively. That is to say, it is looking for mathematical models that describe the fade of quality indicators (such as color, texture, presence or absence of certain flavor compounds and etc.) as a function of conditions in the food chain. Mathematical models consist of equations that provide an output (such as vitamin content) based on a set of input data (for instance time, temperature). It is a concise way to express physical behavior in mathematical terms (Van Boekel, 2008). Kinetic models are also used for an objective, fast and economic assessment of food safety, to predict the influence of processing on critical quality parameters (Patras et al., 2010). Knowledge of degradation kinetic parameters, including reaction order, rate constants and activation energy, is necessary to predict the extent of specific chemical reaction and, consequently, to minimize the undesirable change and to optimize it (Carabasa-Giribet and Ibarz-Ribas, 2000; Patras et al., 2010).

In this respect, thermal degradation kinetics of anthocyanins and color was studied for all concentrates at different temperatures. Anthocyanin pigments, which are natural food colorants, readily degrade during thermal processing which can have dramatic impact on color quality and may also affect nutritional properties. (Patras et al., 2010).

2.6. Rheological studies

Rheology concerns with the flow and deformation of a substance under applied forces, and attempts to define a relationship between the stress acting on a given material and the resulting deformation and/or flow that takes place (Akbulut et al., 2008). Rheology suggests vocabulary, specific terminology and mathematical expressions to discuss foods and their textural properties. Fluids could be characterized by their viscosity and/or by their consistency. Consistency, body term is also used in reference to consistency, can be defined as a quality parameter which is perceptible to touch or as the resistance to permanent deformation. Consistency is also referred as mouth-feel characteristics of semi-solids or liquids, so sensory concepts of mouth-feel and body could be associated with consistency (Balestra et al., 2011). Rheology have many uses in the field of food acceptability, food handling, food processing design and evaluation, process control, product development and etc. (Abu-Jdayil, 2003; Akbulut et al., 2008; Balestra et al., 2011).

The rheological behaviour of fruit juices and concentrates is influenced by their composition (especially type of fruit), treatment performed in its production process and by factors such as temperature and concentration (Juszczak and Fortuna, 2003). Rheological properties are determined by measuring force and deformation as a function of time. (Akbulut et al., 2008). The flow behavior of fruit juices can be described by different rheological models depending on the nature of the juices (Keshani et al., 2012). The fruit juices presents Newtonian behavior when pulp content is low, soluble solid content is lower than 30 °Brix, or if juices have been depectinized (Cepeda and Villarán, 1999). The viscosity does not change with the shear rate for Newtonian fluids at constant temperature and pressure (Marcotte et al., 2001). Presence of pectin substances or/and suspended solid particles causes non-Newtonian behavior of juices and concentrates (Juszczak and Fortuna, 2003). For most non-Newtonian fluids, the viscosity decreases with a rise in shear rate, giving increase in what is known as shear-thinning behavior (pseudoplasticity) and, at the opposite end is dilatancy which is the behavior showing an increase in viscosity with increasing shear rate. Here, the shear-thinning represents an irreversible structural breakdown and, the decrease in viscosity is caused by molecular alignment that takes place within such a substance (Marcotte et al., 2001). Figure 2.4 shows the shear stress and shear rate relationships in liquids.

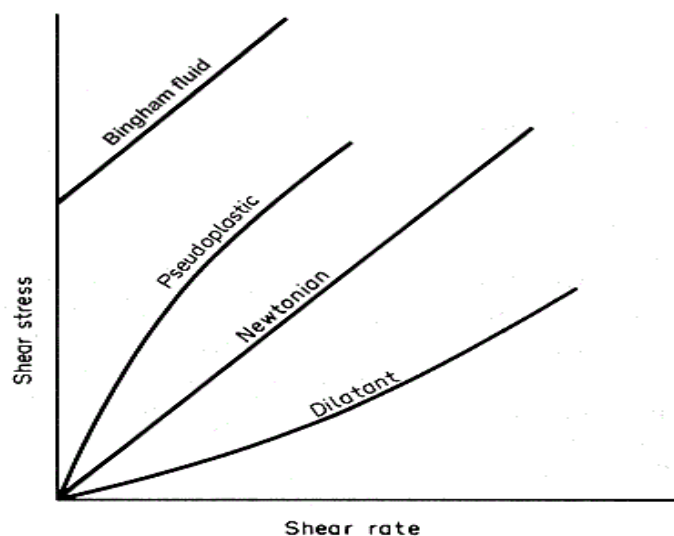


Figure 2.4. Shear stress/shear rate relationships in liquids
(<http://www.nzifst.org.nz/unitoperations/flfltheory3.htm#newtonian>).

In this respect, juices can be classified into three classes: 1) clarified and depectinated concentrates, 2) clarified and no depectinated concentrates, 3) concentrates with suspended solids. Generally, first class shows a Newtonian behavior while other two classes show non-Newtonian behavior (Juszczak and Fortuna, 2003).

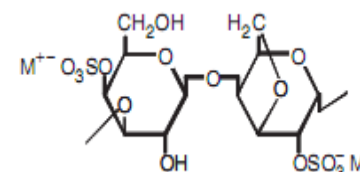
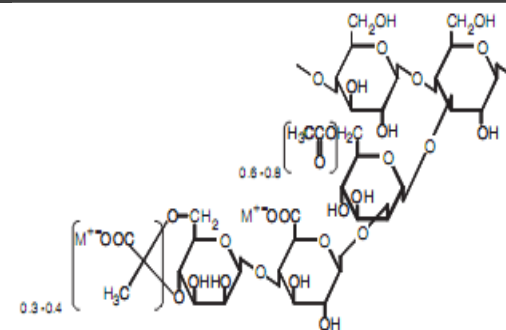
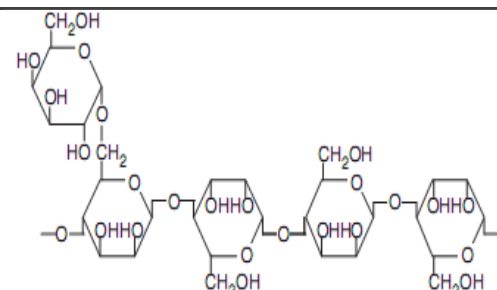
It has been reported that for true solutions, one observes ideal flow behavior with no yield stress and a flow index behavior of unity. In such a condition, flow characteristics of the system can be completely determined by one parameter, Newtonian viscosity. With exception of the ideal fluids, all other fluids do not have proportional relationships between shear stresses and shear rates. To distinguish such shear rate dependent relationships from Newtonian behavior “apparent” viscosity is widely used. Apparent viscosity, naturally a point function which cannot be extended to a wider shear rate, may be defined in two ways: 1) taking simply the ratio of shear stress to shear rate, 2) taking the slope of shear stress to shear rate curve at a particular shear rate, or taking derivative of the mathematical expression describing the shear stress and shear rate relationship (Rha, 1978).

Gums (hydrocolloids) are high molecular weight hydrophilic biopolymers, which serve various functions in food systems, such as enhancing viscosity, creating gel-structures, formation of a film, control of crystallization, inhibition of syneresis, improving texture, encapsulation of flavors and lengthening the physical stability, etc. (Sahin and Ozdemir, 2004; Kayacier and Dogan, 2006). They directly affect overall acceptability of food product via increasing the physical stability and the overall mouth-feel properties (Marcotte et al., 2001). In this respect, Locust bean gum (LBG), it is also known as carob gum or carubin (Rocha et al., 2009), Xanthan gum (XA) and iota-carrageenan (*i*-CARR) were used during sauce preparation to increase viscosity and physical stability of the sauces. The properties of these gums are summarized in Table 2.4.

Gum solutions are generally non-Newtonian pseudoplastic fluids and, power law model has been frequently used to characterize the flow behavior of gum solutions (Kayacier and Dogan, 2006).

Table 2.4. Properties of gums.

Gum type	Charge	Source	Chemical structure ^c	Solubility
Locust bean gum (LBG)	Neutral ^a	Obtained from the seeds of the corob tree (<i>Ceratonia siliqua</i> L.) ^b	β-1,4-D-mannopyranose backbone with α-1,6-D-galactopyranose residues as single unit side chains Man/Gal ratio 3.2 – 3.5	Completely soluble in hot water over 80°C ^d
Xanthan gum (XA)	Anionic ^e	Aerobic fermentation of the microbe <i>Xanthomonas compestris</i> ^e	Linear β-1,4-D glucopyranose backbone with alternating O-3linked trisaccharide side chains of β-Dmannopyranosyl, β-1,4-D- glucuronopyranosyl, α-1,2-D-mannopyranosyl with various amounts of acetyl and pyruvate substituents	Either soluble in hot and cold water ^d
í-carrageenan (í-CARR)	Anionic ^f	Extracted from red seaweed (<i>Rhodophyceae</i>) ^f	Linear chain of alternating β-1,3-D-galactopyranose-4-sulfate and α-1, 4-D-3,6-anhydrogalactose-2-sulfate units	Soluble in hot water over 50°C ^g



^a (Rocha et al., 2009)

^b (Lazaridou, et al., 2000)

^c (De Jong and Van De Velde, 2007)

^d (Sahin and Ozdemir, 2004)

^e (Rodríguez-Hernández and Tecante, 1999)

^f (Černíková et al., 2008)

^g (Trius and Sebranek, 1996)

CHAPTER III
MATERIALS AND METHODS

Experimental design and progress of the thesis work is presented in Table 3.1.

Table 3.1. Experimental design and progress of the thesis work.

Study	Details	Method
I	Fruit collection Cornelian cherry Pomegranate Strawberry Sour cherry Sweet cherry Blackberry Urmu mulberry	
II	Concentration Fresh fruit juices concentrated 40-45 °Brix	Rotary vacuum evaporation
III	Storage of concentrates Freezing at -30 °C	No-frost freeze dryer
IV	Physicochemical properties Total soluble solids pH Titratable acidity Color Total phenolics Total monomeric anthocyanins Total antioxidant activity	Refractometer pH meter Potentiometrically Colorimetrically - CIElab Spectrophotometrically -Folin- Ciocalteu method Spectrophotometrically -pH-differential method Spectrophotometrically -DPPH assay
V	Kinetic study Thermal degradation kinetics of anthocyanins and color	Thermal study was done at preheated ovens at 60, 70 and 80°C.
VI	Sauce preparation Cornelian cherry sauce Pomegranate sauce Strawberry sauce Sour cherry sauce Sweet cherry sauce Blackberry sauce Urmu mulberry sauce	Sauces were prepared with these concentrates with and without gum at three different gum concentrations (0.15, 0.30 and 0.60 % (w/v)) via three different gums (LBG, XA, <i>i</i> -CARR)
VII	Rheology of sauces Flow type and apparent viscosity	Rheometer

3.1. Materials

Cornelian cherry (*Cornus mas* L.) fruits were collected in Elazığ, Eastern Anatolia, Turkey, in September 2010. Pomegranate (*Punica granatum* L.) (in October 2010), Strawberry (*Fragaria x ananassa* Duch.) (in June 2011), sour cherry (*Prunus cerasus* L.) and sweet cherry (*Prunus avium* L.) (both in July in 2011), blackberry (*Rubus fruticosus* sp.) and Urmu mulberry (*Morus nigra* L.) (both in August 2011) fruits were collected in Gaziantep, Southeast Anatolia, Turkey. All fruits were transported to the laboratory for analysis. Pectolytic enzyme, Panzym XXL, was kindly gifted by Sinerji A.Ş., Mersin, TURKEY. The free radical 2,2-dipheynl-1-picrylhydrazyl (DPPH), Folin–Ciocalteu’s reagent, and gallic acid were purchased from Sigma Chemical Co. (St. Louis, MO, USA). Locust bean gum (LBG) (G-0753), xanthan gum (XA) (G-1253) and *ι*-carrageenan (*ι*-CARR) (C-1138) were purchased from Sigma Chemical Company. Buffer salts, potassium dihydrogen orthophosphate and disodium hydrogen orthophosphate were purchased from Analar analytical reagent; BDH chemical Ltd. All the other reagents were of analytical grade.

3.2. Preparation of juices and concentrates

All the foreign materials such as pieces of branches and leaves and also unripe and damaged fruits were removed from fruit samples by hand. The cleaned fruits were washed under cold tap water, stalks and seeds were removed if it is available. Fruits were ground by using a laboratory blender. Juice was immediately filtered through muslin to remove pulp from the juice. Then the juice was depectinized with 1.0 % (w/v) Panzym XXL at 50 °C for 2 h. The depectinized juice was allowed to rest at 4°C for 24 h. The juice was again filtered through five layer muslin and finally double layer filter paper to obtain a clear juice. Clear juices were concentrated using BÜCHİ Rotary Evaporator (Rotavapor R-3 model, BÜCHI Loborthechnik AG, Flawil, Switzerland) at 40 °C up to 40-45 °Brix.

3.3. Physicochemical properties

Total soluble solids (TSS) content was measured with a digital refractometer (PTR 46X, England) at 20 °C. pH measurements were done by using Nel-890 Model pH meter (Ankara, Turkey) calibrated with pH 4 and 7 buffers. Titratable acidity was determined potentiometrically by titrating the sample with 0.1 NaOH until the pH reached 8.2 and expressed as percent citric acid.

3.4. Determination of total phenolics

The total phenolic content in concentrate samples were determined colorimetrically by the Folin-Ciocalteu method (Waterhouse, 2002). Chemical reagents used in this method were prepared as follows:

- *Gallic acid stock solution:* Carefully weighted 0.5 g of drg gallic acid was dissolved in 10 ml of ethanol and completed to 100 ml with twice distilled water in 100 ml volumetric flask.
- *Sodium carbonate solution:* 200 g of anhydrous sodium carbonate was dissolved in 800 ml twice distilled water and brought to boil. After cooling, a few crystals of sodium carbonate was added, and after 24 hour, filtered with Whatman no 1 filter paper and, twice distilled water was added to make up the volume 1 L.
- *Calibration curve:* To prepare calibration curve, 0, 1, 2, 3, 5 and 10 ml of the gallic acid stock were added into 100 ml volumetric flasks, and diluted to volume with twice distilled water. The solutions will have phenolic concentrations of 0, 50, 100, 150, 250 and 500 mg gallic per liter of solution (Appendix A, Figure A1).

100 μ L of sample diluted with methanol up to appropriate dilution factor for each concentrate, and it was mixed with 6 ml of twice distilled water. 500 μ L of Folin-Ciocalteu reagent was added. After waiting 5 minutes at room temperature, 1.5 mL of sodium carbonate (20 % w/v) was added to adjust optimum pH for the reaction. The mixture was vortexed and incubated at room temperature ($\sim 23^{\circ}\text{C}$) for 2 h and then the absorbance was measured at 765 nm using a UV-VIS Lambda 25 spectrophotometer (Perkin Elmer, Shelton, USA). Gallic acid was used as a standard and total phenolic content was expressed in mg gallic acid equivalents (GAE) per liter of concentrate. A mixture of water and reagents was used as a blank. All analyses were done in triplicate.

3.5. Determination of total monomeric anthocyanins

Total anthocyanin content of concentrates was determined using the pH-differential method described by Giusti and Wrolstad (2001), using two buffer systems:

potassium chloride buffer, pH 1.0 (0.025 M), and sodium acetate buffer, pH 4.5 (0.4 M). Buffer solutions were prepared as follows:

- *Potassium chloride buffer, 0.025 M, pH 1.0:* Carefully weighted 1.86 g KCl were dissolved in 980 ml of twice distilled water in a beaker and, pH of the solution was adjusted to 1.0 with concentrated HCl, then the solution was transferred to 1 liter volumetric flask and completed to 1 L with twice distilled water.
- *Sodium acetate buffer, 0.4 M, pH 4.5:* Carefully weighted 54.43 g $\text{CH}_3\text{CO}_2\text{Na}\cdot 3\text{H}_2\text{O}$ were dissolved in 960 ml of twice distilled water in a beaker and, pH of the solution was adjusted to 4.5 with concentrated HCl, then the solution was transferred to 1 liter volumetric flask and completed to 1 L with twice distilled water.

The concentrate samples were diluted up to appropriate dilution factor for each concentrate with twice distilled water. A 0.4 ml of diluted sample was mixed with 3.6 ml of corresponding buffers and allowed to equilibrate for 15 minutes at room temperature. The absorbance of each equilibrated solution was measured at 510 nm (λ_{max}) and 700 nm for haze correction, using UV-VIS Lambda 25 spectrophotometer (Perkin Elmer, Shelton, USA). Total monomeric anthocyanins were calculated as mg cyanidin-3-glucoside per liter concentrate according to the following equation:

$$\text{Total anthocyanins (mg/L)} = A \times \text{MW} \times \text{DF} \times 1000 / (\epsilon \times l) \quad (3.1)$$

where $A = (A_{510} - A_{700})_{\text{pH } 1.0} - (A_{510} - A_{700})_{\text{pH } 4.5}$; MW (molecular weight) = 449.2 g/mol for cyanidin-3-glucoside; DF = dilution factor as final volume per initial volume; l = pathlength in cm; ϵ = 26,900 molar extinction coefficient in L/mol/cm for cyanidin-3-glucoside; 1000 = conversion factor from g to mg. All analyses were done in triplicate. Glass cuvettes of 1 cm path-length were used and all measurements were carried out at room temperature ($\sim 23^\circ\text{C}$). Absorbance readings were made against twice distilled water as blank.

3.6. Determination of antioxidant activity

DPPH assay was done according to the method of Brand-Williams et al. (1995) with some modifications. The stock solution was prepared daily by dissolving 1.2 mg DPPH with 50 mL methanol and special care was taken to minimize the loss of free radical activity of the stock solution during the course of sample preparation. 100 μL of diluted sample up to appropriate dilution factor for each concentrate with methanol was mixed with 3900 μL of $6 \times 10^{-5} \text{ mol L}^{-1}$ DPPH in methanol. The mixture was vortexed and left to stand for 30 min in dark place at room temperature. Then the absorbance was measured spectrophotometrically at 515 nm using UV-VIS Lambda 25 spectrophotometer (Perkin Elmer, Shelton, USA). The percent of reduction of DPPH was calculated by the formula reported by Tural and Koca (2008).

$$\% \text{ DPPH reduction} = [(A_C - A_S)/A_C] \times 100 \quad (3.2)$$

where A_C = absorbance of a control ($t = 0$ min), A_S = absorbance of a tested sample at the end of the reaction ($t = 30$ min). Glass cuvettes of 1 cm path-length were used and all measurements were carried out at room temperature ($\sim 23^\circ\text{C}$). Absorbance readings were made against methanol as blank and control sample was prepared with the same volume of methanol mixed with DPPH stock solution. All analyses were done in triplicate.

3.7. Color measurements

The visual color was evaluated using a HunterLab Colourflex (A-60-1010-615 Model Colourimeter, Hunter Associates Lab. Inc. Reston VA, USA). The instrument was standardized each time with a black and a white ($L = 91.10$, $a = 1.12$, $b = 1.26$) tile. The color values were expressed as L^* (lightness), a^* (redness/greenness) and b^* (yellowness/blueness). Total color difference (TCD*) was calculated and modeled. Color values were the means of triplicate measurements.

3.8. Degradation studies

Thermal degradation of concentrates was studied at 60, 70 and 80°C . Aliquots of 10 ml of concentrates were put into screw-cap test tubes to prevent evaporation and test tubes were placed into oven preheated to a given temperature. At regular time

intervals (0, 2, 4, 6, 8, and 10 h), samples were removed from the oven (NÜVE EN500, Ankara, Turkey) and rapidly cooled by plunging into an ice bath to stop further degradation. The anthocyanin contents and color values of the samples were measured immediately.

3.9. Degradation kinetics of anthocyanins

Previous studies showed that thermal degradation of anthocyanins followed a first-order reaction (Garzón and Wrolstad, 2002; Kırca et al., 2006; Wang and Xu, 2007; Shao-qian et al., 2011). This kinetic type was expressed by the following equation:

$$C = C_o * \exp (\pm k_1 * t) \quad (3.3)$$

where C_o is the initial anthocyanin contents and C is the anthocyanin contents after time t (min) of heating at the given temperature while k_1 is the first order rate constant (min^{-1}). The parameters of first order kinetic model (Eq. (3.3)) were estimated by non-linear regression iterative procedure of the SigmaPlot (SigmaPlot 10.0 Windows version, SPSS Inc.).

Half-lives ($t_{1/2}$) which is the time needed for 50 % degradation was calculated by the following equation:

$$t_{1/2} = -\ln 0.5/k_1 \quad (3.4)$$

where $t_{1/2}$ is the half-lives and, k_1 is the first order degradation rate constant (h^{-1}).

The effect of temperature on the degradation rate constants was expressed by the linearized Arrhenius equation by plotting $\ln k$ against $1/T$ in which the temperature dependence of k was quantified by the activation energy E_a according to Eq. (3.5).

$$\ln k = \ln A_o - E_a/RT \quad (3.5)$$

where the k is the rate constant (min^{-1}), A_o is the frequency factor (min^{-1}), E_a is the activation energy (kJ/mol), R is the universal gas constant (8.314 J/mol/ K) and T is the absolute temperature (Kelvin, K). The E_a value was calculated from the slope of

the straight lines given by Eq. (3.5), using a linear regression procedure of the SigmaPlot (SigmaPlot 10.0 Windows version, SPSS Inc.).

3.10. Kinetics model of visual color

The complexity of fruit juices and derivatives implies a wide range of enzymatic and non-enzymatic browning reactions caused by thermal treatments. Consequently it is difficult to establish a reaction mechanism and to obtain a kinetic model describing the global process adequately (Ibarz et al., 1999). There are numerous references on the kinetics of color of food materials in the literature. The majority of these works report zero-order (Eq. (3.6)) or first-order (Eq. (3.3)) degradation reaction kinetics.

$$C = C_0 \pm k_o * t \quad (3.6)$$

Sometimes the relatively simple models described do not adequately represent color change mechanism. Since these changes can be due to not only to the Maillard reaction but also to the thermal destruction of pigments. That is why a combined kinetics has been developed, in which the non-enzymatic color change reactions are considered to consist of two stages. A first stage of colored polymeric compound formation (i.e., color formation) based on Maillard reactions following zero order kinetics, the second stage supposes decomposition of the colored polymers into non-colored compounds (i.e., pigment destruction) following a first order kinetics. According to this combined kinetic model, the color change mechanism can be expressed by (Garza et al., 1999; Ibarz et al., 1999; Ibarz et al., 2000):

$$C = \frac{k_o}{k_1} - \left[\frac{k_o}{k_1} - C_o \right] \exp(\pm k_1 * t) \quad (3.7)$$

The terms C and C_o are the concentrations of color parameters at any time t and initial concentration, respectively; k_o is the zero-order kinetics constant and k_1 is the first-order kinetics constant in Equations (3.3), (3.6), (3.7). The parameters of combined kinetic model (Eq. (3.7)) were estimated by non-linear regression iterative procedure of the SigmaPlot (SigmaPlot 10.0 Windows version, SPSS Inc.).

Total color difference (TCD*) was calculated by using L^* , a^* , b^* values with (Eq. (3.8)) (Loughrey, 2002):

$$TCD^* = \sqrt{(L_0^* - L^*)^2 + (a_0^* - a^*)^2 + (b_0^* - b^*)^2} \quad (3.8)$$

where, L_0^* , a_0^* and b_0^* refer to initial values, and L^* , a^* and b^* refer to color values at various times during heat treatment.

3.11. Preparation of sauces

Phosphate buffer to dissolve gums and, stock gum solutions used in sauce preparation were prepared as follows:

- *Phosphate buffer, 0.05 M and pH 7.0:* Phosphate buffer was prepared by dissolving potassium dihydrogen orthophosphate (3.76 g) and disodium hydrogen orthophosphate (3.44 g) in 2 liter twice distilled water and, pH was adjusted to 7.0 by using 0.1 M NaOH and 0.1 M HCl.
- *Preparation of stock gum solutions:* LBG, XA and *i*-CARR stock solutions were prepared by dispersing the powders in phosphate buffer and vigorously stirring for 30 min at room temperature by magnetic stirrer, followed heating less than 50 °C until the solution became clear.

Sauces were prepared in the laboratory with previously prepared fruit juice concentrates. For each fruit juice concentrate, sauces prepared as without gum and with gums of LBG, XA and *i*-CARR at three different gum concentrations (0.15, 0.30 and 0.60 % (w/v) by using stock gum solutions. In each case, to make 2 ml of sauce, appropriate quantity of stock gum solution was dissolved in related fruit juice concentrate via vortex in the test tube.

3.12. Rheological measurements

The rheological measurements were performed at 25±0.01 °C by using a CVOR Rheometer (Bohlin, Malvern, Worcestershire, United Kingdom) equipped with Peltier Temperature Controller Unit. The measuring system consisted of a cone and plate sensor with a diameter of 2 cm and cone angle of 2°. Shear rate range was 0–

300 s⁻¹ within 600 s. For each measurement, 1 ml of sample was carefully poured over the plateau of rheometer. Each measurement was done in duplicate. Rheological parameters (shear stress, shear rate, apparent viscosity) were obtained from the Bohlin CVOR 150 data analysis software. Experimental flow curves were fitted to power law model (Krokida, 2001):

$$\sigma = K\gamma^n \quad (3.9)$$

where σ is the shear stress (Pa), γ is the shear rate (s⁻¹), K is the consistency index (Pasⁿ), and the exponent n , called the flow behavior index (dimensionless). The parameters (K , n) of the power law model (Eq. (3.9)) were estimated by linear regression iterative procedure of the SigmaPlot (SigmaPlot 10.0 Windows version, SPSS Inc.). Since for non-Newtonian fluids, apparent viscosity, η_{app} , is reported as a function of shear rate (Rha, 1978), in this study, it was computed at shear rate of 50 s⁻¹ using power law parameters (K , n) due to the following equation:

$$\eta_{app} = K\gamma^{n-1} \quad (3.10)$$

The shear rate of 50 s⁻¹ was selected because of its being known as effective oral shear rate (Marcotte et al., 2001).

CHAPTER IV

RESULTS AND DISCUSSION

4.1. Physicochemical Properties

In this study, fruit juices were concentrated as adjusting total soluble solids within the range of 40-45 °Brix via rotary vacuum evaporator at 40°C to maintain nutritional benefits. All physicochemical properties of related concentrates were given in Table 4.1. Total soluble solids (TSS) contents of Cornelian cherry, pomegranate, strawberry, sour cherry, sweet cherry, blackberry and Urmu mulberry concentrates were measured as 43.52, 40.66, 41.0, 43.55, 45.02, 45.28 and 45.20 °Brix, respectively. While pH of concentrates found in the range of 2.83-3.75, titratable acidity (as percent citric acid) of them changed between 0.87 and 1.85 %. In this respect, the acidity of concentrates based on titratable acidity values were following descending order: strawberry > sour cherry > blackberry > Cornelian cherry > Urmu mulberry > pomegranate > sweet cherry. In addition, it was clearly observed that concentration did not have considerably effect on pH and titratable acidity (TA) values of concentrates. For example, pH and TA values of pomegranate juice were 2.97 and 1.15 %, respectively, which were close to pH (3.02) and titratable acidity (1.18 %) of pomegranate concentrate (Erçelebi and Kara, 2011). Similar trends were also seen in other concentrates. Similar results were observed by Wang and Xu (2007) for blackberry juice and concentrate, and by Garzón and Wrolstad (2002) for strawberry juice and concentrate.

Hunter color parameters have previously proved valuable information in describing visual color deterioration and supplying useful information for quality control of fruit and fruit products such as concentrated fruit pulp (Lozano and Ibarz, 1997), double concentrated tomato paste (Barreiro et al., 1997), blood orange juice (Shao-qian et al., 2011), plum puree (Ahmed et al., 2004), pineapple puree (Chutintrasri and Noomhorm, 2007). The color values were expressed as L^* (lightness) ($L^*=0$ absolute black and $L^*= 100$ absolute white), a^* (redness/greenness) and b

Table 4.1. Physicochemical properties of concentrates.

	Cornelian cherry	Pomegranate	Strawberry	Sour cherry	Sweet cherry	Blackberry	Urnu mulberry
pH	2.90	3.02	2.83	2.95	3.75	3.04	3.30
Total soluble solids (°Brix)	43.52	40.66	41.0	43.55	45.02	45.28	45.20
Titrateable acidity (as percent citric acid) (%)	1.49	1.18	1.85	1.72	0.87	1.63	1.42
Color							
<i>L</i> *	0.98	0.63	0.31	0.70	0.55	0.73	1.00
<i>a</i> *	4.17	0.84	0.70	0.25	0.35	0.12	0.23
<i>b</i> *	0.78	-0.62	-0.29	0.23	0.10	0.10	0.13
Total Monomeric Anthocyanins (mg/L)	207	1101	3236	1767	18	2423	2233
Total phenolics (mg GAE /L)	2180	1190	4760	2390	620	3600	2650
Total antioxidant activity (% reduction)	96	94	91	82	20	84	91

Values represent means calculated from three replicates.

(yellowness/blueness). Wrolstad et al. (2005) have been reported that a very prevalent error is to use the a^* value as a measure of the amount of the redness or greenness and, b^* value as a measure of yellowness or blueness. He also stated that samples with identical a^* values may exhibit colors ranging from purple to red to orange, it is better to examine color as three dimensional in terms of lightness, chroma and hue angle. Table 4.1 shows Hunter color parameters of all concentrates and it was seen that all concentrates have positive a^* values, among them Cornelian cherry concentrate had the the highest a^* value (4.17) and, blackberry had the lowest a^* value (0.12). All concentrates except strawberry and pomegranate had positive b^* values. Table 4.1 shows also that sour cherry concentrate (0.25) and Urmu mulberry concentrates (0.23) had nearly same a^* value, but actually they were not seen at the same color when looked with naked eye, the color of sour cherry was dark red while blackberry was purple. Cornelian cherry and strawberry concentrates were seen nearly at similar red color intensities when looked with naked eye, however, Cornelian cherry had nearly six times higher positive a^* value than strawberry concentrate. All concentrates had L^* values close to zero but none of them was seen black. These differences could be explained by the study of Wrolstad et al. (2005). They have been reported that color perception was the combination of these three parameters and therefore it was inefficient to evaluate them individually.

Strawberry juice was concentrated from 8.0 to 41.0 °Brix and, pH and titratable acidity (% citric acid) were found 2.83 and 1.85, respectively (Table 4.1). Cengiz (2007) has been reported that strawberry genotypes from different regions of Turkey showed different pH and acidity values with respect to changes in plant genotype and ecological conditions. Total monomeric anthocyanin, total phenolic matter and total antioxidant activity of strawberry concentrates were determined as 3236 mg/L, 4760 mg GAE/L and, 91 % reduction, respectively (Table 4.1). In the studies of Garzón and Wrolstad (2002) on stability of pelargonidin-based anthocyanins in strawberry juice (8.06 and 8.25 °Brix) and concentrate (75.0 and 69.0 °Brix), total monomeric anthocyanin content of the juice and concentrate ranged from 268 to 290 mg/L and 210-222 mg/L, respectively, which were lower than our findings (3236 mg/L). Studies of Scalzo et al. (2005) on effect of plant genotype upon total antioxidant capacity and phenolic contents of fruits showed that six different strawberry cultivars had phenolic contents from 2128 to 1093 mg GAE/L due to differential cultivars

which were lower than our findings(4760 mg GAE/L). Previous studies also showed that strawberries have higher antioxidant potential than many fruits (Wang et al., 1996; Scalzo et al., 2005).

Blackberry juice was concentrated from 12.0 to 45.28 °Brix. Titratable acidity, pH, total monomeric anthocyanin, total phenolic matter and total antioxidant activity of blackberry concentrates were determined as 1.63 %, 3.04, 2423 mg/L, 3600 mg GAE/L and 84 % reduction, respectively (Table 4.1). Cemeroğlu et al. (2009) have been reported that total acidity of blackberries changes between 0.4 and 2.5 %, which is consistent with our results. In the studies of Wang and Xu (2007) on degradation kinetics of anthocyanins in blackberry juice and concentrate, total monomeric anthocyanin content of blackberry juice (8.9 °Brix) and concentrate (65.0 °Brix) was found 400.77 and 417.85 mg/L, respectively, which were lower than our results. They also concluded that anthocyanins in blackberries are relatively higher than strawberry, pomegranate and blueberry. In addition, total phenolic content of these blackberry juice (8.9 °Brix) and concentrate (65.0 °Brix) was found 1540.93 mg GAE/L and 1547.84 mg GAE/L, respectively. These variations were probably due to differences among in cultivars, growing seasons, agricultural practices and variations in applied experimental assays. In the studies of Pantelidis et al. (2007) on antioxidant capacity, phenol, anthocyanin and ascorbic acid contents in raspberries, blackberries, red currants, gooseberry and Cornelian cherries, Cornelian cherries were found to have highest anthocyanin content (223 mg/ 100 g fresh weight) expressed as cyanidin-3-glucoside, followed by blackberry and raspberry x blackberry cultivars (104–198 mg/100 g fresh weight), whereas raspberry and red gooseberry cultivars (35–49 mg/100 g fresh weight) were found to have lowest amounts of anthocyanins. Moreover, blackberry and raspberry x blackberry cultivars had highest phenolic content and highest antioxidant activity as compared to other species of their study. In addition, Koca and Karadeniz (2009) have been reported that anthocyanin contents, phenolic contents and antioxidant activity of wild blackberries were higher than those of cultivated blackberries.

Cornelian cherry juice was concentrated from 18.46 to 43.52 °Brix. Titratable acidity and pH of Cornelian cherry concentrates were determined as 1.49 % and 2.90 (Table 4.1), respectively and, these results were relevant with previous findings (Demir and

Kalyoncu 2003; Didin et al., 2000; Tural and Koca 2008). Total monomeric anthocyanin, total phenolic matter and total antioxidant activity of Cornelian cherry concentrates were determined as 207 mg/L, 2180mg GAE/L and, 96 % reduction, respectively (Table 4.1). As compared to the studies of Tural and Koca (2008) on physico-chemical and antioxidant properties of Cornelian cherry fruits grown in Turkey, there has been a small difference which possibly caused by differences in sampling and applied experimental assays, plant genotype, harvesting time, and ecological conditions.

Fully ripened Urmu mulberry juice was concentrated from 15.02 to 45.20 °Brix. Titratable acidity as percent citric acid and pH of concentrates were determined as 1.42 % and 3.30, respectively (Table 4.1). Ercisli and Orhan (2008) have been reported that total soluble solids and pH of black mulberry fruits which grown in different agro climatic region of Turkey were between 13.91-18.36 % and 3.31-3.80, respectively, and also, the variation of these parameters could be the result of heterozygote nature of seed propagated genotypes and the effect of different environmental conditions where the genotypes grown. Our results showed that Urmu mulberry has slightly acidic character which was relevant with previous findings (Ercisli and Orhan, 2007; 2008). Orhan and Ercisli (2010) have been reported that most of mulberry species, except *Morus alba*, has a distinct flavor with juicy and acidic characteristics making them attractive for use in the processing industry for products such as fruit juice, ice cream, jelly and jam. Table 4.1 shows that Urmu mulberry concentrates had high total monomeric anthocyanin (2233 mg/L), total phenolic matter (2650 mg GAE/L) and total antioxidant activity (91 % reduction). Ercisli and Orhan (2008) have been reported that black mulberry genotypes from Northeast Anatolia region of Turkey had high total phenolic content (1943-2237 mg GAE/100 g fresh mass) and their wide differences among genotypes as a result of plant genotype and cultivation site and technique. Similar results were found by Ercisli and Orhan (2007), in their studies black and red mulberries had higher phenolic matter than white mulberries. Studies of Özgen et al. (2009) on phytochemical and antioxidant properties of red and black mulberries had been demonstrated that black mulberry exhibited higher total phenolics, total monomeric anthocyanin and total antioxidant capacity than red mulberries, which supports our findings. In addition, Bae and Suh (2007) have been reported that anthocyanins are

considered as very good antioxidant agents and the antioxidant capacity has been correlated to a significant degree with anthocyanin content in small fruits, indicating that anthocyanins may govern to a certain extent the antioxidant capacity of several plant tissues. Moreover, in their studies mulberries which were rich in anthocyanin compounds showed strong antioxidant activity, In addition, Du et al. (2008) have been reported that mulberry anthocyanins are excellent antioxidant agents. Aramwit et al. (2010) in their studies over various colors of mulberry fruits (*Morus alba*), have been reported that, purple-colored mulberry fruit extract contains the highest levels of anthocyanins and strong antioxidants compared with other colors mulberry fruit extracts.

Sour and sweet cherry juices were concentrated from 16.56 and 15.0 total soluble solid content to 45.02 and 43.55 °Brix, respectively. Titratable acidity, pH, total monomeric anthocyanin, total phenolic matter and total antioxidant activity of sour cherry concentrates were determined as 1.72 %, 2.95, 1767 mg/L, 2390 mg GAE/L and 82 % reduction, respectively (Table 4.1). Although pH value was a bit lower than the studies of Cemeroglu et al. (2009), pH and titratable acidity values were in accordance with their results. Titratable acidity, pH, total monomeric anthocyanin, total phenolic matter and total antioxidant activity of sweet cherry concentrate determined as 0.87 %, 3.75, 18 mg/L, 620 mg GAE/L and 20 % reduction, respectively (Table 4.1). Titratable acidity and pH values of sweet cherry concentrate were in consistent with previous studies (Karlidag et al., 2009). Chaovanalikit and Wrolstad (2004) in a study on total anthocyanins and total phenolics of fresh and processed cherries (one sour and three sweet cherry cultivars) their antioxidant properties, have been reported that both sour and sweet cherries rich in anthocyanin and polyphenolics. In their study sour cherry cultivar of Montmorency contained higher phenolics and exhibited higher antioxidant activity than sweet cherry cultivars (Bing, Royal Ann, Rainier), which supports our findings. In our study, sweet cherry concentrates had relatively low phenolic content, anthocyanin content and showed vividly low antioxidant activity. In another study by Usenik et al. (2008) on sugar, organic acids, phenolic composition and antioxidant activity of 13 sweet cherry cultivars, sweet cherries found to have good antioxidant activity. They also suggested that antioxidant activity of sweet cherries depend on different chemical attributes (in some cultivars depend on phenolics, in others on anthocyanins and also with some

other compounds) which were specific for cultivars. Chaovanalikit and Wrolstad (2004) have been reported that total phenolics and anthocyanins for all cultivars were concentrated in the skin. So, in the light of all these data, it can be concluded that the low results of our sweet cherries can be caused by losing anthocyanin rich skin during depectinization and clarification process resulting in low anthocyanin content (18 mg/L), which may cause to low antioxidant activity (20 % reduction) (Table 4.1).

Pomegranate juice was concentrated from 15.33 to 40.66 °Brix. Titratable acidity and pH of pomegranate concentrates were determined as 1.18 and 3.02 (Table 4.1), respectively and, these results were relevant with previous findings (Miguel et al., 2004; Akbarpour et al., 2009). In addition, total monomeric anthocyanin, total phenolic matter and total antioxidant activity of concentrates were determined as 1101 mg/L, 1190 mg GAE/L and, 94 % reduction, respectively (Table 4.1). When compared to the studies of Tezcan et al. (2009) on commercial pomegranate juices sold in Turkish markets, total phenolic matter was lower while antioxidant activity was higher than their findings. Ozgen et al. (2008) have been reported that phenolic content of six pomegranate arils from Mediterranean region of Turkey are between 1245 and 2076 mg/L, which was close to our findings. Poyrazoğlu et al. (2002) have been reported that the pomegranate juices prepared from pomegranates grown in different regions of Turkey had different amount and composition of phenolic matter. In addition, total monomeric anthocyanin content of our pomegranate concentrate (1101 mg/L) was found to be higher than previous studies on different pomegranate genotypes by Çam et al. (2009) (8.1-36.9 mg/100ml) and Ozgen et al. (2008) (6.1-219.0 mg/L). They claimed that the differences in anthocyanin contents were probably caused by the differences due to genotype, harvesting time and ecological conditions. Similar assumptions could also be made for other physicochemical properties. Besides, Tezcan et al. (2009) and Gil et al. (2000) suggested that anthocyanins play only minor role in total antioxidant activity while punicalagin originating from the peels of pomegranate is one of the major contributors of this activity. So, it can be concluded that total monomeric anthocyanin content may not have direct impact on total antioxidant activity of pomegranate concentrate.

Finally, when these fruit concentrates were compared in general with respect to their total phenolic contents (as mg gallic acid equivalents/L concentrate), following descending order was observed: strawberry (4760 mg GAE/L) > blackberry (3600 mg GAE/L) > Urmu mulberry (2650 mg GAE/L) > sour cherry (2390 mg GAE/L) > Cornelian cherry (2180 mg GAE/L) > pomegranate (1190 mg GAE/L) > sweet cherry (620 mg GAE/L). Following descending order was found in terms of total monomeric anthocyanin contents (cyanidin-3-glucoside/L concentrate): strawberry (3236 mg/L) > blackberry (2423 mg/L) > Urmu mulberry (2233 mg/L) > sour cherry (1767 mg/L) > pomegranate (1101 mg/L) > Cornelian cherry (207 mg/L) > sweet cherry (18 mg/L). The total antioxidant activities (as % reduction) of our concentrates were in following descending order: Cornelian cherry (96 %) > pomegranate (94 %) > strawberry (91 %) = Urmu mulberry (91 %) > sour cherry (82 %) \cong blackberry (84 %) > sweet cherry (20 %). In the studies of Jakobek et al. (2007) on anthocyanin content and antioxidant activity of various red fruit juices, the high concentrations of phenolics were found in sour cherry juice (2054 mg GAE/L) and blackberry juice (1831 mg GAE/L) while sweet cherry juice (1567 mg GAE/L) and strawberry juice (1272 mg GAE/L) had relatively lower concentrations of phenolics. In addition, following hierarchy of anthocyanin concentrations (mg cyanidin-3-*O*-glucoside equivalents/L fruit juice) was found: blackberry juice (740 mg/L) > sour cherry juice (369 mg/L) > sweet cherry juice (257 mg/L) > strawberry juice (206 mg/L). They also reported the following the following hierarchic order in terms of total antioxidant activity (as μ mol Trolox equivalents (TE)/ml of juice): sour cherry juice (13 μ mol TE/ml) > blackberry juice (9 μ mol TE/ml) > strawberry (4 μ mol TE/ml) = sweet cherry (4 μ mol TE/ml). In the studies of Wolfe et al. (2008) on cellular antioxidant activity of common fruits, related fruits in order of total phenolics (as mg GAE/100 g fruit) were blackberry (412 mg GAE/100 g) > pomegranate (338 mg GAE/100 g) > strawberry (235 mg GAE/100 g) > cherry (151 mg GAE/100 g). They reported following descending order in terms of antioxidant activities (as μ mol Trolox equivalents (TE)/100 g fruit): strawberry (8348 μ mol TE/100 g) > blackberry (6221 μ mol TE/100 g) > cherry (5945 μ mol TE/100 g) > pomegranate (4479 μ mol TE/100 g). Variations in these orders probably have been caused by differences in plant genotype, harvesting time, ecological conditions and etc.

4.2. Degradation kinetics of total monomeric anthocyanins

Thermal stability of anthocyanins was studied at 60, 70, 80 °C. Sweet cherry concentrate had relatively low initial anthocyanin content (18 mg/L), so thermal degradation kinetics of sweet cherry anthocyanins was not studied. The use of a first order model to describe the thermal degradation of anthocyanins has previously been reported (Cemeroglu et al., 1994; Garzón and Wrolstad, 2002; Reyes and Cisneros-Zevallos, 2007; Wang and Xu, 2007; Yang et al., 2008; Patras et al., 2010; Verbeyst et al., 2011).

Degradation of anthocyanins during heating in related concentrates (except sweet cherry concentrate) was plotted as a function of time (Figure 4.1-4.6) and fitted to first order reaction kinetics. Thermal degradation of strawberry anthocyanins was shown in Figure 4.1. Strawberry concentrate has initially 3236 mg/L Total monomeric anthocyanins (TMA) content and decrease in anthocyanin content was 88.4 %, 94.0 % and 96.2 % for heating at 60, 70, 80 °C, respectively. Figure 4.2 illustrates the thermal degradation of blackberry anthocyanins. It has 2423 mg/L TMA content initially. Reduction in anthocyanin content was 85.9 %, 91.1 % and 97.1 % for heating at 60, 70, 80 °C, respectively. Initial TMA content of Cornelian cherry concentrate was 207 mg/L and decrease in anthocyanin content was 63.77 %, 71.50 % and 89.37 % for heating at 60, 70, 80 °C, respectively, at the end of 600 min. (Figure 4.3). Figure 4.4 shows that the thermal degradation of Urmu mulberry anthocyanins with initial 2233 mg/L TMA content. Decrease in anthocyanin content of Urmu mulberry was 56.02 %, 83.74 % and 91.67 % for heating at 60, 70, 80 °C. Sour cherry concentrate has initially 1767 mg/L TMA content and decrease in anthocyanin content was 22.5 %, 36.5 % and 50.5 % for heating at 60, 70, 80 °C, respectively (Figure 4.5). Figure 4.6 illustrates the thermal degradation of pomegranate anthocyanins. Pomegranate concentrate has initial 1101 mg/L TMA content and decrease in anthocyanin content was 47.9 %, 66.9 % and 82.5 % for heating at 60, 70, 80 °C, respectively.

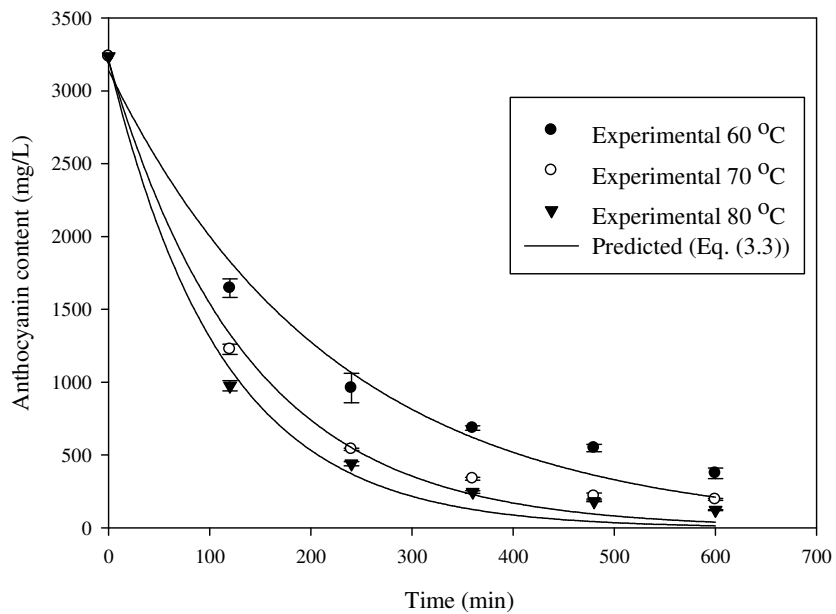


Figure 4.1. Degradation of anthocyanins in strawberry concentrates during heating at 60, 70 and 80 °C.

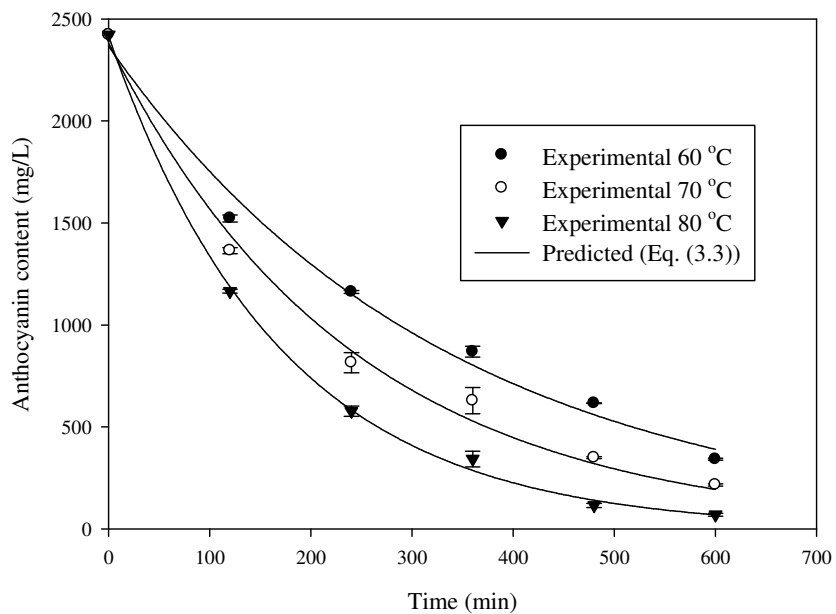


Figure 4.2. Degradation of anthocyanins in blackberry concentrates during heating at 60, 70 and 80 °C.

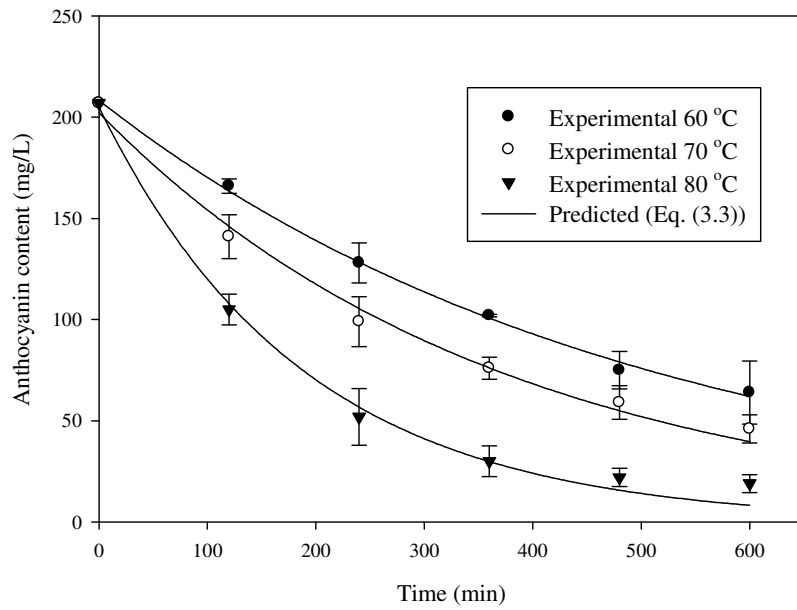


Figure 4.3. Degradation of anthocyanins in Cornelian cherry concentrates during heating at 60, 70 and 80 °C.

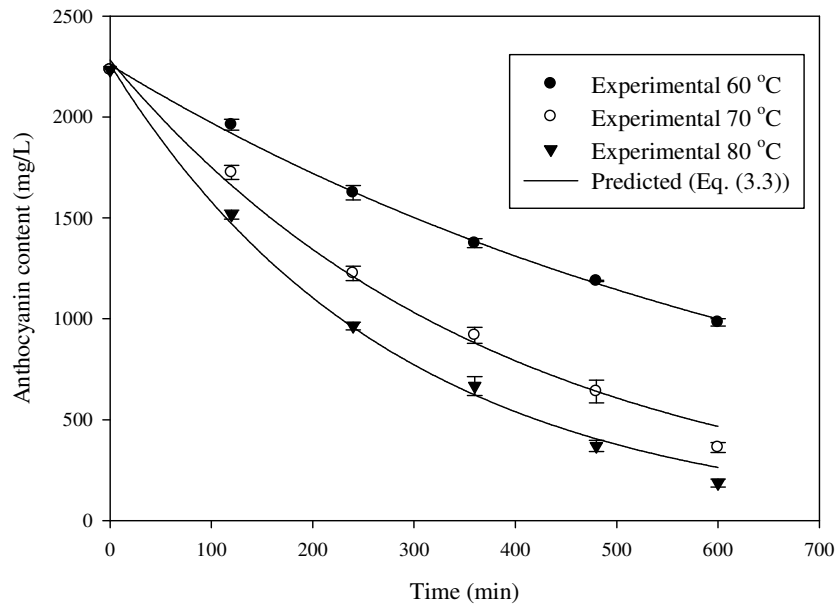


Figure 4.4. Degradation of anthocyanins in Urmu mulberry concentrates during heating at 60, 70 and 80 °C.

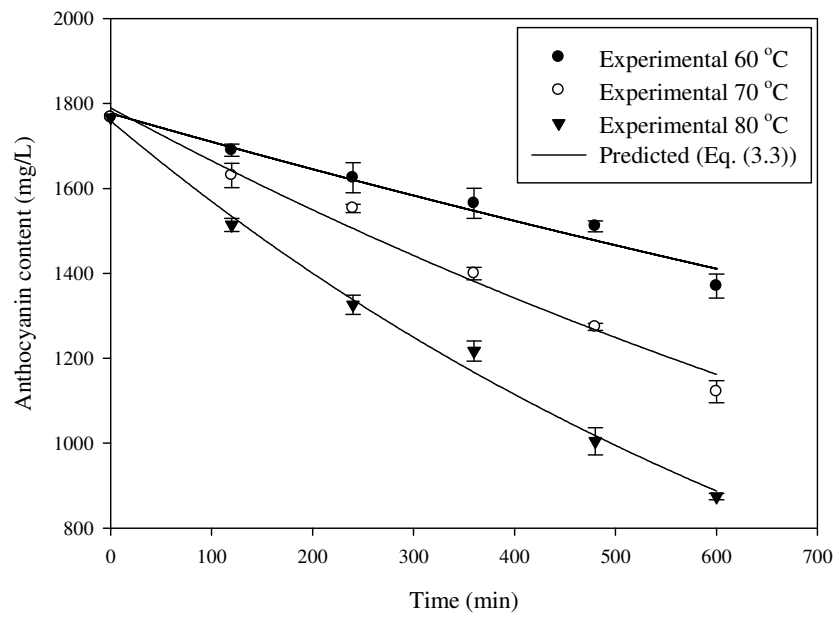


Figure 4.5. Degradation of anthocyanins in sour cherry concentrates during heating at 60, 70 and 80 °C.

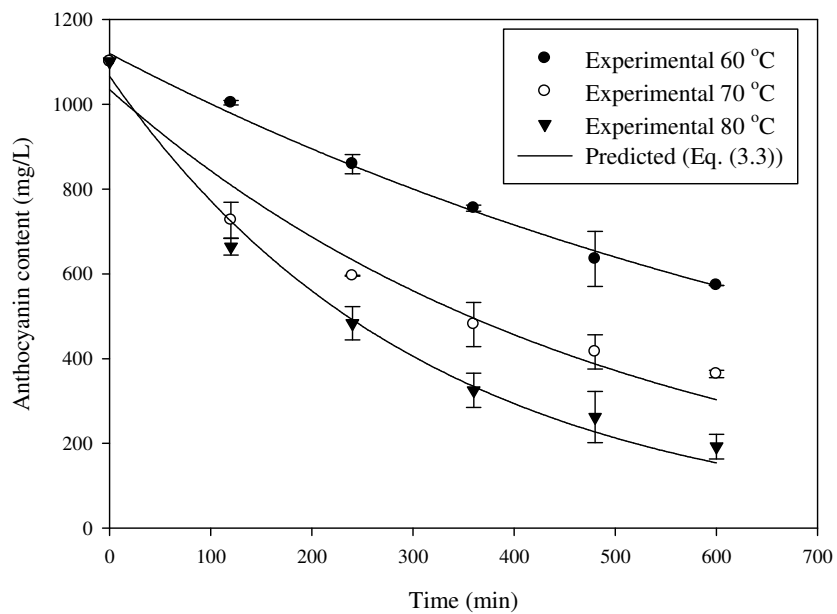


Figure 4.6. Degradation of anthocyanins in pomegranate concentrates during heating at 60, 70 and 80 °C.

Thermal degradation of anthocyanins of all these concentrates were fitted to first order kinetic model with respect to temperature and, the extent of anthocyanin degradation increased with increasing temperature and time (Figures 4.1-4.6). Moreover, it can be concluded that as anthocyanin concentration decreased the degradation rate also decreased. These results show that the rate of the degradation is directly proportional to the concentration of pigment, agree with those of previous studies reporting first order degradation kinetics of anthocyanins (Cemeroğlu et al., 1994; Garzón and Wrolstad, 2002; Kırca et al., 2006, Shao-qian et al., 2011).

The first order reaction rate constants (k_1), half-life of anthocyanins ($t_{1/2}$) and activation energy for defined temperature range were shown in Table 4.2. The comparison of k_1 values at selected temperatures showed the following order $(k_1)_{80^\circ\text{C}} > (k_1)_{70^\circ\text{C}} > (k_1)_{60^\circ\text{C}}$ for all concentrates. For example, the k_1 values for anthocyanin degradation were 0.002, 0.027 and 0.054 min^{-1} in Cornelian cherry concentrate at 60, 70 and 80 °C, respectively. Similar trends were observed for others also. As shown in Table 4.2, as temperature increased k_1 values increased. As expected, the degradation rate was dependent on temperature, being faster at high temperatures. So, it can be concluded that anthocyanin degradation was greatly dependent on temperature as indicated by higher k_1 values at higher temperatures (Kırca et al., 2003). Table 4.2 also shows that as temperature increased $t_{1/2}$ values decreased in consistent with faster reaction rates accompanied by higher k_1 values. For example, the $t_{1/2}$ values for anthocyanin degradation were 28.9, 16.5 and 10.5 h in sour cherry concentrate at 60, 70 and 80 °C, respectively (Table 4.2). Cemeroğlu et al. (1994) reported that the $t_{1/2}$ values for anthocyanin degradation were 24.0, 10.9 and 4.4 h in sour cherry concentrate (45° Brix) at 60, 70 and 80 °C, respectively, which were lower than our findings. That is, our sour cherries were found to be more heat stable. In addition, the $t_{1/2}$ values for anthocyanin degradation were 3.9, 2.8 and 2.0 h in blackberry concentrate at 60, 70 and 80 °C, respectively (Table 4.2). Wang and Xu (2007) reported that the $t_{1/2}$ values for anthocyanin degradation were 16.7, 8.8 and 4.7 h in blackberry juice (8.90 °Brix) at 60, 70 and 80 °C, respectively. This difference could be resulted from difference in total soluble solid content and blackberry genotype. Our concentrates were ordered to the decreasing heat susceptibilities as follows: strawberry, blackberry, Cornelian cherry, Urmu mulberry, pomegranate and sour cherry. These different susceptibilities of concentrate

anthocyanins to heat might be due to their varying anthocyanidin composition as reported by Wang and Xu (2007) and Yang et al. (2008).

Table 4.2. Effect of temperature on k_1 , $t_{1/2}$ and E_a values of anthocyanin degradation in concentrates.

Concentrate type	Temperature (°C)	$k_1^a \times 10^3$ (min ⁻¹)	$t_{1/2}$ (h) ^b	E_a (kJ/mol) ^c
Cornelian cherry	60	2.0 (0.9980) ^d	5.7	48.38 (0.9428) ^d
	70	2.7 (0.9920)	4.3	
	80	5.4 (0.9929)	2.1	
Pomegranate	60	1.1 (0.9935)	10.5	52.27 (0.9973)
	70	2.0 (0.9529)	5.8	
	80	3.2(0.9865)	3.6	
Strawberry	60	4.5(0.9792)	2.6	34.02 (0.9574)
	70	7.3 (0.9909)	1.6	
	80	9.0 (0.9911)	1.3	
Sour cherry	60	0.4 (0.9665)	28.9	49.51 (0.9980)
	70	0.7 (0.9828)	16.5	
	80	1.1(0.9936)	10.5	
Blackberry	60	3.0 (0.9893)	3.9	33.07 (0.9996)
	70	4.2 (0.9933)	2.8	
	80	5.9 (0.9989)	2.0	
Urmu mulberry	60	1.4 (0.9973)	8.3	46.32 (0.9744)
	70	2.6 (0.9922)	4.4	
	80	3.6 (0.9959)	3.2	

^a Rate constant.

^b Half-life.

^c Activation energy.

^d Numbers in parentheses are the correlation coefficients.

To determine the effect of temperature on degradation rate constants, the constants (k) obtained from Eq. (3.3) were fitted to Arrhenius equation Eq. (3.5) at 60, 70 and 80 °C (Figures 4.7-4.12). The calculated activation energy E_a for Cornelian cherry, pomegranate, strawberry, sour cherry, blackberry and black mulberry were 48.38 kJ/mol, 52.27 kJ/mol, 34.02 kJ/mol, 49.51 kJ/mol, 33.07 and 46.32 kJ/mol, respectively (Table 4.2). As shown, strawberry and blackberry concentrates has close but lower E_a values when compared to others. Also, Cornelian cherry, pomegranate, sour cherry and Urmu mulberry concentrates had nearly similar E_a values. Wang and Xu (2007) reported that at 60- 90 °C, the activation energy for degradation of anthocyanins for blackberry juice (8.9 °Brix) was 58.95 kJ/mol. Cemeroğlu et al. (1994) reported that at 50-80 °C, the activation energy for degradation of anthocyanins for sour cherry concentrate (45 °Brix) was 75.85 kJ/mol (18.13 kcal/mol). Low activation energy signified a higher rate of reaction for anthocyanins

whereas higher activation energy indicated a retarded rate of degradation (Ahmed et al., 2000). These results were consistent with $t_{1/2}$ values since strawberry and blackberry concentrates had the least $t_{1/2}$ values when compared to our other concentrates. The difference in activation energy values could be due to different soluble solid contents (Cemeroglu et al., 1994) and compositional change in samples being treated (Kırca et al., 2007).

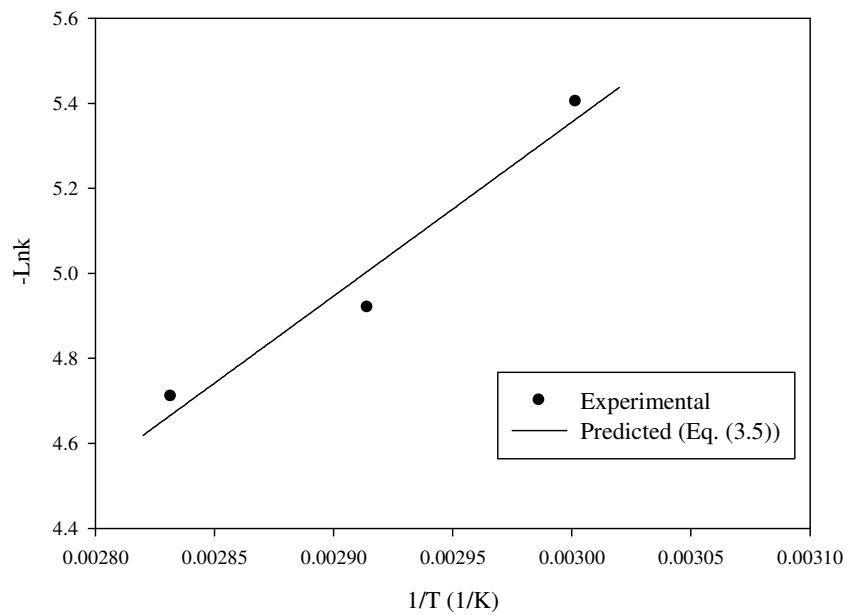


Figure 4.7. The Arrhenius plots for degradation of anthocyanins in strawberry concentrate during heating.

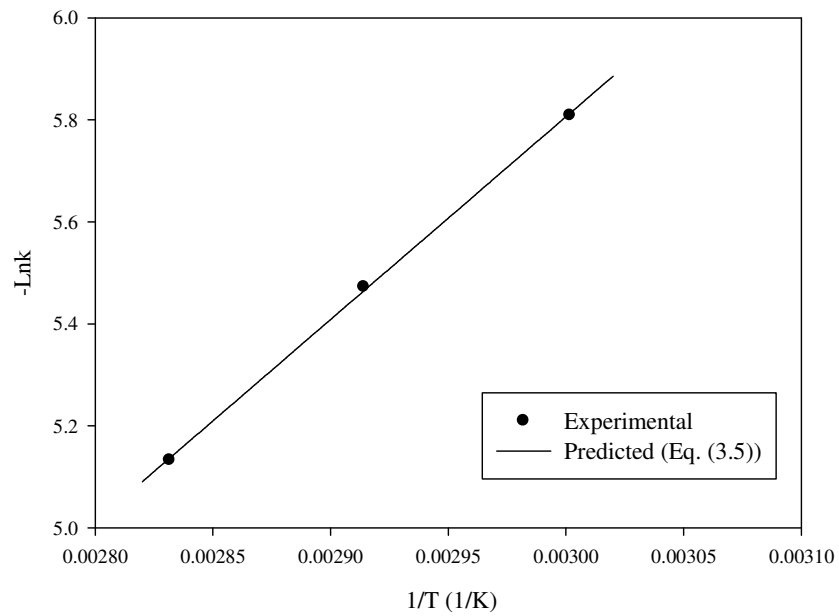


Figure 4.8. The Arrhenius plots for degradation of anthocyanins in blackberry concentrate during heating.

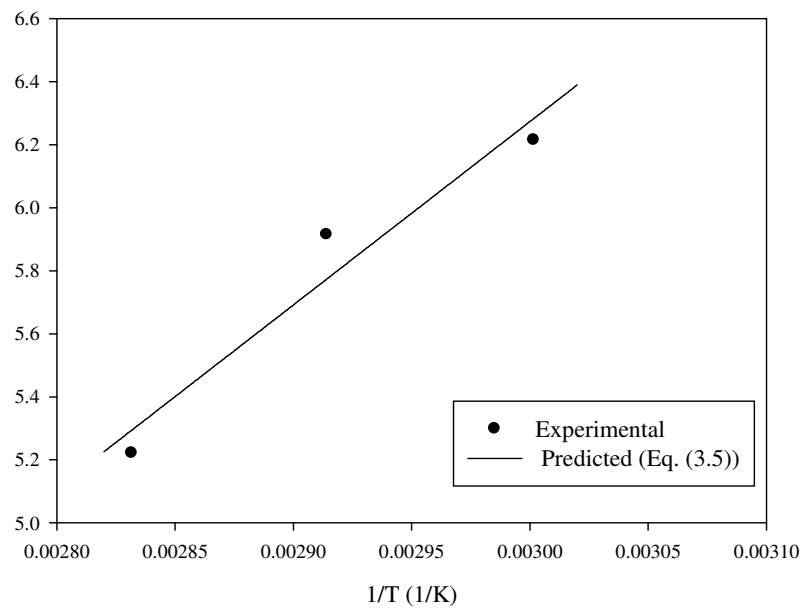


Figure 4.9. The Arrhenius plots for degradation of anthocyanins in Cornelian cherry concentrate during heating.

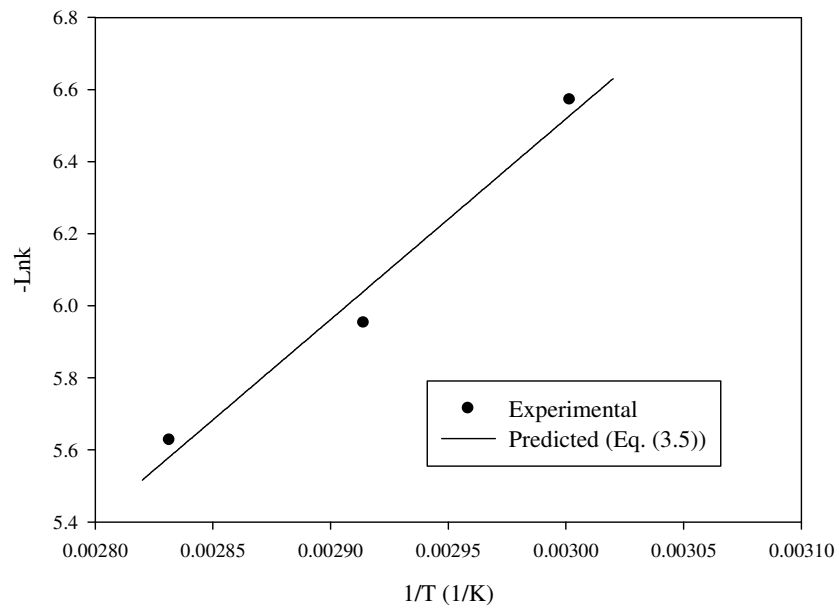


Figure 4.10. The Arrhenius plots for degradation of anthocyanins in Urmu mulberry concentrate during heating.

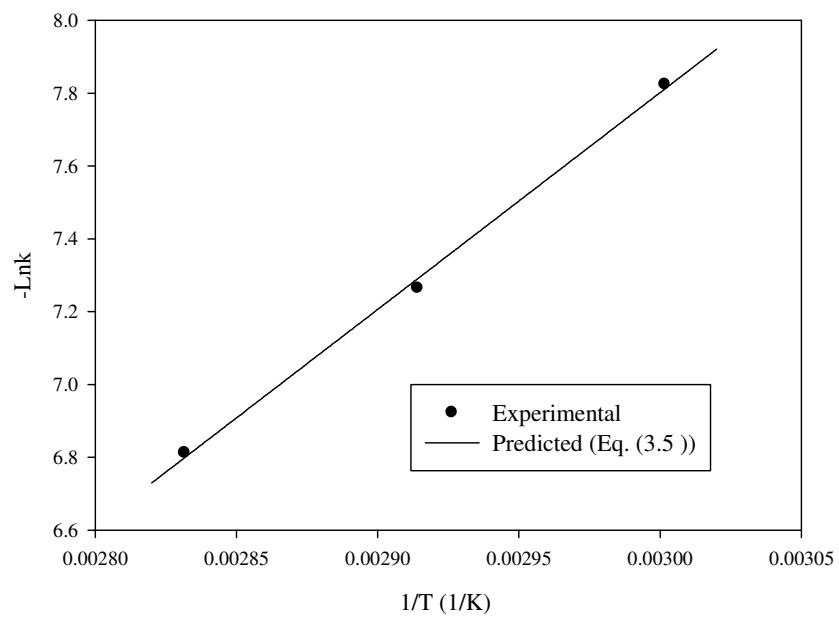


Figure 4.11. The Arrhenius plots for degradation of anthocyanins in sour cherry concentrate during heating.

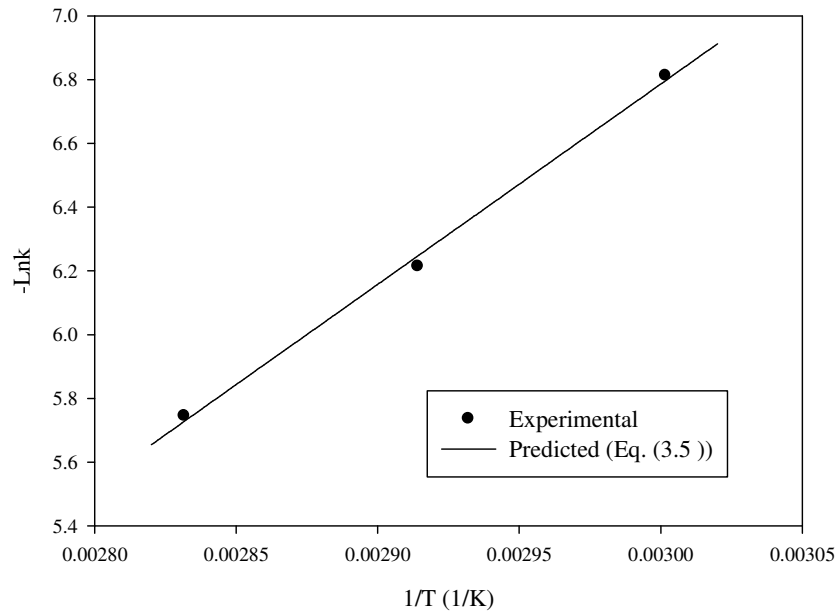


Figure 4.12. The Arrhenius plots for degradation of anthocyanins in pomegranate concentrate during heating.

4.3. Degradation kinetics of visual color

Since perception of color is the result of three coordinate axes of L^* , a^* , b^* and, difficult to interpret independently, an overall examination of these three coordinate axes of CIELAB colourimetric space was needed (Loughrey, 2002; Wrolstad et al., 2005). One of the best parameters for describing the color variation is the total color difference (TCD^*) since it is the combination of parameters L^* , a^* and b^* (Ibarz et al., 1999). Therefore, TCD^* parameters were calculated by using L^* , a^* , b^* values (Eq. (3.8)). Variation of TCD^* value of concentrates fitted to zero order (Eq. (3.6)), first order (Eq. (3.3)) and combined model (Eq. (3.7)) during heating at 60, 70 and 80 °C for 600 minutes. Since combined model was chosen the best model with highest correlation coefficients (R^2) values and only the graphs of this model were given (Figures 4.13-4.19).

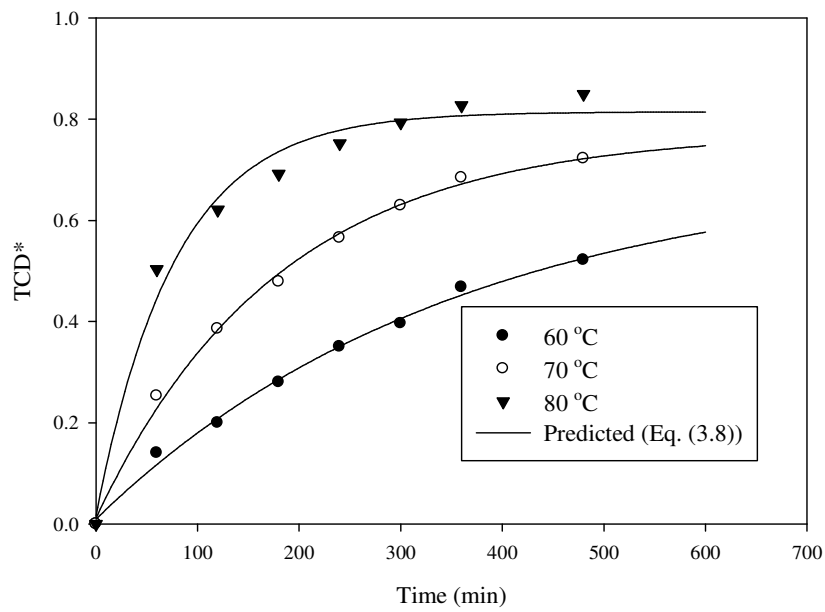


Figure 4.13. Change in total color difference (TCD*) value of strawberry concentrate during heating at 60, 70 and 80 °C.

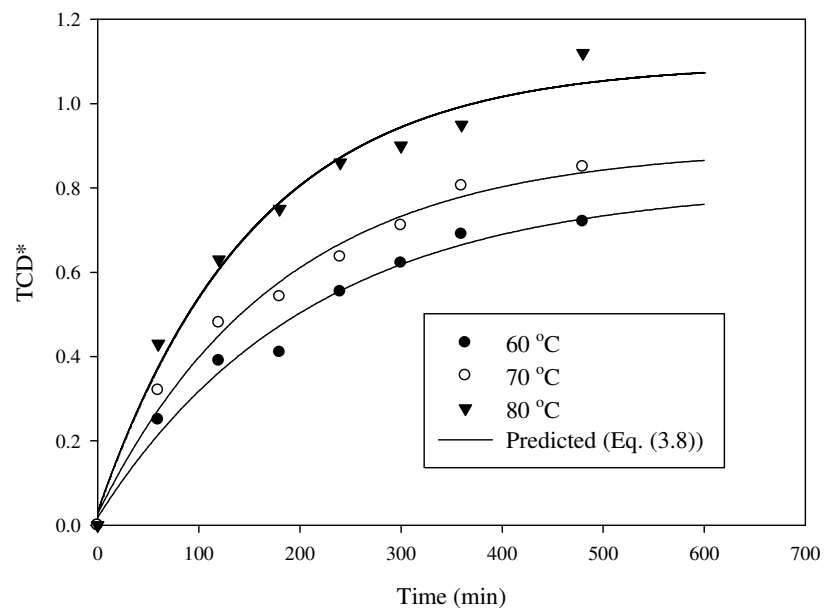


Figure 4.14. Change in total color difference (TCD*) value of blackberry concentrate during heating at 60, 70 and 80 °C.

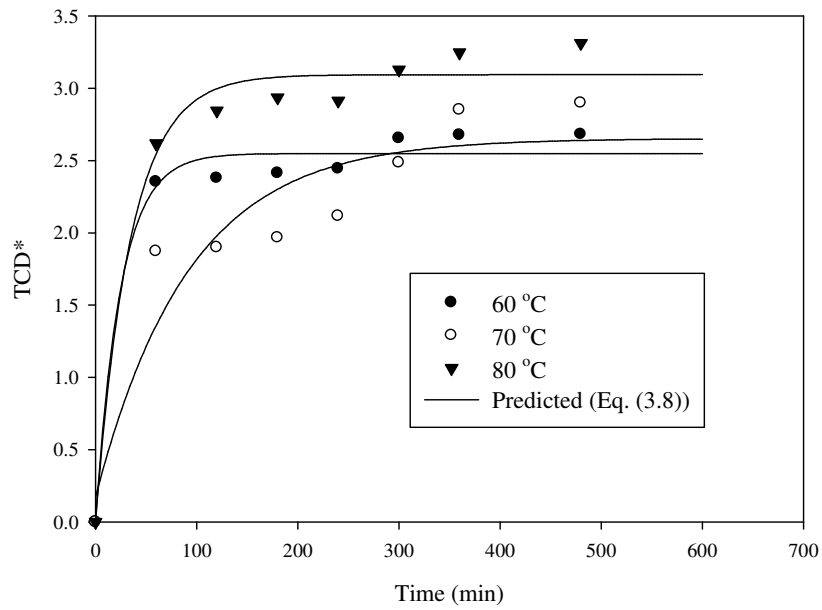


Figure 4.15. Change in total color difference (TCD*) value of Cornelian cherry concentrate during heating at 60, 70 and 80 °C.

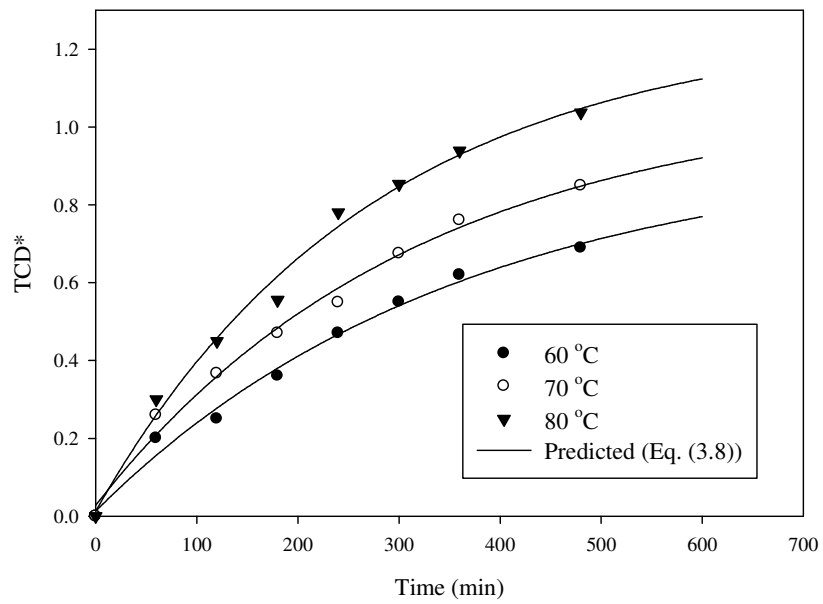


Figure 4.16. Change in total color difference (TCD*) value of Urmu mulberry concentrate during heating at 60, 70 and 80 °C.

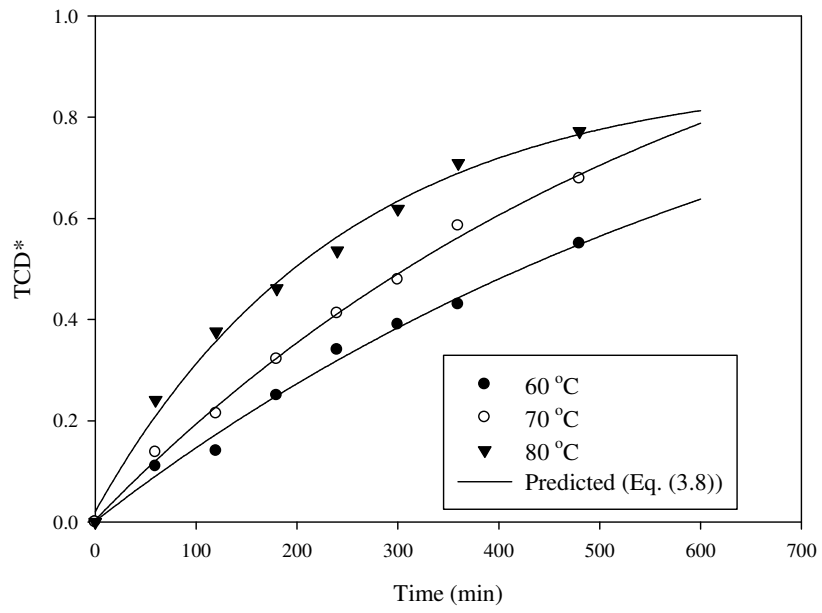


Figure 4.17. Change in total color difference (TCD*) value of sour cherry concentrate during heating at 60, 70 and 80 °C.

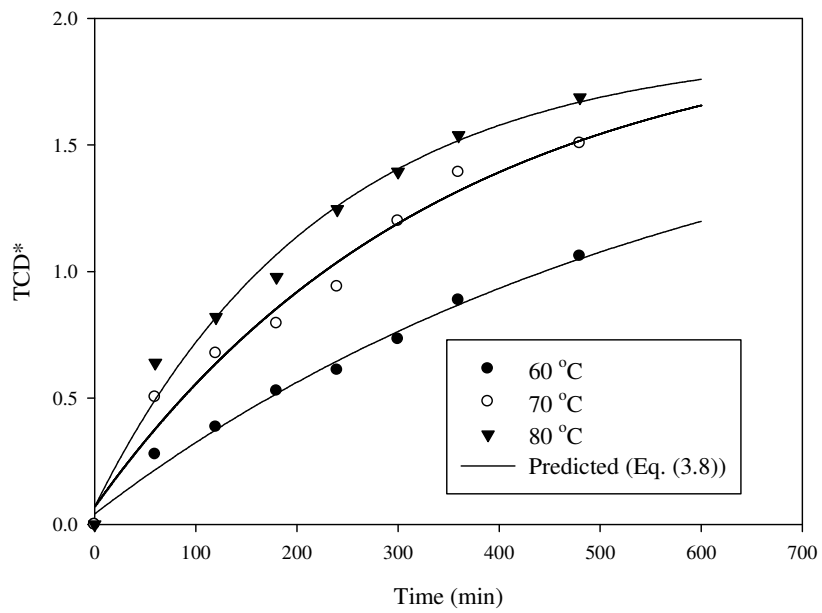


Figure 4.18. Change in total color difference (TCD*) value of sweet cherry concentrate during heating at 60, 70 and 80 °C.

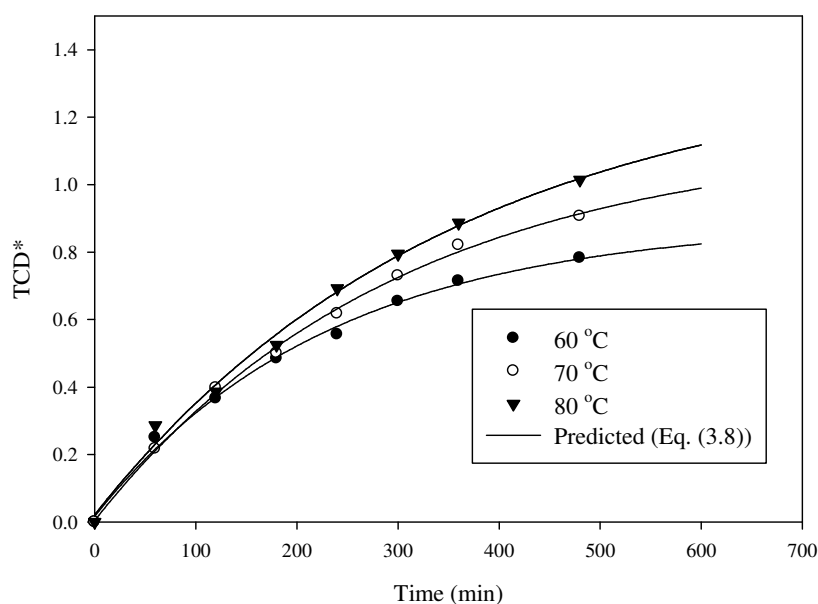


Figure 4.19. Change in total color difference (TCD*) value of pomegranate concentrate during heating at 60, 70 and 80 °C.

Figure 4.13 shows the variation of TCD* value for strawberry concentrate with respect to temperature. TCD* value was 0.52, 0.72 and 0.85 for heating at 60, 70, 80 °C, respectively, at the end of 600 min. Change in TCD* value of blackberry concentrate was 0.72, 0.85 and 1.12. for heating at 60, 70, 80 °C, respectively (Figure 4.14). The variation in TCD* value of Cornelian cherry concentrate was shown in Figure 4.15 TCD* value was 2.68, 2.90 and 3.31 for heating at 60, 70, 80 °C, respectively, at the end of 600 min. Change in TCD* value of Urmu Mulberry concentrate was 0.69, 0.85 and 1.04 for heating at 60, 70, 80 °C, respectively (Figure 4.16). Variation in TCD* value of sour cherry concentrate was 0.55, 0.68 and 0.77 at 60, 70, 80 °C, respectively (Figure 4.17). Figure 4.18 illustrates change in TCD* value of sweet cherry concentrate, which reached the TCD* value of 1.06, 1.51 and 1.69 at the end of 600 minutes heating at 60, 70, 80 °C, respectively. Finally, Figure 4.19 represents the change in TCD* value of pomegranate concentrate, which reached the TCD* value of 0.78, 0.91 and 1.01 at the end of 600 minutes heating at 60, 70, 80 °C, respectively. Figures 4.13-4.19 clearly indicates that The TCD* value increased with increase in time and treatment temperature for all concentrates.

There are numerous references on the kinetics of color of food materials in the literature. The majority of these works report zero-order kinetics (Eq. (3.6)) (Chutintrasri and Noomhorm; 2007; Tiwari et al., 2009), first-order kinetics (Eq. (3.3)) (Ahmet et al., 2000; Shao-qian et al., 2011) and combined kinetic model (Eq. (3.7)) (Garza et al., 1999; Ibarz et al., 1999). Combined model consist of two stages: the first one includes color formation based on Maillard reactions and it follows zero order kinetics and the second includes the color destruction (pigment destruction) which follows a first order kinetics (Garza et al., 1999; Ibarz et al., 1999). Experimental data for change in parameters TCD* were fitted to zero-order (Eq. (3.6)), first-order (Eq. (3.7)) and combined kinetic model (Eq. (3.7)). Kinetic parameters of zero, first and combined model were given in Table 4.3, Table 4.4 and Table 4.5, respectively. Regression analysis revealed that the combined kinetic model described the experimental data of TCD* better than zero and first order kinetics models due to having highest correlation coefficients and reasonable C_o values. So, only graphs of this model were given. For example, in the light of regression analysis, combined kinetic described variation in TCD* of Cornelian cherry concentrate better than zero and first order kinetics models due to having highest correlation coefficients (R^2) ranging between 0.8849-0.9828 (Table 4.5) when compared to ones of zero (0.4364-0.7196) (Table 4.3) and first order kinetics (0.3663-0.6267) (Table 4.4).

Correlation coefficients of TCD* fitted to first order (Table 4.4) and combined model (Table 4.5) were not considerably different from each other for pomegranate, Urmu mulberry, sour cherry and blackberry concentrates. So, both first order and combined model was found to be appropriate for these concentrates. Table 4.5 clearly shows that, k_o and k_l values increased as temperature increased for all concentrates except for Cornelian cherry and pomegranate concentrates. As defined in literature (Ibarz et al., 2000), temperature increase gives rise to rates of the both two steps of combined model (color formation and pigment destruction). In Cornelian cherry concentrate, as temperature increased rate of color formation (k_o) and pigment destruction (k_l) steps of combined model did not show a definite trend but at each temperature k_o were higher than k_l (Table 4.5). In pomegranate concentrate, as temperature increased, rate of color formation (k_o) did not changed considerably while rate of pigment

destruction (k_I) decreased resulting in more pronounced affect on TCD* by Maillard reaction than pigment destruction (Table 4.5).

According to Ibarz et al. (2000), when the ratio of kinetic constants k_o (color formation) and k_I (pigment destruction) is greater than unity, Maillard reaction predominates over pigment destruction. In this respect, as temperature increased increase in TCD* was predominantly caused by Maillard reaction for Cornelian cherry and sweet cherry concentrates at each temperature (Table 4.5). For pomegranate, Urmu mulberry concentrates, Maillard reaction start to predominate over pigment destruction as temperature increased from 60 to 70 and 80 °C (Table 4.5). Similar trend was seen in blackberry concentrate over 70 °C (Table 4.5). These results are correlated with the results of previous studies (Garza et al., 1999; Ibarz et al., 1999; Ibarz et al., 2000). However, in sour cherry concentrate, effect of Maillard reaction on TCD* were predominant under 80 °C, that is, at high temperatures effect of Maillard reaction on TCD* decreases while the effect of pigment destruction increases (Table 4.5). Moreover, in strawberry concentrate, pigment destruction rate was higher than color formation at 60, 70 and 80 °C, that is, TCD* of strawberry concentrate may predominantly caused by pigment destruction instead of Maillard reaction under 80°C (Table 4.5).

Table 4.3. Kinetics parameters of zero-order model (Eq. (3.6)) for TCD* values.

Concentrate type	Temperature (°C)	$C_o \pm SE$	$ko \pm SE$	R^2
Strawberry	60	0.0618±0.0245	0.0011±0.0001	0.9568
	70	0.1582±0.0569	0.0014±0.0002	0.8780
	80	0.3216±0.1048	0.0014±0.0004	0.6816
Blackberry	60	0.1415±0.0550	0.0014±0.0002	0.8884
	70	0.1878±0.0670	0.0016±0.0003	0.8736
	80	0.2620±0.0917	0.0020±0.0003	0.8516
Cornelian cherry	60	1.3928±0.4546	0.0037±0.0017	0.4364
	70	0.9616±0.3247	0.0048±0.0012	0.7196
	80	1.5883±0.5184	0.0048±0.0020	0.4957
Urmu mulberry	60	0.0825±0.0347	0.0014±0.0001	0.9515
	70	0.1217±0.0443	0.0017±0.0002	0.9448
	80	0.1517±0.0637	0.0021±0.0002	0.9285
Sour cherry	60	0.0278±0.0170	0.0011±0.0001	0.9814
	70	0.0438±0.0204	0.0014±0.0001	0.9826
	80	0.1313±0.0483	0.0015±0.0002	0.9212
Sweet cherry	60	0.1020±0.0354	0.0021±0.0001	0.9763
	70	0.2233±0.0834	0.0030±0.0003	0.9377
	80	0.3254±0.1151	0.0033±0.0004	0.9040
Pomegranate	60	0.1362±0.0513	0.0016±0.0002	0.9152
	70	0.1150±0.0491	0.0019±0.0002	0.9445
	80	0.1234±0.0485	0.0021±0.0002	0.9548

SE: Standard error, R^2 : correlation coefficients.

Table 4.4. Kinetics parameters of first-order model (Eq. (3.3)) for TCD* values.

Concentrate type	Temperature (°C)	$C_o \pm SE$	$k_f \pm SE$	R^2
Strawberry	60	1.0275±0.0155	-0.0015±0.0001	0.9876
	70	1.0520±0.0381	-0.0029±0.0004	0.9699
	80	0.8716±0.0482	-0.0121±0.0028	0.9148
Blackberry	60	1.0436±0.0401	-0.0028±0.0004	0.9672
	70	1.0341±0.0413	-0.0041±0.0006	0.9769
	80	1.0544±0.0413	-0.0070±0.0011	0.9814
Cornelian cherry	60	1.6014±0.4117	0.0014±0.0008	0.3663
	70	1.2512±0.2927	0.0020±0.0007	0.6267
	80	1.8614±0.4682	0.0015±0.0008	0.4117
Urmu mulberry	60	1.0177±0.0208	-0.0025±0.0002	0.9897
	70	1.0256±0.0268	-0.0035±0.0003	0.9898
	80	1.0420±0.0559	-0.0051±0.0010	0.9733
Sour cherry	60	0.9975±0.0143	-0.0016±0.0001	0.9907
	70	0.9946±0.0148	-0.0023±0.0001	0.9944
	80	1.0328±0.0259	-0.0031±0.0003	0.9879
Sweet cherry	60	1.0418±0.0728	-0.0042±0.0010	0.9520
	70	1.2536±0.1777	-0.0062±0.0040	0.8455
	80	1.3813±0.1965	-0.0072±0.0054	0.8232
Pomegranate	60	1.0275±0.0242	-0.0033±0.0003	0.9902
	70	1.0055±0.0246	-0.0042±0.0003	0.9933
	80	1.0331±0.0545	-0.0045±0.0008	0.9729

SE: Standard error, R^2 : correlation coefficients.

Table 4.5. Kinetics parameters of combined model (Eq. (3.7)) for TCD* values.

Concentrate Type	Temperature (°C)	$C_o \pm SE$	$ko \pm SE$	$k_1 \pm SE$	R^2
Strawberry	60	0.0095±0.0127	0.0020±0.0002	0.0028±0.0005	0.9951
	70	0.0114±0.0145	0.0043±0.0002	0.0056±0.0004	0.9970
	80	0.0161±0.0406	0.0105±0.0013	0.0129±0.0018	0.9844
Blackberry	60	0.019±0.0314	0.0039±0.0005	0.0048±0.0010	0.9833
	70	0.0274±0.0352	0.0050±0.0006	0.0056±0.0009	0.9868
	80	0.0317±0.0492	0.0071±0.0009	0.0065±0.0011	0.9842
Cornelian cherry	60	0.0014±0.1397	0.1027±0.0275	0.0403±0.0111	0.9828
	70	0.1738±0.3564	0.0288±0.0098	0.0109±0.0044	0.8849
	80	0.0068±0.1744	0.0893±0.0168	0.0289±0.0057	0.9815
Urmu mulberry	60	0.0133±0.0240	0.0026±0.0003	0.0028±0.0007	0.9902
	70	0.0218±0.0288	0.0034±0.0004	0.0032±0.0007	0.9903
	80	0.0134±0.0337	0.0046±0.0004	0.0037±0.0006	0.9919
Sour cherry	60	0.0015±0.0174	0.0016±0.0002	0.0014±0.0006	0.9911
	70	0.0040±0.0131	0.0021±0.0001	0.0016±0.0004	0.9968
	80	0.0205±0.0231	0.0036±0.0003	0.0041±0.0006	0.9928
Sweet cherry	60	0.0420±0.0347	0.0031±0.0004	0.0017±0.0006	0.9898
	70	0.0709±0.0792	0.0058±0.0010	0.0029±0.0010	0.9765
	80	0.0702±0.0759	0.0083±0.0011	0.0044±0.0010	0.9835
Pomegranate	60	0.0167±0.0188	0.0038±0.0003	0.0043±0.0005	0.9955
	70	0.0046±0.0148	0.0038±0.0002	0.0033±0.0003	0.9979
	80	0.0215±0.0282	0.0039±0.0003	0.0028±0.0005	0.9936

SE: Standard error, R^2 : correlation coefficients.

4.4. Flow properties of fruit sauces

All fruit concentrates had a pH value between 2.83-3.75 and total soluble solids content of 40-45 °Brix. Shear stress and shear rate data were taken for all sauces prepared without gum and with gums of LBG, XA and *i*-CARR at temperature of 25°C, separately. Power law model was used to fit the measured data to determine flow behavior of sauces. Power law model (Eq. (3.9)) $\sigma = K\gamma^n$ where σ is the shear stress (Pa), γ is the shear rate (s^{-1}), K is the consistency index (Pas^n), and the exponent n , called the flow behavior index (dimensionless), reflects the closeness to Newtonian flow (Chin et al., 2009). When $n = 1$, the fluid is Newtonian and hence K becomes the viscosity η (Pas) (Nindo et al., 2005). If n is less than 1, the material is shear-thinning (pseudoplastic), if n is more than 1, then material is shear thickening (dilatant) (Krokida, 2001).

The parameters (n , K) obtained by fitting the power law model to the shear stress versus shear rate (Eq. (3.9)), and correlation coefficients, R^2 , and calculated η_{app} of sauces (Eq. (3.10)) at $50 s^{-1}$ by fitting power law model were presented in Table 4.6. The model appeared to be suitable for describing the flow behavior of sauces with

high correlation coefficients (0.9133- 0.9971). Typical rheograms of sauces prepared without and with gum at selected gum concentrations of 0.15, 0.30 and 0.60 % (w/v) were shown in Figures 4.20-4.40. The curves in these figures represent the Power law model fitted to the measured data.

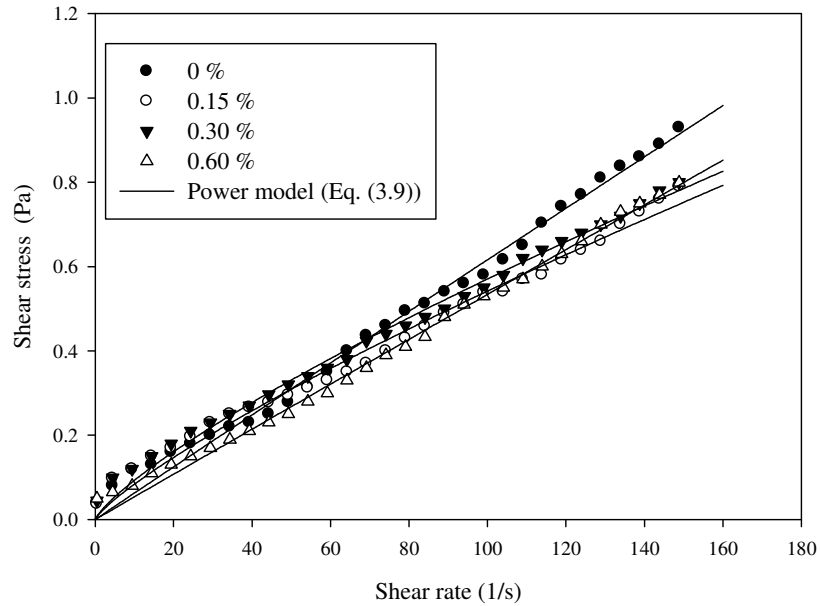


Figure 4.20. Changes in shear stress with shear rate in LBG added strawberry sauces at different gum concentrations.

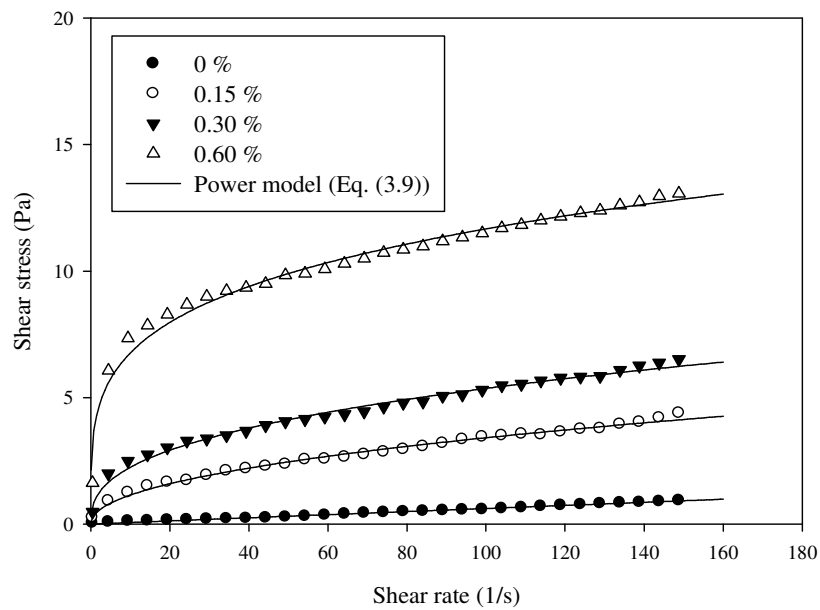


Figure 4.21. Changes in shear stress with shear rate in XA added strawberry sauces at different gum concentrations.

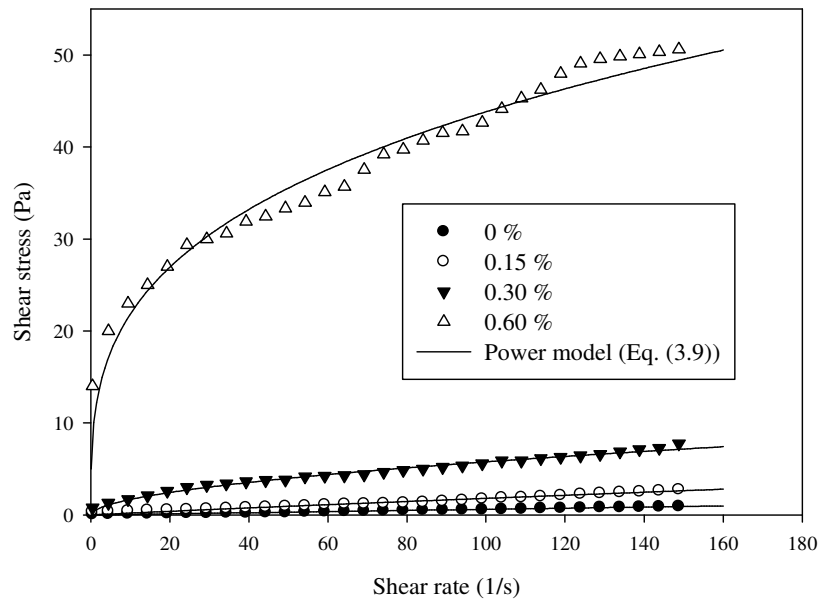


Figure 4.22. Changes in shear stress with shear rate in *i*-CARR added strawberry sauces at different gum concentrations.

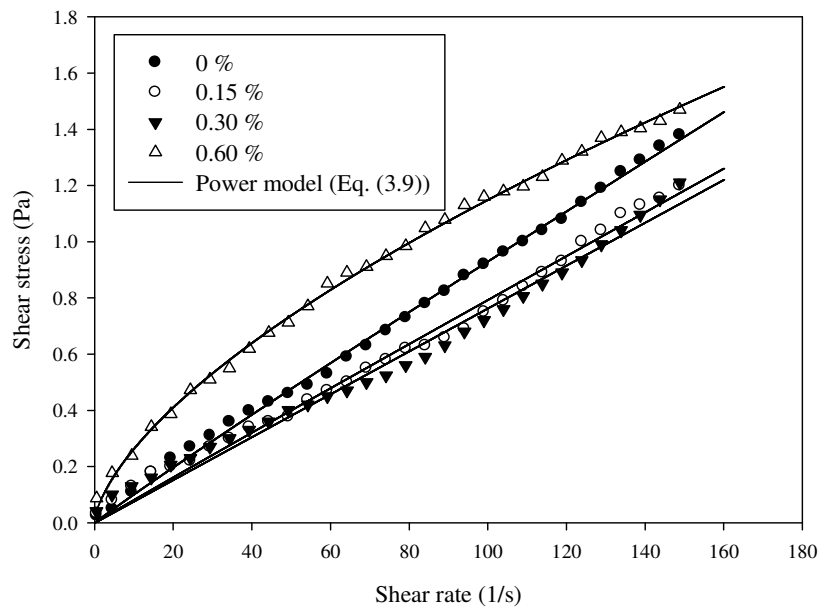


Figure 4.23. Changes in shear stress with shear rate in LBG added blackberry sauces at different gum concentrations.

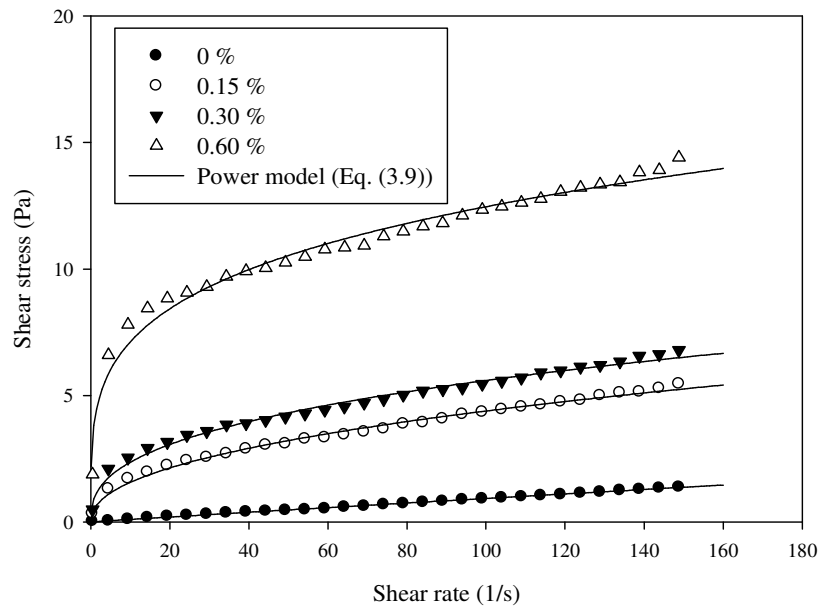


Figure 4.24. Changes in shear stress with shear rate in XA added blackberry sauces at different gum concentrations.

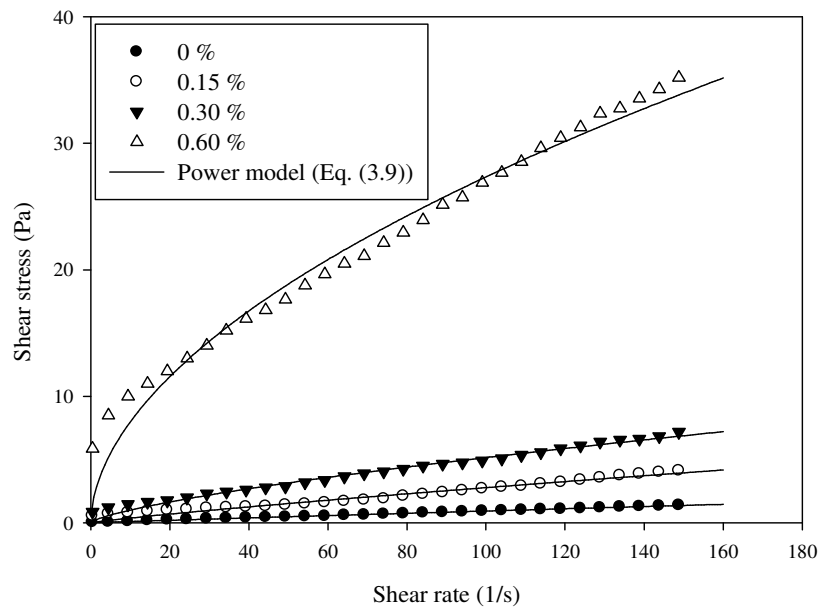


Figure 4.25. Changes in shear stress with shear rate in *i*-CARR added blackberry sauces at different gum concentrations.

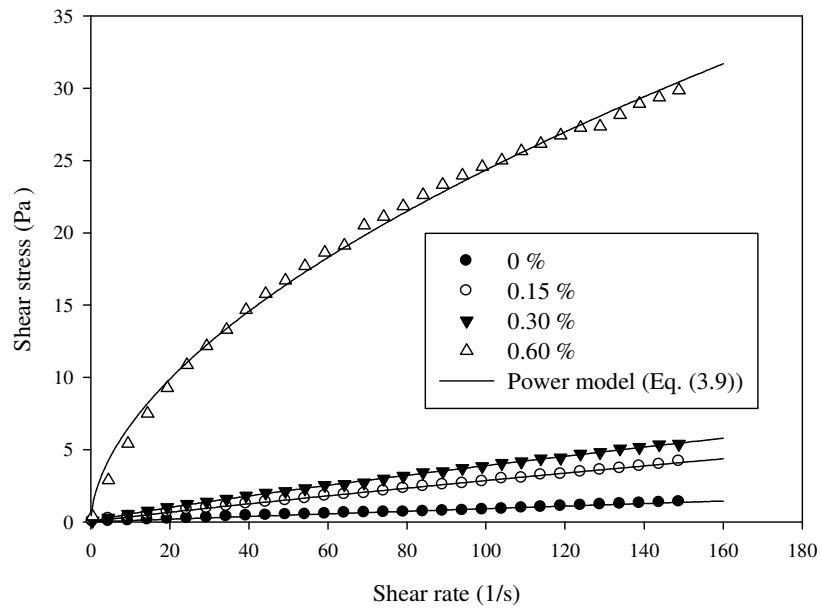


Figure 4.26. Changes in shear stress with shear rate in LBG added Cornelian cherry sauces at different gum concentrations.

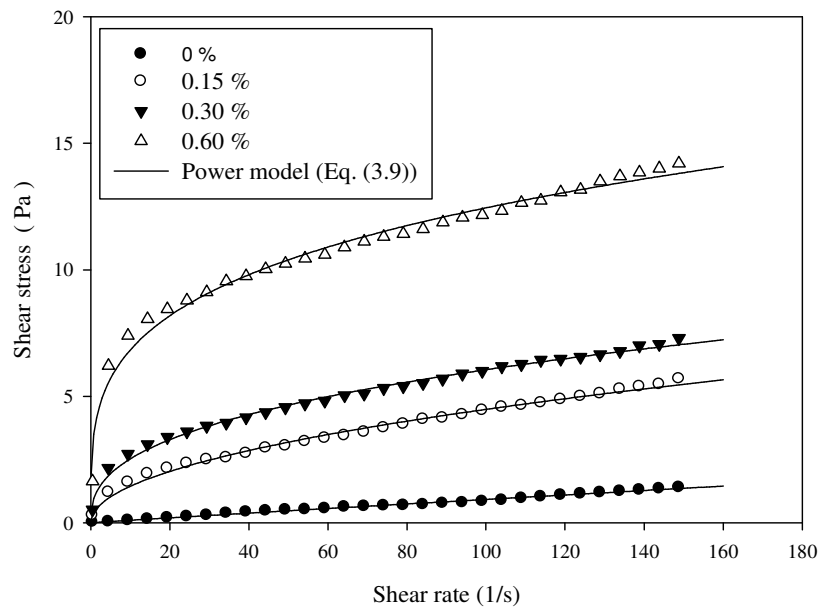


Figure 4.27. Changes in shear stress with shear rate in XA added Cornelian cherry sauces at different gum concentrations.

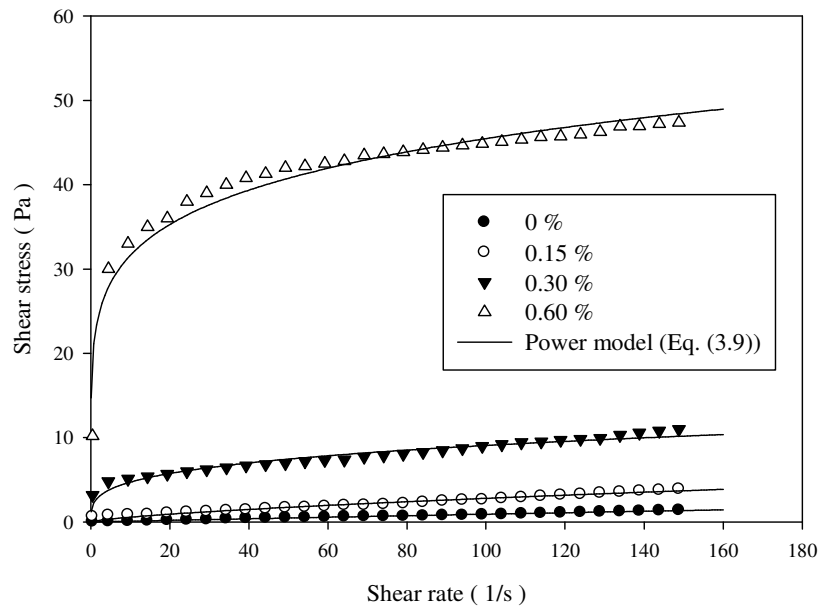


Figure 4.28. Changes in shear stress with shear rate in *i*-CARR added Cornelian cherry sauces at different gum concentrations.

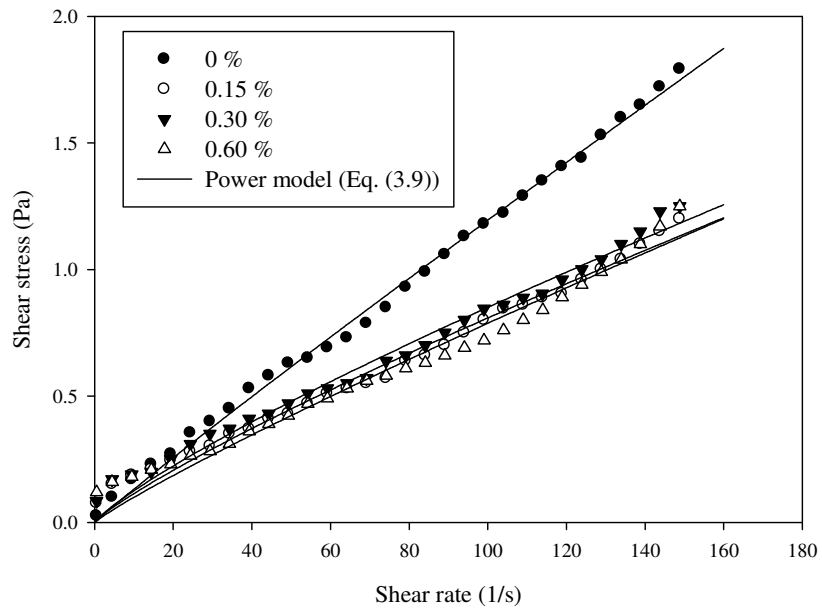


Figure 4.29. Changes in shear stress with shear rate in LBG added Urmu mulberry sauces at different gum concentrations.

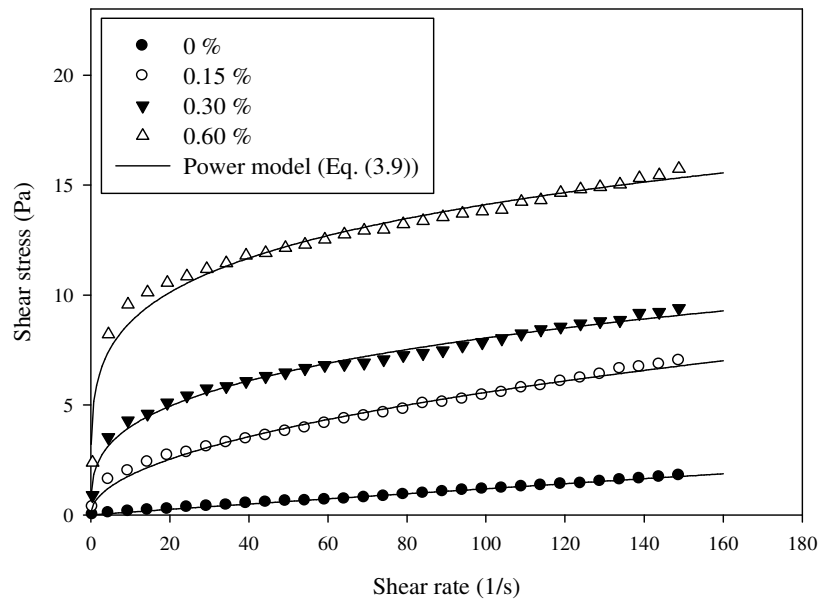


Figure 4.30. Changes in shear stress with shear rate in XA added Urmu mulberry sauces at different gum concentrations.

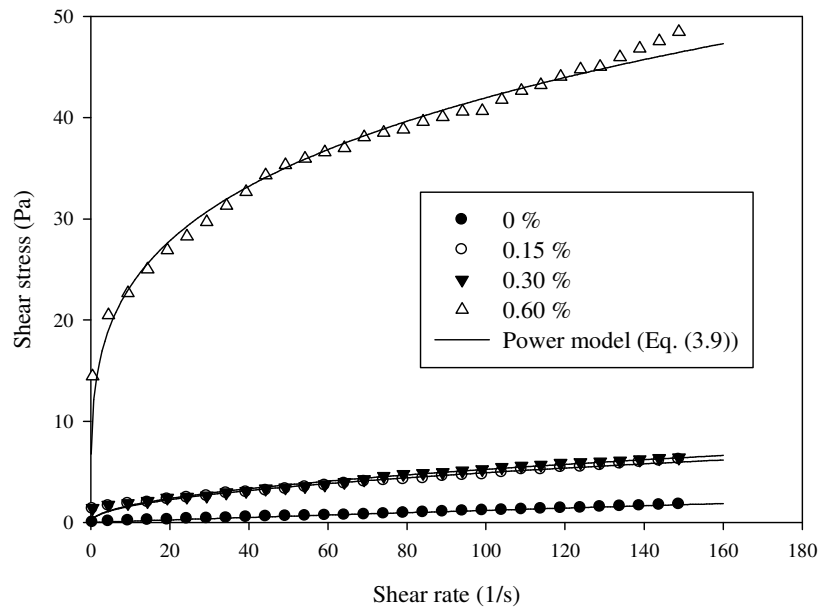


Figure 4.31. Changes in shear stress with shear rate in *i*-CARR added Urmu mulberry sauces at different gum concentrations.

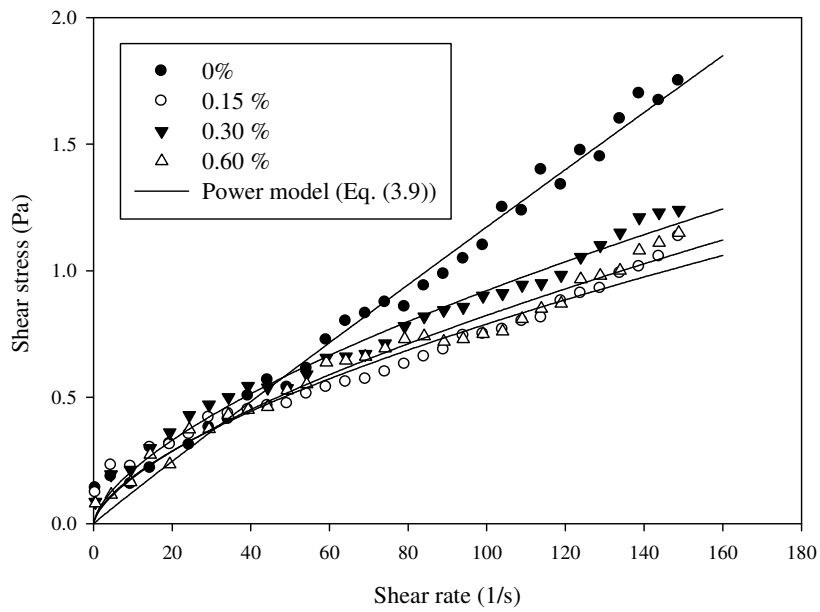


Figure 4.32. Changes in shear stress with shear rate in LBG added sour cherry sauces at different gum concentrations.

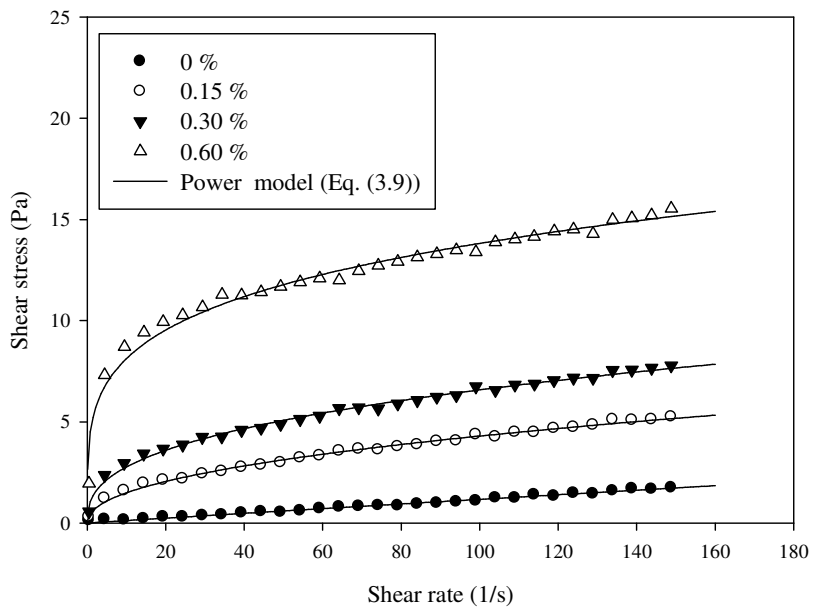


Figure 4.33. Changes in shear stress with shear rate in XA added sour cherry sauces at different gum concentrations.

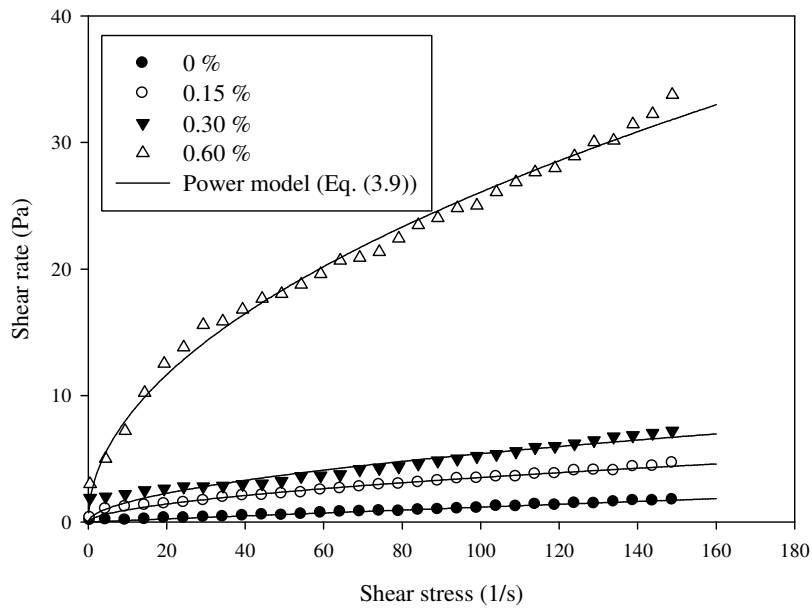


Figure 4.34. Changes in shear stress with shear rate in *i*-CARR added sour cherry sauces at different gum concentrations.

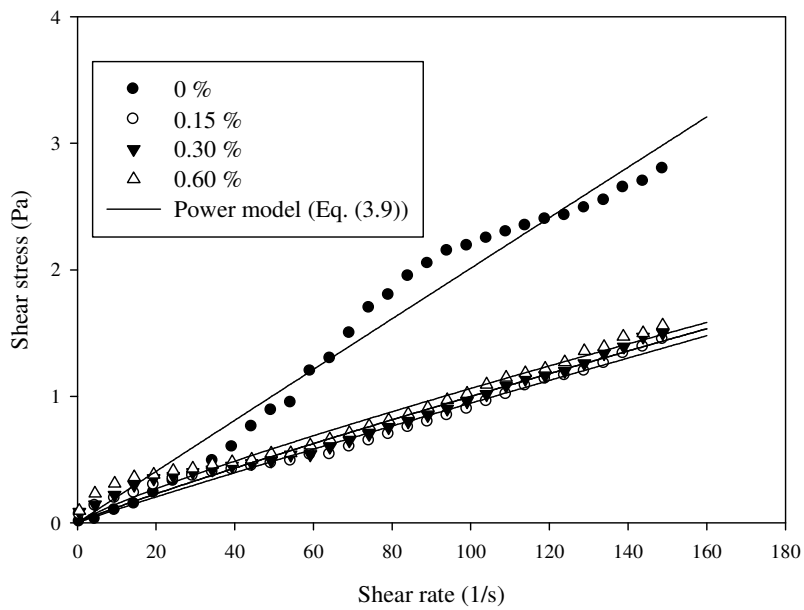


Figure 4.35. Changes in shear stress with shear rate in LBG added sweet cherry sauces at different gum concentrations.

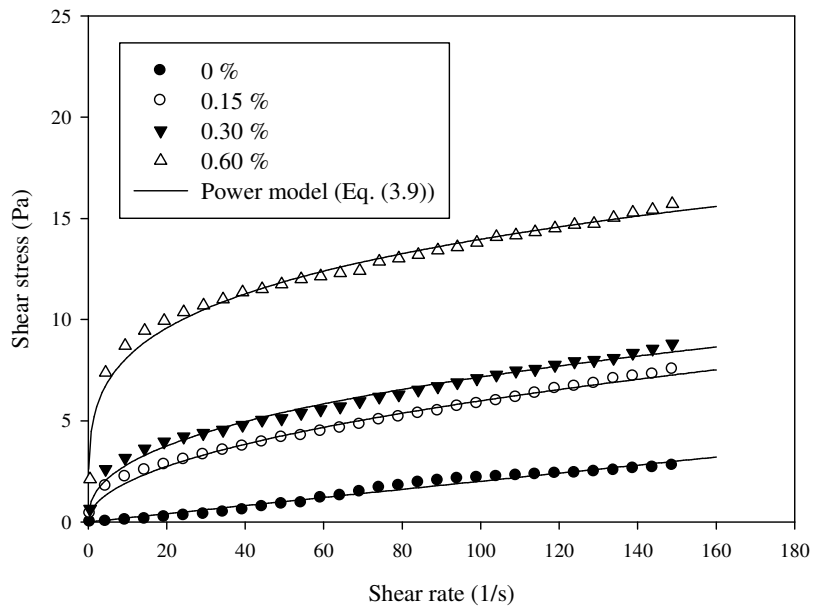


Figure 4.36. Changes in shear stress with shear rate in XA added sweet cherry sauces at different gum concentrations.

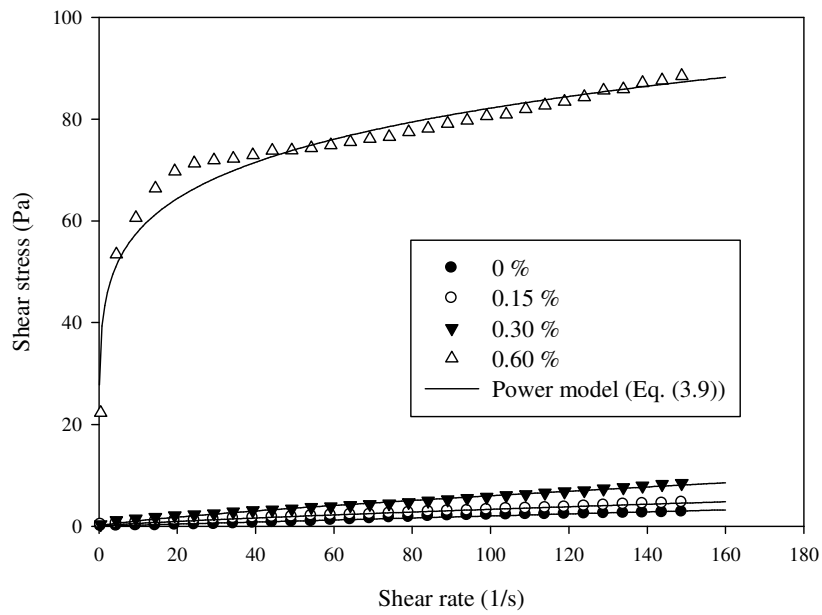


Figure 4.37. Changes in shear stress with shear rate in *i*-CARR added sweet cherry sauces at different gum concentrations.

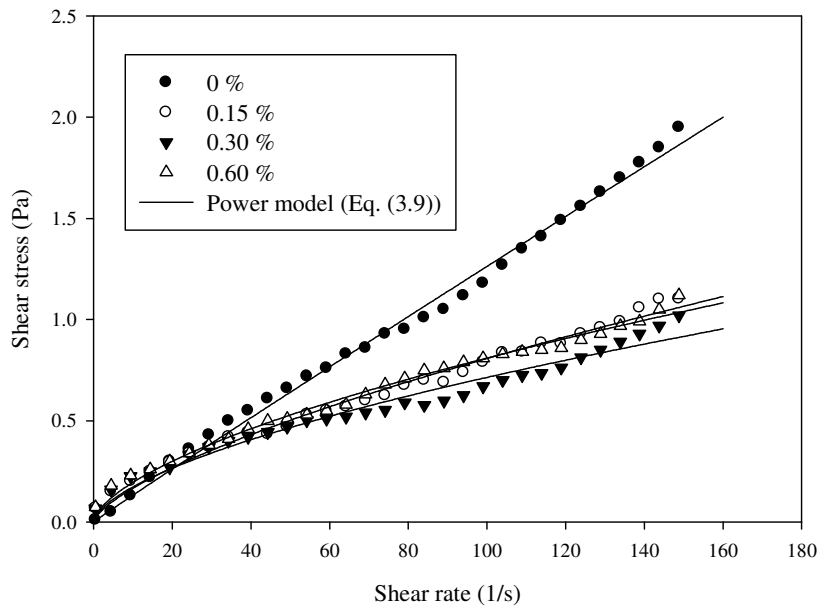


Figure 4.38. Changes in shear stress with shear rate in LBG added pomegranate sauces at different gum concentrations.

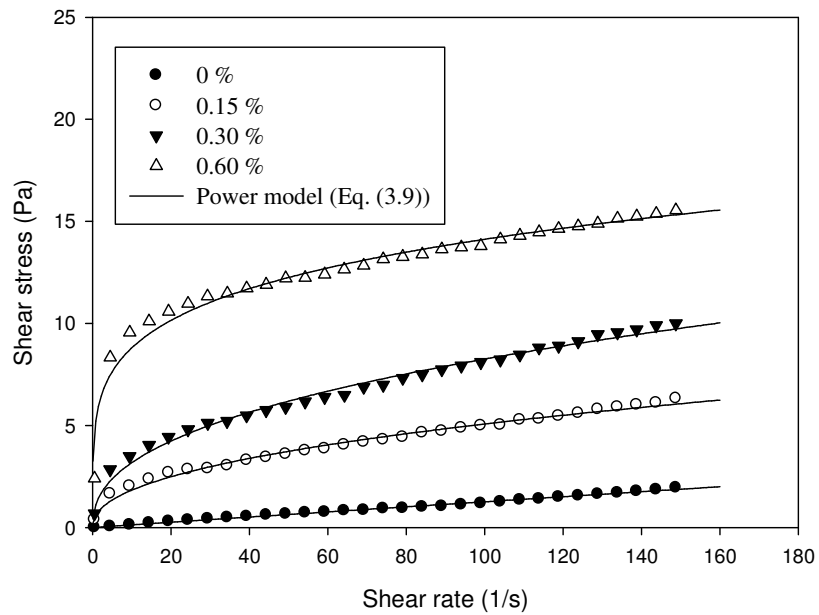


Figure 4.39. Changes in shear stress with shear rate in XA added pomegranate sauces at different gum concentrations.

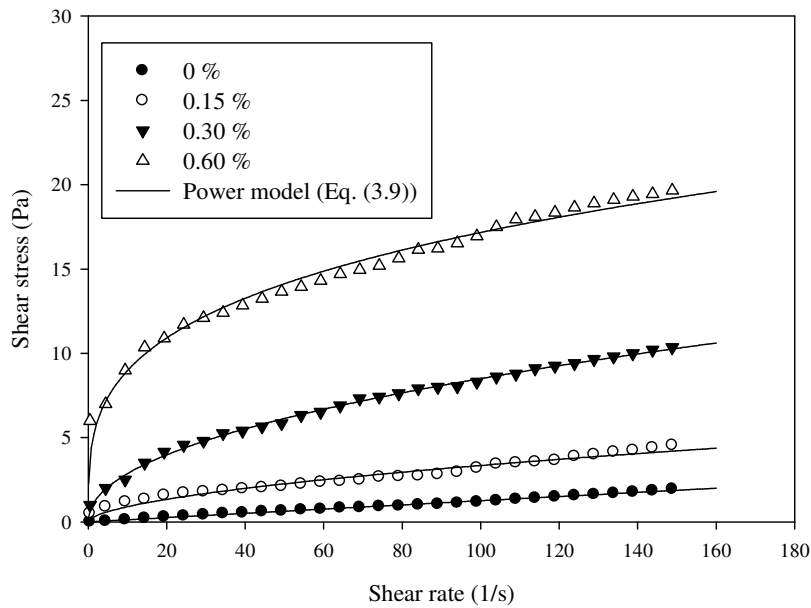


Figure 4.40. Changes in shear stress with shear rate in *i*-CARR added pomegranate sauces at different gum concentrations.

It was seen from Table 4.6 that flow behavior indexes (n) were close to 1 (0.9572-0.9925), which clearly shows that all sauces prepared without gum shows Newtonian behavior, that is, at constant temperature and pressure, the viscosities of these sauces does not change with shear rate (Marcotte et al., 2001). Since our sauces prepared from clarified and depectinized fruit concentrates, they exhibited Newtonian flow characteristics, which are supported by literature data, and even a small pseudoplasticity could be acceptable due to presence of some soluble solids, mostly pectins and tartarates (Giner et al., 1996; Juszczak and Fortuna, 2003; Goula and Adamopoulos, 2011). Generally, gum addition caused a clear shift from Newtonian behavior to Non-Newtonians shear-thinning behavior except LBG, as shown by a noticeable decrease in values of flow behavior index (n). There was no definite trend in K , n and η_{app} values and they indicated that LBG did not show definite change in flow properties of related sauces (Table 4.6). Actually, LBG has many uses in food industry due to its ability to form very viscous solutions at a relatively low concentrations and their high stability upon pH or heat processing, mainly due to neutral character of this gum (Camacho et al., 2005). In this study, LBG even caused the reduction in apparent viscosity of sauces when compared to sauces prepared without gum, as in the case of Urmu mulberry, pomegranate, and sweet cherry

sauces (Table 4.6). It can be concluded that LBG could not show its potential thickening ability in these sauces. It can be possibly caused by not being completely dissolved at related study temperature of 25 °C. In literature, it is stated that LBG needs heating to 80°C for complete solubility (Sahin and Ozdemir, 2004). Wei et al. (2001) have been reported in a study related to flow properties of fruit fillings that some gums may even decrease the η_{app} under certain circumstances. In addition, they stated that when gums are not properly hydrated, their potential for increasing viscosity does not fully appear.

Table 4.6. Parameters from power law model ((Eq. 3.9)) fitting; consistency coefficient, K , and flow behaviour index, n , and apparent viscosity, η_{app} calculated (Eq. (3.10)) at 50 s⁻¹ of sauces.

Source	Gum added	Gum conc. (%) (w/v)	Consistency index (Pa.s ⁿ) $K \pm SE$	Flow index (Dimensionless) $n \pm SE$	R^2	(50/s) (Pa.s) η_{app}
Strawberry	LBG	0	0.0064±0.0008	0.9915±0.0249	0.9918	0.0062
		0.15	0.013±0.0015	0.8096±0.0225	0.9863	0.0062
		0.30	0.0152±0.0013	0.7871±0.0180	0.9928	0.0066
	XA	0.60	0.0054±0.0005	0.9957±0.0209	0.9943	0.0053
		0.15	0.3857±0.0195	0.4734±0.0111	0.9917	0.0492
		0.30	0.9390±0.0446	0.3784±0.0106	0.9877	0.0825
	<i>i</i> -CARR	0.60	3.9189±0.1631	0.2369±0.0095	0.9731	0.1980
		0.15	0.0247±0.0050	0.9323±0.0436	0.9692	0.0190
		0.30	0.4928±0.0388	0.5344±0.0172	0.9844	0.0797
Blackberry	LBG	0.60	10.8725±0.6514	0.3027±0.0135	0.9648	0.7106
		0	0.0111±0.0007	0.9616±0.0128	0.9978	0.0096
		0.15	0.0085±0.0010	0.9857±0.0250	0.9917	0.0080
	XA	0.30	0.0076±0.0012	0.9994±0.0332	0.9856	0.0076
		0.60	0.0608±0.0021	0.6383±0.0077	0.9980	0.0148
		0.15	0.5592±0.0246	0.4473±0.0097	0.9928	0.0643
	<i>i</i> -CARR	0.30	0.9989±0.0470	0.3741±0.0105	0.9876	0.0863
		0.60	4.0696±0.1817	0.2430±0.0102	0.9705	0.2106
		0.15	0.0515±0.0113	0.8663±0.0470	0.9573	0.0305
Cornelian cherry	LBG	0.30	0.1964±0.0233	0.7097±0.0257	0.9808	0.0631
		0.60	2.3263±0.2304	0.5351±0.0217	0.9741	0.3774
		0	0.0110±0.0013	0.9619±0.0253	0.9914	0.0095
	XA	0.15	0.0451±0.0017	0.9016±0.0083	0.9989	0.0307
		0.30	0.0803±0.0027	0.8432±0.0071	0.9991	0.0435
		0.60	1.8422±0.0831	0.5607±0.0099	0.9958	0.3303
	<i>i</i> -CARR	0.15	0.4643±0.0231	0.4924±0.0110	0.9926	0.0637
		0.30	1.0550±0.0383	0.3793±0.0081	0.9929	0.0930
		0.60	3.7494±0.1537	0.2606±0.0093	0.9788	0.2078
Urmu mulberry	LBG	0.15	0.1179±0.0185	0.6882±0.0340	0.9629	0.0348
		0.30	2.4581±0.1796	0.2837±0.0165	0.9392	0.1491
		0.60	21.9939±1.0066	0.1577±0.0106	0.9222	0.8152
	XA	0	0.0146±0.0011	0.9572±0.0157	0.9966	0.0123
		0.15	0.0162±0.0021	0.8484±0.0276	0.9854	0.0090
		0.30	0.0186±0.0024	0.8302±0.0283	0.9840	0.0096
	<i>i</i> -CARR	0.60	0.0126±0.0024	0.8975±0.0410	0.9710	0.0084
		0.15	0.5848±0.0320	0.4896±0.0120	0.9909	0.0794
		0.30	1.9963±0.0838	0.3027±0.0095	0.9842	0.1305
	0.60	5.4440±0.2396	0.2069±0.0101	0.9593	0.2446	
	0.15	0.5301±0.0500	0.4838±0.0210	0.9701	0.0704	
	0.30	0.5403±0.0515	0.4938±0.0210	0.9711	0.0746	
	0.60	12.9588±0.4195	0.2552±0.0074	0.9848	0.7033	

Table 4.6. continued.

Sour cherry		0	0.0135±0.0019	0.9693±0.0299	0.9875	0.0120
	LBG	0.15	0.0438±0.0064	0.6277±0.0319	0.9614	0.0102
		0.30	0.0399±0.0048	0.6571±0.0259	0.9785	0.0104
		0.60	0.0487±0.0049	0.6383±0.0219	0.9830	0.0118
	XA	0.15	0.5211±0.0216	0.4583±0.0092	0.9940	0.0626
		0.30	1.1698±0.0437	0.3752±0.0083	0.9923	0.1015
		0.60	4.7838±0.2071	0.2304±0.0099	0.9692	0.2356
	<i>i</i> -CARR	0.15	0.2617±0.0210	0.5642±0.0175	0.9856	0.0476
		0.30	0.4506±0.0818	0.5395±0.0398	0.9107	0.0744
0.60		2.6010±0.1479	0.5005±0.0125	0.9908	0.3685	
Sweet cherry		0	0.0208±0.0049	0.9925±0.0496	0.9724	0.0202
	LBG	0.15	0.0119±0.0021	0.9507±0.0372	0.9795	0.0098
		0.30	0.0149±0.0026	0.9133±0.0380	0.9764	0.0106
		0.60	0.0212±0.0039	0.8502±0.0399	0.9690	0.0118
	XA	0.15	0.6428±0.0342	0.4847±0.0117	0.9912	0.0856
		0.30	1.1309±0.0589	0.4009±0.0116	0.9870	0.1085
		0.60	4.7522±0.1863	0.2342±0.0089	0.9753	0.2376
	<i>i</i> -CARR	0.15	0.0887±0.0078	0.7861±0.0190	0.9919	0.0384
		0.30	0.1849±0.0200	0.7550±0.0233	0.9867	0.0709
0.60		40.8932±1.7382	0.1515±0.0099	0.9246	1.4794	
Pomegranate		0	0.0140±0.0014	0.9784±0.0208	0.9943	0.0129
	LBG	0.15	0.0346±0.0032	0.6844±0.0201	0.9878	0.0101
		0.30	0.0421±0.0056	0.6150±0.0291	0.9675	0.0093
		0.60	0.0474±0.0036	0.6165±0.0167	0.9894	0.0106
	XA	0.15	0.6641±0.0343	0.4416±0.0114	0.9897	0.0747
		0.30	1.2265±0.0617	0.4140±0.0112	0.9887	0.1239
		0.60	5.4931±0.2388	0.2051±0.0100	0.9594	0.2451
	<i>i</i> -CARR	0.15	0.2461±0.0323	0.5671±0.0287	0.9612	0.0453
		0.30	0.9702±0.0288	0.4714±0.0066	0.9971	0.1227
0.60		4.6987±0.2056	0.2814±0.0099	0.9778	0.2825	

LBG: Locust bean gum.

XA: Xanthan gum.

i-CARR: *i*-carrageenan.

SE: Standard error.

 R^2 : Correlation coefficients.

All sauces prepared with XA and *i*-CARR showed non-Newtonian, shear thinning behavior ($n < 1$). Similar shear-thinning behavior also reported by Sikora et al. (2007) in dessert sauces thickened by starch-xanthan gum combinations. For all sauces prepared with these two gums, an increase in gum concentration was accompanied with an increase in pseudoplasticity, shown by a decrease in n values, a measure of departure from Newtonian flow (Table 4.6). The smaller the n values the greater the departure from Newtonian behavior (Farhoosh and Riazi, 2007). When compared to the sauces without gum and sauces prepared with these two gums, gum addition led to rise in K , thereby resulting in an increase in the η_{app} of sauces. The η_{app} of sauces showed an agreeing trend to K with respect to concentration levels (Table 4.6). Similar results were found by Sahin and Ozdemir (2004) in hydrocolloid addition to

different formulated ketchups. As expected, consistency coefficient and η_{app} increased with increase in gum concentration. It was resulted from decrease in fluidity possibly as a result of binding of water by hydrocolloid molecules leading to an increase in the resistance to flow (Sahin and Ozdemir, 2004). When looked flow curves of sauces prepared with XA and *i*-CARR, it is clear that XA caused a more steadily increase in pseudoplasticity when compared to *i*-CARR. That is, *i*-CARR showed a slight transition in flow regimes as increasing gum concentration from 0 to 0.15 and 0.30 %, respectively, but showed a sharp increase at 0.60 % gum concentration. Gamonpilas et al. (2011) have been reported that the transition point between dilute and semi-dilute regimes, of XA gum is relatively low, making it very advantageous to achieve the desirable viscosity in food products, which supports our findings.

Trius and Sebranek (1996) reported that *i*-CARR has good gelling property but it becomes soluble in hot water (at 50°C). They also informed that carrageenans are quite stable at pH levels of seven or higher, but below pH 7 chemical stability decreases, especially at high temperatures. At pH 5 to 7, changes are small, but as the pH is further lowered, hydrolysis of the carrageenan occurs with loss of viscosity and gelling ability. Once the gel is formed, however, hydrolysis is no longer a problem even at low pH levels, and the gel is stable. So, in this study, possibly carrageenan did not reached optimum solubility or could suffer from low pH. However, XA showed good thickening and steady increase in pseudoplasticity. XA is an effective stabilizer which has a three dimensional network consisting of the unique rigid, rod-like conformation (Gamonpilas et al., 2011). XA is either soluble in hot and cold water (Sahin and Ozdemir, 2004) and become affected only at pH values more than 11 and less than 2.5 (Uan-On and Senge, 2008). That is both temperature (25°C) and pH ranges of the concentrates (2.83-3.75) were suitable for XA activity. Besides, it is reported that pseudoplastic characteristics of XA gives the advantage in terms of organoleptic quality, e.g. flavour release and mouth-feel, in food products and promotes mixability, pumpability and flowability characteristics which are important factors for the design of flow systems. (Gamonpilas et al., 2011). Consequently, XA can be regarded as a suitable stabilizer for all these fruit sauces. However, for high viscosity and good mouth-feel characteristics, the gum choice should be a gum system having low n value, since high n value tends to feel slimy in the mouth

(Farhoosh and Riazi, 2007). In this respect, not only rheological characteristics but also sensory evaluation of sauces should be taken into consideration. Similar assumptions were done by Sahin and Ozdemir, 2004.

CHAPTER 5

CONCLUSION

The outcomes of this study can be summarized as follows:

- Concentration via rotary vacuum evaporator at 40 °C did not make noticeable change in physicochemical properties. Since these fruits have brief harvest seasons and highly perishable, their shelf life can be increased by concentration with this way with maintaining their nutritional and health promoting benefits.
- Red colored fruits are the source of food phenolics since they contain high amounts of phenolics, which are important due to their being coloring agent, flavoring agent (mainly astringency and bitterness), potential odorants and they have antioxidant properties.
- Red colored fruits are rich in anthocyanins and, anthocyanins are responsible for their attractive red color. Anthocyanins also have many beneficial activities which guarantee human health. (e.g., they are natural antioxidants) Consumption of these fruits may be protective against various diseases.
- Monomeric anthocyanins are found to be highly unstable and susceptible to degradation at high temperatures, which followed first order reaction kinetics, and the rate of degradation increased with increase in treatment time and temperature. In conclusion, it can be advised that red fruits of this study should be handled below 60 °C to prevent monomeric anthocyanin degradation, which will result in color loss and decrease in nutritional value.
- Color is the first property the consumer observes so, it is important quality parameter, whose degradation mechanism is found to be quite complex.

Combined model has chosen adequate model when compared to both zero order and first order model to describe this complex physical behavior in terms of mathematical expressions. Modeling total color change of red fruits by measuring instantaneously via Hunter colorimeters could be online quality parameter which, will give clues about (pigment concentration) anthocyanin concentration since their attractive color is granted by anthocyanins.

- Power law model was found to be suitable to define flow characteristics of sauces. As expected, sauces prepared without gum has exhibited Newtonian flow characteristics ($n \cong 1$) since they are clarified and depectinized, while sauces prepared with gums has exhibited non-Newtonian pseudoplastic flow characteristics ($n < 1$), that is apparent viscosity of these sauces were decreased as shear rate increased. Pseudoplasticity has increased as gum concentration increased. LBG caused the reduction in apparent viscosity of sauces when compared to sauces prepared without gum. So it concluded that some gums may even decrease the apparent viscosity under certain circumstances. In the case of sauces prepared with XA and *i*-CARR, as compared to the sauces prepared without gum, consistency coefficient (K) and apparent viscosity (η_{app}) increased with increase in gum concentration resulting in more physically stable sauces. Finally, sauces prepared with xanthan gum at 0.30 % (w/v) gum concentration were selected as the best sauces with desired consistency.

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APPENDICES
APPENDIX A

FIGURE A.1. Calibration curve of gallic acid.

