HEMICELLULOSE COATING AS A SUBSTITUTE OF SULFURING FOR APRICOT DRYING

A THESIS SUBMITTED TO
THE GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES
OF
MIDDLE EAST TECHNICAL UNIVERSITY

BY

ALİ ÜBEYİTOĞULLARI

IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR
THE DEGREE OF MASTER OF SCIENCE
IN
FOOD ENGINEERING

AUGUST 2014

Approval of the thesis:

HEMICELLULOSE COATING AS A SUBSTITUTE OF SULFURING FOR APRICOT DRYING

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ABSTRACT

HEMICELLULOSE COATING AS A SUBSTITUTE OF SULFURING FOR APRICOT DRYING

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August 2014, 118 pages

Dry apricot is one of the most exported fruits in Turkey. However, there are some quality problems faced with sulfuring before drying. Sulfuring is a chemical method that is used to prevent/delay oxidation and fungal-bacterial growth. Indeed, sulfuring is harmful to human health. Therefore, alternatively to sulfuring, hemicellulose coating was investigated.

In this study, hemicellulose was extracted from hazelnut shells by using alkaline peroxide solutions. The extraction conditions were optimized with respect to temperature (40, 50 and 60 °C), alkaline concentration (10, 15 and 20 %) and extraction time (4, 8 and 12 h) and the highest hemicellulose purity was found as 64.24 % (w/w) by Box-Behnken response surface methodology at optimum conditions (10 % NaOH at 40 °C for 4 h).

Hemicellulose coated apricots were dried in a tray dryer with various conditions; hemicellulose concentration (1-3 %), air velocity (0.5-1.5 m/s) and air temperature (60-80 °C). The effects of hemicellulose coating on apricot during drying was evaluated by color parameters (ΔE* and Δb*) and final moisture content. The optimum drying conditions were found as 1 m/s of air velocity, 80 °C of air

temperature, and 3 % (w/v) hemicellulose coating which gave experimental values of 15.2, -8.3 and 26 % for ΔE*, Δb* and final moisture content, respectively. The models prediction of the responses were successful with close values of 13.2, -8.3 and 24.9 % for ΔE*, Δb* and final moisture content. Comparison of color values of dried apricots indicated that hemicellulose coated apricots had significantly better color values than uncoated and chitosan coated apricots.

Apricot drying kinetics was evaluated by four models: Newton, Page, Henderson and Pabis and Logarithmic model. The best drying kinetics model for 2 % hemicellulose coated apricots at 60 and 70 °C was found as Logarithmic model. Page model described best the drying kinetic model for 2 % hemicellulose coated apricots at 80 °C.

Effective diffusion coefficients increased with increasing temperature and ranged at 2.499-5.742 x 10^{-9}. Arrhenius type equation used for description of the temperature dependency of effective diffusion coefficient was resulted in 33.78 kJ/mol of activation enegy during apricot drying.

Comparison of dried apricots with respect to rehydration rates revealed that hemicellulose coated dried apricots had slightly higher rehydration rate (0.011 min^{-1}) than the uncoated dried apricots (0.010 min^{-1}).

In conclusion, this study shows that hazelnut shell is an effective feedstock for the hemicellulose extraction and hemicellulose coating has promising results to be used prior to apricot drying.

Keywords: Hazelnut shells, hemicellulose, extraction, edible coating, drying, modelling, apricot

ÖZ

KAYISI KURUTMADA KÜKÜRTLEME YERİNE HEMİSELÜLOZ KAPLAMASININ KULLANILMASI

Übeyitoğulları, Ali
Yüksek Lisans, Gıda Mühendisliği Bölümü
Tez Yöneticisi: Doç. Dr. Deniz Çekmecelioğlu

Ağustos 2014, 118 sayfa

Kuru kayısı Türkiye'den en çok ihracaat edilen meyvelerden biridir. Ancak kayısı kuruturken kükürtlemeye (SO_2) bağlı olarak bazı kalite sorunları ortaya çıkmaktadır. SO_2 çözeltisi, oksidasyonu ve bakteri-küf oluşumunu engelleyen/geciktiren bir kimyasaldır. Burada asıl husus SO_2'nin insan sağlığına zararlı olmasıdır. Bu yüzden hemiselüloz ile kaplamanın etkisi, kükürtlemeye alternatif olarak araştırılmıştır.

Bu çalışmada, fındık kabuğundan bazik peroksit ortamda hemiselüloz özütlenmiştir. Özütleme koşulları sıcaklık (40, 50 ve 60 °C), alkali yoğunluğu (% 10, 15 ve 20) ve özütleme süresi (4, 8 ve 12 saat) bakımından optimize edilmiş ve Box-Behnken tepki yüzeyi yöntemi ile en yüksek hemiselüloz saflık oranı % 64.24 olarak elde edilmiştir (% 10 NaOH, 40 °C ve 4 saat).

Hemiselüloz ile kaplanan kayısılar tepsili kurutucuda değişen hemiselüloz yoğunluğu (% 1-3), hava hızı (0.5-1.5 m/s) ve hava sıcaklığı (60-80 °C) kullanılarak kurutulmuştur. Hemiselüloz kaplamanın, kurutma esnasında kayısının renk değerleri (ΔE^* and Δb^*) ve nihai nem içeriğine etkisi değerlendirilmiştir. Optimum kurutma koşulları, 1 m/s hava hızı, 80 °C hava sıcaklığı ve % 3 (w/v) hemiselüloz

yoğunluğu olarak bulunmuş ve deneysel sonuçlar 15.2, -8.3 ve % 26 sırasıyla ΔE*, Δb* ve nihai nem içeriği icin hesaplanmıştır. Kurutmanın model tahminleri, ΔE* değerini 13.2, -Δb* değerini -8.3 ve nihai nem içeriğini % 24.9 olarak başarılı bir şekilde bulmuştur. Hemiselüloz ile kaplanan kayısıların renk değerleri, kaplamasız ve kitosan ile kaplı kuru kayısılara kıyasla önemli ölçüde daha iyi olarak bulunmuştur.

Kayısı kuruma kinetikleri Newton, Page, Henderson ve Pabis ve Logarithmic model olmak üzere dört model ile değerlendirilmiştir. Logarithmic model, 60 ve 70 °C'de % 2 hemiselüloz ile kaplanan kayısılar için en iyi kuruma kinetik modeli olarak belirlenmiştir. 80 °C'de % 2 hemiselüloz ile kaplanan kayısılar için ise en iyi kuruma kinetik modeli Page model olarak bulunmuştur.

Etkin nem yayınma katsayıları sıcaklık ile doğru orantılı olarak artmış ve 2.499-5.742 x 10^{-9} değerleri arasında değişim göstermiştir. Etkin nem yayınma katsayısının sıcaklığa bağlı değişimi Arrhenius tipi denklem ile açıklanmış ve kayısı kuruma aktivasyon enerjisi 33.78 kJ/mol olarak hesaplanmıştır.

Kuru kayısıların rehidrasyon hızları karşılaştırıldığında; hemiselüloz ile kaplı kuru kayısıların rehidrasyon hızının (0.011 dk^{-1}) kaplamasız kuru kayısılarınkine (0.010 dk^{-1}) oranla daha hızlı olduğu bulunmuştur.

Sonuç olarak, bu çalışma fındık kabuğunun hemiselüloz özütlemesi için etkili bir hammadde olduğunu ve hemiselüloz kaplamanın kayısı kurutmadan önce uygulanmasının umut verici sonuçlar verdiğini göstermiştir.

Anahtar Kelimeler: Fındık kabuğu, hemiselüloz, özütleme, yenebilir kaplama, kurutma, modelleme, kayısı

To all my beloved…

ACKNOWLEDGEMENTS

First and foremost, I would like to express my sincere gratitude to my advisor, Assoc. Prof. Dr. Deniz Çekmecelioğlu for his endless support, understanding and encouragement throughout this study and guidance in life. His assistance and knowledge was invaluable.

I would like to thank my examining comitee members, Prof. Dr. Meryem Esra Yener, Assoc. Prof. Dr. Behiç Mert, Asst. Prof. Dr. Mecit Öztop and Asst. Prof. Dr. Cem Baltacıoğlu for their valuable comments.

I would like to thank METU-BAP coordination (BAP-03-14-2013-002) for funding this study, Department of Food Engineering, METU for experimental support and to The Scientific and Technological Council of Turkey (TÜBİTAK) for the financial support during my graduate education.

I owe a debt of gratitude to my lab friend and office mate Sibel Uzuner for her supervision and helpful contributions. I would also like to thank to all my colleagues and friends; Özlem Yüce, Abduvali Valiev, Sevil Çıkrıkcı, Elif Yıldız, Hazal Turasan, Hande Baltacıoğlu, Sinem Acar, Sertan Cengiz, Oğuz Kaan Öztürk, Meltem Karadeniz, Elçin Bilgin, Gözde Erbuğa and Onur Yüce for their friendship and support.

I would like to say thank to my home mate Ahmet Yıldız and also to my lab mate/colleague Önay Burak Doğan for their friendship. Life would be boring without them. Ece Bulut, I love and appreciate all that you have done for me.

I would like to thank my uncle Özgür Çiçekli for his kind support during my study. I would like to express my deepest and biggest appreciation to my parents, Zarife-Şefik Übeyitoğulları and also to my brothers, Ahmet, İsmail, Mehmet and Cemil. I would like to thank them for always believing in me.

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CHAPTER 1

INTRODUCTION

Drying is the oldest technique used for preservation of apricots for centuries. Nevertheless, drying alone does not provide stable dried apricots with respect to color, nutritive value and other quality parameters.

Sulfuring is applied to apricots to prevent the browning reactions and enhance the dried apricot quality. However, sulfuring can cause some health problems such as sore throat, pyrosis, headache, vomiting and also asthma attacks (Sobutay, 2003).

In this study, hemicellulose coating prior to apricot drying was investigated. As a feedstock of hemicellulose, hazelnut shells were used. Hemicellulose was extracted from hazelnut shells by alkaline peroxide method. The extraction conditions were optimized with respect to extract purity.

Drying conditions were optimized according to concentration of hemicellulose coating, air velocity and temperature. Besides, chitosan coated, sulfured and uncoated dried apricots were also tested. The responses were color parameters and final moisture content. Drying mechanisms of dried apricot was analyzed by moisture ratio models, effective diffusion coefficients, activation energy and rehydration ratios.

Optimizations were conducted by Box-Behnken response surface methodology with 95 % confidence level.

The aim of this study was to apply edible coatings as a substitute of sulfuring before drying. Objectives of hemicellulose coating were to:

- ✓ Dry apricots without any chemical usage (sulfur dioxide)
- ✓ Retard color changes (due to prevention of browning reactions)

- ✓ Preserve its physical integrity
- ✓ Retain microbial stability
- ✓ Overcome some exportational problems due to sulfuring
- ✓ Contribute to food sector and environment due to usage of food waste for production of hemicellulose

In chapter 2, a literature review was given about apricot, browning reactions, preservation techniques, edible coatings, hemicellulose isolation methods and drying.

In chapter 3, materials and methods were presented to give detailed information about the experiments conducted.

In chapter 4, extraction optimization results were discussed. Experimental results of drying was analyzed and the optimum drying conditions were found. It was followed by comparison of dried apricots due to color parameters. Drying mechanisms were reported at the end of this chapter.

In chapter 5, the study was concluded with the outcomes and recommendations for future work.

CHAPTER 2

LITERATURE REVIEW

2.1 Apricot

Apricot (*Prunus armeniaca* L.) is a fruit with high β-carotene and cellulosic compounds which are required for a healthy diet (Erdogan-Orhan & Kartal, 2011). There are many types of apricot produced in Turkey such as hacihaliloglu, hasanbey, kabaası, cataloglu, alyanak and sekerpare. Hacihaliloglu, cultivated in Malatya region, is the main apricot type used for drying (Ünal, 2010). Moreover, apricot is a climacteric fruit which ripens with increased respiration and ethylene production (Knee, 2002). Apricot has a crucial importance in daily intake due to its beta carotene content. The detailed information about the composition of the apricot is given in Table 2.1 (Sobutay, 2003).

The total annual production of raw apricot is 3 500 000 tons in the world and Turkey produces 700 000 tons of the total. Thus, with this production amount, Turkey has 20 % share in the world as the top fresh apricot producer (Ünal, 2010). It is also known that 100 000 tons of dried apricot are annually produced in Turkey and almost all (95 %) of this amount is exported. Therefore, Turkey is the leader of the dried apricot sector in the world with 76 % share (T. C. Ministry of Economy, 2012).

Table 2.1 Composition of the fresh and dried apricots (100 grams)

Content	Raw (Fresh) Apricot	Dried Apricot
Water (%)	86.3	30.9
Calorie (Cal)	48.0	241.0
Protein (g)	1.4	3.4
Fat (g)	0.2	0.5
Carbohydrate (g)	11.2	62.6
Dietary Fiber (g)	2.0	7.3
Vitamin A (IU)	1926	3604
Vitamin C (mg)	10	2
Calcium (mg)	13	55
Potassium(mg)	259	1162
Phosphorus (mg)	23	71

There are two types of dried apricots. In the first type, apricots are pretreated with sulphur and subsequently dried. However, in the second one, which is called sun dried apricot, pretreatment is not used. Nevertheless, the use of sulfur dioxide is restricted due to some health problems. Consuming more than recommended daily intake (0.7 mg/kg body mass) can cause some side effects (especially on people suffering from asthma) like heartburn, headache, vomiting and some severe allergic reactions (Vavasour, 1999). For this reason, FDA removed sulfites usage on fresh fruits and vegetables from GRAS (generally recognized as safe) list (Taylor, 1993). According to the Turkish Food Codex, the sulfur usage limit in dried apricot is 2000 ppm. However, this value is much less in other countries such as Austria, Italy and France; 300 ppm, 600 ppm and 1000 ppm, respectively (Sobutay, 2003). Therefore, there are still some problems about exports due to high sulfur residual in the dried apricots in Turkey.

2.2 Browning reactions in fruits

Browning is the discoloration of foods due to enzymatic and non-enzymatic reactions which result in food deterioration (Friedman, 1996; Mujumdar, 2007).

Enzymatic browning reactions occur because of the enzymes called polyphenol oxidase (PPO), catechol oxidase and peroxidase (POD) (Ioannou, 2013). Monophenols are oxidized to diphenols and later to quinones by the help of PPO (Queiroz et al., 2008). The final product of these series of reactions is melanin a dark brown pigment (Queiroz et al., 2008).

Enzymatic browning is observed in fruits such as apple (İyidoğan & Bayındırlı, 2004; Nicolas et al., 1994), pear (Franck et al., 2007), banana (Quevedo et al., 2009) and litchi (Yueming et al., 2004).

Maillard reaction and caramelization are the two major categories of non-enzymatic browning reactions. In the absence of amino acids, caramelization occurs when sugars are heated to high temperature (Hodge, 1953). On the other hand, Maillard reactions are serial reactions between reducing sugars and amino acids. In the first step, a reducing sugar and an amino group react to form the Amadori product. Afterwards, this compound results in furfural or hydroxyl-methyl furfural according to the sugar type present and by further step, they form aldols and aldehydes owing to nitrogen (amino groups). In the last step, the outcome is brown pigments, called melanoidins (Martins et al., 2000; Waller & Feather, 1983).

Some fruits like kiwi (Mohammadi et al., 2008), plum (Singh et al., 2012), apple (Mogol et al., 2010), blueberries (López et al., 2010), citrus fruits (Mrak, 1951), pear (Coimbra et al., 2011), figs, apricots (Sanz et al., 2001) and grape (Frank et al., 2005) are affected by non-enzymatic browning reactions.

Browning reactions on the surface of the fruits are detected by color change. For this reason, colorimeters are used. There are several color determination methods. To begin with, CIELab (CIE 1976) color space indicates a uniform color scale and L* value stands for lightness and L* differentiates from black to white. a* and b*

axes correspond to red/green and yellow/blue, respectively (Sharifzadeh et al., 2014). The other color output spaces are Hunter 1948 Lab, CIE 1931 XYZ, CIE Lch, CIE L*u*v*, RGB (red, green and blue) and CMYK (cyan, magenta, yellow and key) (Hunter, 1958; Karabulut et al., 2007; Ladaniya, 2008; León et al., 2006).
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2.3 Fruit Preservation Techniques

Fresh fruits have a short shelf life and are highly perishable (Sousa Gallagher & Mahajan, 2011). The main reason is the high moisture content which enables transportation of enzymes and microorganisms within fruits (James, 2003).

There are several preservation methods of fruits. The traditional ones are jam making, canning and drying (Morris, 1946). Novel technologies are also used as preservation techniques. To illustrate, ultrasound was applied to the strawberry to increase the shelf-life (Aday et al., 2013; São José et al., 2014). In addition, high hydrostatic pressure is subjected to apple, pear, melon and strawberry (Prestamo et al., 2000). Edible coatings are also used for preservation of several fruits such as mango, kiwi, grape, apple, pear, pumpkin and banana (Kittur et al., 2001; Krochta et al., 2012).

Among all, drying is the oldest and the most effective method. The main principle of drying is to decrease moisture content to about 10-15 %. As a result, enzymatic reactions and growth of microorganisms are inhibited (James, 2003). However, some fruits, especially apricot, has some problems with the browning reactions. To delay browning reactions, apricots are exposed to sulfur dioxide in sulfuring room by burning sulfur or dipped to the sulfite or bisulfite ($Na_2S_2O_5$, $K_2S_2O_5$ and $NaHSO_3$) salt solutions (Menges & Ertekin, 2006b). Sulfur dioxide prevents both enzymatic and non-enzymatic browning reactions (Türkyılmaz et al., 2013). The mechanism is that SO_2 prevents the oxidation of quinones and inhibits the PPO and also the carbonyl groups in Maillard reactions (Embs & Markakis, 1965; McWeeny,

1981; McWeeny et al., 1969; Sapers, 1993). The aim of sulfuring is not only to retard browning reactions but also to prevent the microbial growth (Sağırlı et al., 2008). Nonetheless, high residual of sulfur dioxide causes undesired taste and bad smell in the apricots (James, 2003).

In the light of this information, drying does not accomplish the preservation of apricot alone. It also needs a reliable technique such as edible coating to prevent browning and microbial growth.

2.3.1 Edible Coatings

Coating is a thin layer (film) formation on the surface of a product. Coating material also acts as an edible packaging for food. Edible coating provides the following characteristics to the food (Bourtoom, 2008; McHugh et al., 2012):

- Control the exchange of important gases, such as oxygen, carbon dioxide, water vapor and ethylene
- Retard ripening of fruits
- Prevent rancidity of fatty products
- Delay the browning reactions
- Provide surface sterility
- Improve appearance and physical integrity
- Extend shelf life and quality of foods.

Every food requires a different storage condition with various parameters. Therefore, coating materials should provide the necessary conditions to the food. These coating materials are applied by several methods such as dipping, spraying, dripping, foaming and fluidized-bed coating (Krochta et al., 2012).

Coating materials are classified into four groups according to their chemical structure and properties; polysaccharide, protein and lipid based coatings and composite coating.

2.3.1.1 Polysaccharide based coatings

All polysaccharide based coatings are hydrophilic. Therefore, they have poor moisture barrier ability. On the contrary, polysaccharide coatings have low oxygen permeability so they are generally used for fruit and vegetable coatings (Gennadios et al., 1997; Lacroix & Le Tien, 2005). Polysaccharide based coatings are composed of cellulose and derivatives, starch and starch derivatives, pectins, gums and chitosan.

Cellulose $(C_6H_{10}O_5)_n$ is made up of linear chains of β(1→4) linked D-glucose units (Updegraff, 1969). Cellulose based edible coatings can be used for high fat foods because they have very low oxygen permeability (Park et al., 1993). Ayranci (2004) coated apple and green pepper with methyl cellulose to reduce both water loss and vitamin C loss.

Hemicellulose is the second most abundant biopolymer in the nature (Saha, 2003). It constitutes 20-30 % of the weight of annual plants (Table 2.2). Hemicellulose, like lignin and cellulose, is one of the major part of the plant cell walls (Plackett, 2011). Hemicellulose (Figure 2.1) is composed of pentoses (xylose and arabinose), hexoses (glucose, galactose and mannose), hexuronic acids (glucoronic acids) and deoxy-hexose (rhamnose) (Coma, 2013). 4-*O*-methyl-$_D$-glucoruno-$_D$-xylan forms more than 90 % of the hemicellulose monomers (Ebringerová, 2005).

Table 2.2 Composition of some agricultural wastes (Saha, 2003)

	Composition (%, dry basis)		
	Cellulose	Hemicellulose	Lignin
Corn cob	45	35	15
Corn stover	40	25	17
Rice straw	35	25	12
Wheat straw	30	50	20
Sugarcane bagasse	40	24	25
Switchgrass	45	30	12
Hazelnut shells	22	25	37

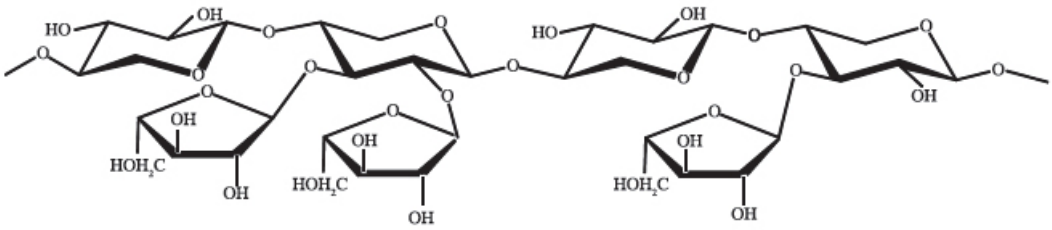


Figure 2.1 Structure of hemicellulose: L-arabino-D-xylane (Heinze, 2005)

Hemicellulose is also hydrophilic like cellulose so that it has the same properties about water vapor transmission rate. Hemicellulose is categorized to hemicellulose A as water insoluble and hemicellulose B as water soluble (Doner & Hicks, 1997; Ebringerová et al., 2005). Therefore, many hemicellulose based coating materials are formed by aqueous solution. The hemicellulose coating solutions are opaque and do not affect the taste of the product (Hansen & Plackett, 2008). Besides,

hemicellulose coating has an antimicrobial activity (Campos et al., 2010; Li et al., 2011). Hemicellulose derivatives were also found to be effective against some Gram-positive and Gram-negative bacteria (Ebringerová et al., 2005).

Hemicellulose based edible coatings were reviewed (Hansen & Plackett, 2008). However, hemicellulose based coating is not common yet. Arabinoxylan, a type of hemicellulose, was used as a coating material for grapes. It was observed that coating material prolonged postharvest shelf life by decreasing the water loss rate by 18 % after 7 days (Zhang & Whistler, 2004).

Hemicellulose was used as coating material for retention of physical quality and enhancing the shelf life of banana. The color of banana was preserved and the coating material prevented the fungal growth (Celebioglu & Cekmecelioglu, 2013).

Starch and derivatives are also applied as coating material. The effect of starch coating on the osmotic rehydration of carrots were investigated. It was reported that starch coating increased the solid content 30 % more than the uncoated carrots (Levic et al., 2008). Furthermore, pumpkin was coated with native and modified starches prior to drying in the study of Lago-Vanzela et al. (2013). According to this study, edible starch coating decreased the color changes and retained the carotenoids in the pumpkin during drying at 70 °C for 8-10 h.

Pectin and gum coatings were compared with the starch based coatings. Shelf-life and quality of raisins were tested with different coatings and pectin coating was better than starch and gum coatings in terms of shelf-life, sensory and chemical properties of raisin. In addition, microbial growth was significantly decreased with all coating materials (Ghasemzadeh et al., 2008).

Chitosan is the other polysaccharide based coating material and one of the most applied coating material in biomedical, food and chemical industries (Li et al., 1992; No et al., 2007). Deacetylated chitin in alkali conditions forms chitosan which is found in the cell wall of the green algae, fungi and yeast (Arvanitoyannis et al., 1998). The structure of chitosan is given in the Figure 2.2.

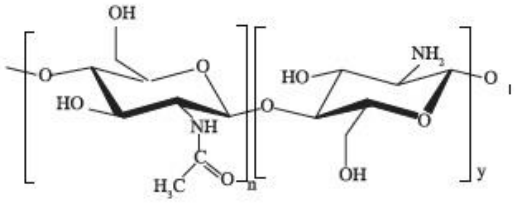


Figure 2.2 Structure of chitosan (Coma, 2013)

Chitosan is produced by extraction from crab or shrimp cells and fungal cell wall (Bourtoom, 2008; Ravi Kumar, 2000). The extraction includes alkaline treatment as mentioned before. For example, extraction of chitosan from *Aspergillus terreus* has several steps such as homogenization, deproteinization, centrifugation and fermentation as a pretreatment for the growth of fungal culture. After homogenization, alkaline extraction of the dried biomass takes place in the autoclave for 20 min at 121 °C with 1.0 N NaOH (Cheng et al., 2014; White et al., 1979). Therefore, chitosan production is a long and complicated process.

Chitosan solutions are generally prepared by using dilute acid (Rinaudo, 2006). Antimicrobial effect of chitosan was proved by many studies (El Ghaouth et al., 1991; No et al., 2006; Roller & Covill, 1999). Specifically, chitosan solutions prevented the contamination of rot pathogen *Burkholderia seminalis* within apricot fruit (Lou et al., 2011). Additionally, microbial quality of fresh squash slices was provided by chitosan coating during drying (Moreira et al., 2009).

Chitosan based edible coatings also extend the shelf life, retard color changes and improve postharvest quality of the foods. Chitosan coatings provided longer cold storage life, postponed the color changes and regulated the inside oxygen and carbon dioxide concentrations of the papaya fruit (Asgar et al., 2011). In another study, sliced mango fruit was coated with chitosan edible coating. Although, mango

can be easily spoiled, chitosan coating prolonged shelf life, prevented the water loss and increased ascorbic acid content (Chien et al., 2007).

2.3.1.2 Protein based coatings

Proteins are composed of amino acids. Properties of protein based coating changes due to the extrinsic factors such as temperature, relative humidity and pH. Besides, protein based coating materials have low oxygen barrier properties at high relative humidity (Salame, 1986). Some of the proteins used as coating materials are gelatin, corn zein, wheat gluten, soy protein and milk proteins (Plackett, 2011).

Protein based coatings extend food shelf life, delay microbial contamination and chemical reactions. Particularly, they are known to be perfect oxygen barriers under controlled conditions. Thus, protein based coatings are mainly used for fatty foods to prevent oxidation (Embuscado & Huber, 2009). For example, whey protein based coatings were used for coating peanuts and it was reported that whey protein coating significantly decreased the oxidation rate compared to uncoated peanuts (Lee & Krochta, 2002). Additionally, corn zein coating resulted in better color compared to the uncoated apricots. The ΔE values of coated and uncoated apricots were found as 7.9±1.1 and 13.8 ±0.6, respectively (Baysal et al., 2010). Lastly, shelf life of kinnow fruits was lengthened by 20 days with casein coating (Alam & Paul, 2001).

2.3.1.3 Lipid based coatings

The main purpose of the lipid based edible coatings is to prevent moisture loss due to its hydrophobic structure. Triglycerides, acetoglycerides, waxes, fatty acids and resin are commonly used lipid based coatings (Bourtoom, 2008). Lipid based

coating materials are generally used with combination of other coating materials due to their weak mechanical strength.

Waxes are applied to many fresh fruits to minimize the water loss and to improve microbiological stability. For instance, oranges and mandarins coated with wax were well protected and 80 % of the sporulation was inhibited (Njombolwana et al., 2013). Meanwhile, shellac coating was conducted as a coating material for grapefruit to minimize chilling injury during two months storage at 4 °C and 92 % relative humidity (Dou, 2004).

2.3.1.4 Composite coating

Composite coating is the combination of multiple coating types. The permeability, mechanical strength, solubility of the coating material and other properties are optimized by composite coating. Examples of composite coatings are arabinoxylan-lipid combination (Phan The et al., 2002), sodium caseinate-lipid (Fabra et al., 2008), whey protein-hydroxypropyl methylcellulose (Perez-Gago et al., 2005) and glucomannan and chitosan-soy protein (Jia et al., 2009).

Integration of lipid with polysaccharide or protein has various advantages. While lipids have good water barrier properties, on the other hand their mechanical strength is very weak. Therefore, polysaccharides or proteins mixed with lipids is required to increase coating stability and integrity (Bravin et al., 2006; Roberto et al., 1994).

2.4 Hazelnut shells as a source of hemicellulose

Turkish hazelnut accounts for 69 % of the world hazelnut market followed by Italy, Azerbaijan and the USA in 2013 (TGB, 2013). This means that 549 000 tons of

hazelnut is annually produced (INC, 2013). Hereby, 250 000 tons of hazelnut shells are manufactured every year. This amount of hazelnut shell is burned in Turkey (TGB, 2013). On the contrary, these agricultural wastes are composed of 24.8 % hemicellulose, 37 % lignin and 22.2 % cellulose (Arslan, 2007).

The studies on hazelnut shells are limited so far. Hazelnut shells studies are focused on production of ethanol (Arslan & Eken-Saraçoğlu, 2010; Arslan et al., 2012) and biodiesel (Demirbas, 2008). Antioxidant capacity of the shells is also studied (Altun et al., 2013; Contini et al., 2008; Xu et al., 2012). Demirbas (2002) investigated liquefaction of hazelnut shells by direct and alkaline glycerol. Furthermore, activated carbon is produced from hazelnut shells (Demirbas et al., 2009; Sencan et al., 2014; Sharifan & Fowler, 2014)

2.5 Hemicellulose Isolation Methods

Hemicellulose has been isolated by several methods for bioprocess applications and it is generally obtained by biorefining of agricultural wastes (Table 2.3).

Table 2.3 Hemicellulose isolation methods

Method	Feedstock	Study
Alkaline Extraction	Caragana Korshinskii	(Bian et al., 2010)
Water and alkaline extraction	Sugarcane bagasse	(Peng et al., 2009)

Table 2.3 (continued)

Dilute acid	Giant bamboo	(Vena et al., 2010)
Hydrogen peroxide	Destarched corn fiber	(Doner & Hicks, 1997)
Steam explosion and ultrafiltration	Barley husks	(Krawczyk et al., 2008)
Ultrasonic extraction	Buckwheat hulls	(Hromádková & Ebringerová, 2003)
Enzymatic hydrolysis	Wood residues	(Kim et al., 2001)

Most of the hemicelluloses are isolated by extraction. The commonly used extraction techniques of hemicellulose are alkaline and acidic methods (Yılmaz Celebioglu et al., 2012).

Cunningham et al. (1987) used annual plants (wheat straw, kenaf and sorghum bagasse) for hemicellulose extraction in alkaline conditions. A maximal yield of 80-84 % of the kenaf hemicelluloses and 88-90 % of the hemicelluloses in the wheat straw and sorghum bagasse were obtained with 12 % NaOH solution at 80 °C for 4 h. Corn fiber was utilized for the ethanol production but hemicellulose was removed from the corn fiber by alkaline extraction prior to ethanol fermentation. Hemicellulose extraction was accomplished at 120 °C and 2 bars for 1h with 1 and 2 % NaOH and KOH solutions (Gáspár et al., 2007). Approximately, 80 % of the

total hemicellulose was precipitated by ethanol (Gáspár et al., 2007). Some other studies reported alkaline extraction with optimum hemicellulose recoveries of 56.1 % (Juan et al., 2013), 50.3% (Yuan et al., 2013), 26.2 % (Luo et al., 2012), 42.7 % (Bian et al., 2010) and 12.4 % (Vena et al., 2013).

Hydrogen peroxide is also used as a pretreatment agent in alkaline extraction. An improvement in the extraction efficiency and other quality parameters was reported (Doner & Hicks, 1997; Harmsen & Huijgen, 2010; Rabetafika et al., 2014; Sun, 2002; Sun et al., 2000).

Acidic extraction methods have been compared with alkaline extraction by several studies (Geng et al., 2003; Xu et al., 2008; Yılmaz Celebioglu et al., 2012). Other extraction methods are heat (over 100 °C) (Benko et al., 2007; Tunc & Adriaan, 2008), ultrasonically assisted (Sun & Tomkinson, 2002), ozone treated (Ben-Ghedalia & Rubinstein, 1986), microwave assisted (Buranov & Mazza, 2010) and high pressure methods (Hanim et al., 2012).

2.6 Drying

Drying has been used as a preservation method for centuries. The stability of foods increases with drying due to loss of water (Van Arsdel & Copley, 1963). The soluble solid content of the dried foods becomes high enough to prevent microbial growth (Nury & Brekke, 1963). Moreover, drying reduces the burden of transportation and packaging requirements (Sagar & Suresh Kumar, 2010).

Most important physical change during drying is shrinkage (reduction in its original volume) (Mayor & Sereno, 2004; Ratti, 1994). Shrinkage has negative effects on the consumers and also decreases the rehydration capacity of the dried food (Jayaraman et al., 2007; McMinn & Magee, 1997) . Rehydration is the water absorption capacity of the dried food (Krokida & Philippopoulos, 2005; Maskan, 2001) and is an important quality parameter for the dried fruits, snacks and instant soups (Krokida & Marinos-Kouris, 2003). Particularly, rehydration properties of

dried apple slices, kiwi, avocado, banana and potato were studied (Atarés et al., 2009; Giraldo et al., 2006; Lee et al., 2006).

There are various drying technologies used for food drying. Vacuum dryers (Cui et al., 2004), spray dryers (Chegini & Ghobadian, 2007), rotary dryers (Savaresi et al., 2001), continuous fluid-bed dryers (Temple & Van Boxtel, 2000), tray dryers (Kiranoudis et al., 1997) and freeze dryers (Fissore et al., 2014) are generally preferred dryer types in food dehydration.

Drying is widely used in foods; meat (Soydan Karabacak et al., 2014), fish (Jain & Pathare, 2007), vegetables (Kim et al., 2004), coffee and tea (Vijayavenkataraman et al., 2012), dairy products (Schuck, 2002) and egg (Franke & Kießling, 2002).

Perishability of the fruits is prevented by the help of drying. Drying is practically applied to nearly every fruit such as apple (Ben Mabrouk et al., 2012), banana (Guine & Dias, 2007), kiwi (Mohammadi et al., 2008), raisins (Pangavhane & Sawhney, 2002), figs (Doymaz, 2005a), pineapple (Bala et al., 2003) and cherries (Mabellini et al., 2010). Fruit drying is usually practiced with tray dryers (Kiranoudis et al., 1997; Misha et al., 2013).

Apricots are largely dried by the solar energy (Piga et al., 2004; Toğrul & Pehlivan, 2002, 2004). However, this drying technique takes a long time and has some problems due to safety of the apricot. Hence, controlled drying methods have been introduced for apricot drying and tray dryers are the most used ones (Abdelhaq & Labuza, 1987; Ertekin & Yaldiz, 2004; Karabulut et al., 2007; Mirzaee et al., 2009; Toğrul & Pehlivan, 2003).

2.6.1 Drying Mechanism

Drying follows different patterns during removal of volatile compounds. Drying lasts until a constant weight reached under the given conditions, temperature and relative humidity which leads to the equilibrium moisture content. The water

removed before that point is called free water (Geankoplis, 2003). The water exerting less vapor pressure than the water at the same temperature is named as bound water and it has strong forces due to its availability in fine capillaries (Keey, 1972). The foods having bound water are known as hygroscopic (Bender, 2014; Lopez et al., 1995; Rockland, 1957). The moisture other than bound water is the unbound moisture. These water types determine the sorption behavior of the foods. Furthermore, Figure 2.3 shows the sorption isotherms which are observed by adsorption process (wetting) or by desorption process (drying) (Aguerre et al., 1989). The difference between these process curves is called hysteresis. Three moisture retention regions are seen in Figure 2.3. Specifically, in the region A of the Figure 2.3, water is found in the finest capillaries as bounded, water is located in small capillaries in the region B and water is unbound in large capillaries in region C (Keey, 1972).

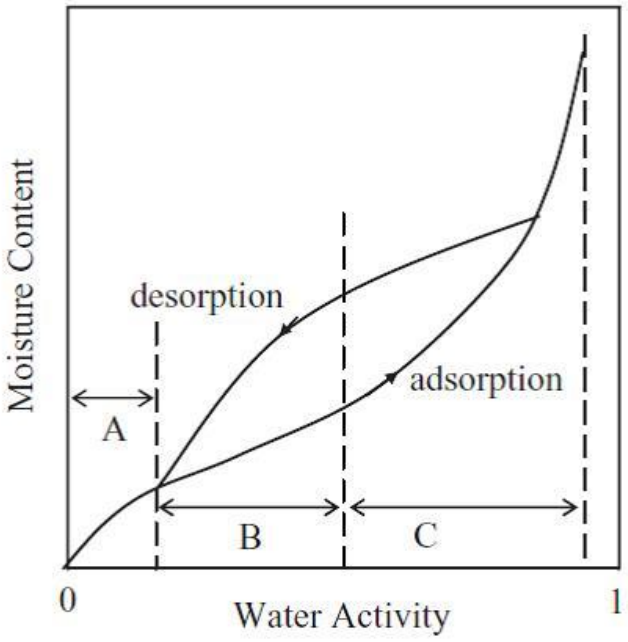


Figure 2.3 Sorption behavior of a typical food (Sahin & Sumnu, 2006)

According to water type (bound or unbound), drying rate differs. Two periods of drying are observed in foods; constant rate and falling rate of drying (Figure 2.4) (Van Arsdel & Copley, 1963). Constant rate of drying is observed until all the unbound water evaporates. Actually, drying continues in a constant rate as long as evaporation rate is constant. Nevertheless, after a point (C) known as critical free moisture content drying rate starts to decrease because of no enough water supplied to the surface of the food. This phenomenon results in the second drying period, falling rate drying. In addition, water is transferred by capillary movements to the surface of the material in falling rate. In the same manner, when surface of the material is completely dried, the second falling rate period (after point D in the Figure 2.4) is observed and the migration of water vapor is maintained by diffusion. Falling rate period takes most of the drying time (Geankoplis, 2003; Mujumdar, 2000; Mujumdar & Devahastin, 2008).

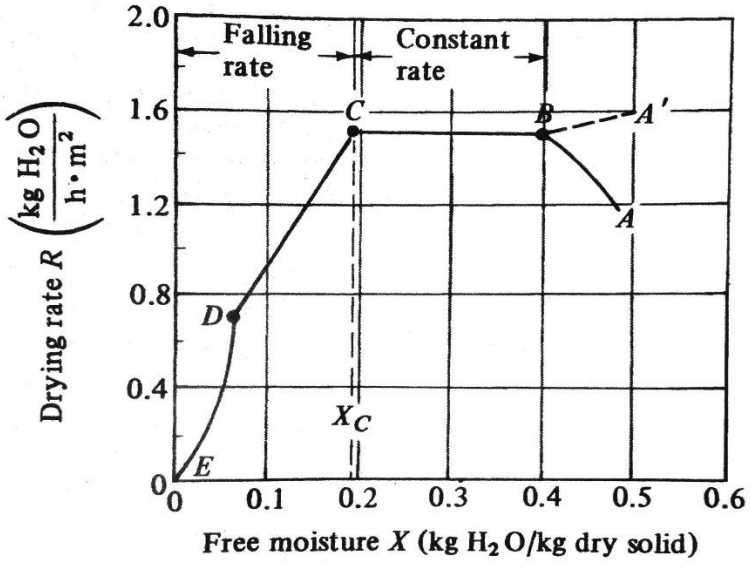


Figure 2.4 Drying rate curve under constant external conditions (Geankoplis, 2003)

2.6.2 Mathematical Modelling of Drying

Models are deterministic if their probability is equal to one, else are named as stochastic model (Mujumdar, 2007). There are numerous drying models based on different aspects; experimental (Baini & Langrish, 2008; Ben Mabrouk et al., 2012), transport phenomena (Hussain & Dincer, 2003), and porous media theory (de Boer, 2002).

Thin-layer drying (drying kinetics) is expressed by experimental and diffusion models (da Silva et al., 2014). These theoretical drying models are based on the Fick's second law (Sander, 2007). Thin layer drying is based on the equation 1 (Jayas et al., 1991).

$$-\frac{dX}{dt} = k(X - X_{eq}) \quad (1)$$

where X (kg H_2O/kg db) is the moisture content, X_{eq} (kg H_2O/kg db) is the equilibrium moisture content and t denotes the drying time. Thin-layer equation is applied for many foods such as mushrooms (Midilli et al., 2002), pistachio (Kashaninejad et al., 2007), apricot (Mirzaee et al., 2010; Toğrul & Pehlivan, 2002), eggplant (Ertekin & Yaldiz, 2004), plum (Goyal et al., 2007), apple (Menges & Ertekin, 2006a), mango (Goyal et al., 2006), garlic slices (Ponciano et al., 1996), black tea (Panchariya et al., 2002), carrot (Doymaz, 2004a) and red pepper (Akpinar et al., 2003a).

The solution of the first order differential equation by Lewis in 1921 (equation 2) and by Page in 1949 (equation 3) is given below (Jayas et al., 1991; Karathanos, 1999).

$$MR = \frac{X - X_{eq}}{X_0 - X_{eq}} = exp(-kt) \quad (2)$$

$$MR = \frac{X - X_{eq}}{X_0 - X_{eq}} = exp(-kt^n) \quad (3)$$

where MR stands for the moisture ratio (dimensionless moisture content), k and n are the model constants. Lewis's solution is similar to the Newton's law of cooling

and suggested for the falling rate of the drying of porous hygroscopic materials. It is also known as Newton model (Lewis, 1921; Toğrul & Pehlivan, 2003). Page is derived as the third equation for the thin layer drying of shelled corn as the best fitted model (Page, 1949; Sokhansanj et al., 1987).

The other drying kinetic models are derived from these two primarily equations. Some of the best fitted models in food materials are

Henderson and Pabis model (Pabis, 1998):

$$MR = \frac{X - X_{eq}}{X_0 - X_{eq}} = a\ exp(-kt) \quad (4)$$

Modified Page equation (Overhults et al., 1973):

$$MR = \frac{X - X_{eq}}{X_0 - X_{eq}} = exp(-(kt)^n) \quad (5)$$

Logarithmic model (Akpinar et al., 2003b):

$$MR = \frac{X - X_{eq}}{X_0 - X_{eq}} = a\ exp(-kt) + c \quad (6)$$

and two term model (Henderson, 1974):

$$MR = \frac{X - X_{eq}}{X_0 - X_{eq}} = a\ exp(-k_0 t) + b\ exp(-k_1 t) \quad (7)$$

The best fit models calculated for drying of foods are the logarithmic model for pistachio (Midilli & Kucuk, 2003) and white mulberry (Doymaz, 2004b); Page model for whole banana (da Silva et al., 2014), avocado and kiwi (Ceylan et al., 2007), okra (Doymaz, 2005b) and potato slices (Aghbashlo et al., 2009); modified Page model for carrot (Erenturk & Erenturk, 2007); two term drying model for grape (Yaldiz et al., 2001).

Appropriate models found for apricot drying are Page model (Igual et al., 2012; Menges & Ertekin, 2006b) and logarithmic model (Mirzaee et al., 2010; Toğrul & Pehlivan, 2003) for air drying and two term model (Ghatrehsamani et al., 2012) for solar drying.

2.6.3 Effective Diffusion Coefficient and Activation Energy

Effective diffusion coefficient can be calculated by unsteady-state diffusion formula based on Fick's second law for fruits and vegetables (Mirzaee et al., 2009; Sander, 2007). The equation can be written as follows for thin-layer drying (Geankoplis, 2003):

$$\frac{\partial X}{\partial t} = D_{eff} \frac{\partial^2 X}{\partial x^2} \tag{8}$$

where D_{eff} is the effective diffusion coefficient in m^2/s and x is thickness of the solid in m. This equation is valid for the falling rate drying because the main mechanism of the water removal is by diffusion (Keey, 1972). Solution of the equation 8 is given below for infinite slab, negligible shrinkage and constant diffusion coefficient (Bird et al., 2001; Tosun, 2007):

$$\frac{X-X_{eq}}{X_0-X_{eq}} = \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} exp\left(\frac{-(2n+1)^2 \pi^2 D_{eff} t}{4L^2}\right) \tag{9}$$

where L is the half thickness of the fresh food when dried from two sides or the thickness of the fresh food when dried from one side in m. This equation can be reduced to the first term only if the Fourier number is greater than 0.1. Thus, lumped model is applicable for long drying times (Akpinar et al., 2003b; Crank, 1975; Seth & Sarkar, 2004):

$$\frac{X-X_{eq}}{X_0-X_{eq}} = \frac{8}{\pi^2} exp\left(\frac{-\pi^2 D_{eff} t}{4L^2}\right) \tag{10}$$

By some configuration, drying time (Geankoplis, 2003) and activation energy by Arrhenius type equation are written as follows (Lopez et al., 2000; Mirzaee et al., 2009):

$$t = \frac{4L^2}{\pi^2 D_{eff}} \ln\left[\frac{8}{\pi^2}\left(\frac{X_0-X_{eq}}{X-X_{eq}}\right)\right] \tag{11}$$

$$D_{eff} = D_0 exp\left(-\frac{E_a}{RT_a}\right) \tag{12}$$

where t is the drying time, E_a is the activation energy (kJ/mol), R is universal gas constant (kJ/mol K), T_a is the absolute air temperature (K) and D_0 is constant (m^2/s). The average diffusion coefficient (m^2/s) was reported as 7.517×10^{-10} for carrot, 2.553×10^{-10} for potato (Mulet, 1994), 8.121×10^{-9} for apple (Zogzas & Maroulis, 1996), 8.56×10^{-10} for mango and 4.93×10^{-10} for cassava (Hernández et al., 2000).

In addition, effective diffusion coefficient of apricot found between 1.7×10^{-10} and 1.15×10^{-9} m^2/s and the activation energy changes in the range of 29.35-33.78 kJ/mol (Mirzaee et al., 2009). According to another study, effective diffusion coefficient (m^2/s) of apricot ranged from 4.76×10^{-9} to 8.32×10^{-9} (Toğrul & Pehlivan, 2003).

2.6.4 Effects of Coating on Drying

Edible coating can be applied prior to drying to take advantage of preservation properties of the coating materials. However, drying mechanism is affected by the coating material. For instance, osmotic dehydration rate increases with starch or pectin coating (Lenart & Dabrowska, 1997; Lenart & Dabrowska, 1999; Lewicki et al., 1984). Besides, the efficiency of osmatic dehydration of carrot in saccharose and molasses is enhanced by starch coating (Levic et al., 2008). The color, texture and microbial stability of raisins are also improved by pectin film coating during storage (Ghasemzadeh et al., 2008).

Some foods are coated prior to drying to retain color. For example, pumpkin slices are coated with native and modified starches to preserve the carotenoids during air drying. Significant improvements were obtained by edible coatings and carotene loss was decreased by 12-15 % (Lago-Vanzela et al., 2013). Furthermore, carrots were coated with corn starch before drying and compared with sulfites. It was reported that corn starch coating has a slower rate of carotene loss than sulfites during storage (Zhao & Chang, 1995).

2.7 Objectives of the Study

Hazelnut industry produces a large amount of hazelnut shells as waste every year. These agro food wastes were aimed to be used as the source of hemicellulose. Usage of food waste for production of hemicellulose will contribute to food sector and the environment. The extraction of hemicellulose was optimized using different values of temperature, alkaline concentration and extraction time.

Currently, apricots are sulfured before drying to enhance the dried apricot quality. However, some harmful side effects have been reported. Therefore, hemicellulose coating prior to drying of apricot will be a substitute to sulfuring for prevention its side effects. Color and kinetic parameters of dried apricots were investigated and optimum drying conditions (air temperature, air velocity and hemicellulose concentration) were determined in the light of responses; color parameters and final moisture content.

By this study, it is aimed to retard color changes, preserve its physical integrity and retain microbial stability during and after drying of apricots. The usage of hemicellulose coating will also overcome some exportational problems due to excess usage of sulfur dioxide in Turkey.

CHAPTER 3

MATERIALS AND METHODS

3.1 Materials

3.1.1 Raw materials and chemicals

Hazelnut shells were obtained from a local factory in Giresun. Hacihaliloglu type apricot was used for drying and it was provided from local producers in Malatya. All the chemicals used for the extraction, coating and other analysis are given in Table A.1.

3.1.2 Dryer

A laboratory scale tray dryer (Eksis Endustriyel Kurutma Sistemleri, Isparta, Turkey) was used for the drying experiments (Figure 3.1). Air flow rate, air temperature and tray revolution speed were adjustable. The air was moving parallel throughout the steel trays. The dimensions of the trays were 30 cm x 30 cm x 2 cm. A shematic drawing of the dryer is given in the Figure 3.2. The tray dryer had five perforated trays. The experimental data was recorded by the dryer every min for temperature (0.1 ℃) and every 5 min for weight (1 g). The temperature was kept constant within the range ±1 °C during the experiment. Before the weight measurement, the dryer fan and rotation stops automatically for 1-2 seconds to prevent any external measurement errors. Dryer working conditions were optimized by selecting the best response curve to the different PID controller gain due to its

oscillation rate, overshoot and steady-state time. The relative humidity were set to ±1% before all of the experiments. The experiment was started after the dryer reached the steady-state conditions.

Figure 3.1 Laboratory scale tray dryer

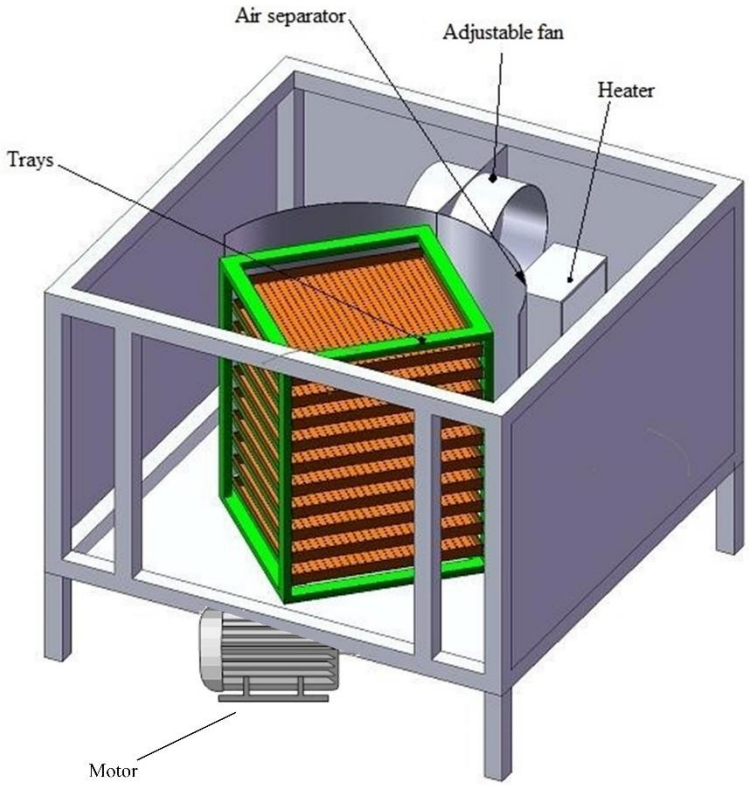


Figure 3.2 Schematic drawing of the scale tray dryer

3.2 Methods

3.2.1 Sample preparation

The hazelnut shells were dried at 70 °C for 24 h and then granulated by a grinder (Thomas Model 4 Wiley® Mill (Thomas Scientific, Swedesboro, NJ 08085, USA)). Prior to extraction, the hazelnut shells were sieved to have a uniform distributed particle size at 0.85 mm to 1 mm in diameter. The granulated hazelnut shells were kept at the room temperature in zipper storage bags until use.

Apricots were halved and the stone was separated. Then, the apricot halves were subsequently dipped to the coating material for just a few seconds to minimize undesirable reactions. The apricots were kept at 4 °C before the experiments.

3.2.2 Hemicellulose extraction methods

3.2.2.1 Direct Alkali Extraction

Alkaline extraction was conducted by using NaOH solutions for 24 h at 30 °C. The mixture was filtered to separate the insoluble parts (cellulose). The pH of filtrate was adjusted to 5.5 by 37 % HCl and subsequently 3 x volumes of 98 % ethanol was added in order to precipitate the hemicellulose and kept at 4 °C for 24 h (Gáspár et al., 2007). It was not required to separate the hemicellulose A and hemicellulose B for the coating (Yılmaz Celebioglu et al., 2012). The precipitated hemicellulose was filtrated by filter cloth and dried.

3.2.2.2 Alkaline Hydrogen Peroxide Extraction

Three different alkaline extraction methods with hydrogen peroxide pretreatment were tested.

In the first method, 1:20 ratio of hazelnut shells to H_2O_2 solution was obtained by adding 100 ml of 1 % aqueous solution of hydrogen peroxide to 5 g hazelnut shells. pH of the solution was adjusted to 11.5 with 2*N* NaOH. The mixture was kept at 120 rpm in the shaking incubator. After filtration, pH of the supernatant was adjusted to 4.0 by titrating with 4*N* HCl. Finally, three times ethanol by volume was added to the solution and the mixture was kept for 24 h at 4 °C to precipitate the crude hemicellulose (Doner & Hicks, 1997).

In the second method, the hazelnut shells were dewaxed by extraction with toluene-ethanol (2:1, v/v) for 6 h with 1:20 ratio of hazelnut shells to the toluene-ethanol solution. For the next step, namely delignification, the dewaxed hazelnut shell powder was treated with 6% sodium chlorite at 75 °C for 2 h. The pH of the sodium chlorite solution was adjusted to 3.6-3.8 with 10% acetic acid before the treatment. Subsequently, the residue washed with ethanol and dried. Then, the hemicellulose was extracted from dried powder with different concentrations of KOH solution at the same solid-liquid ratio. The extract pH was adjusted to 5.5 with 6 M HCl and the extract was washed by ethanol. Finaly, the solution was kept at 4 °C to precipitate hemicelluloses in the solution (Peng et al., 2012).

In the last method, as in the previous method, the hazelnut shell powder was extracted with the same toluene-ethanol ratio for 6 h. Then, the dewaxed shell powder was treated with different NaOH concentrations for various times at 120 rpm in the shaking incubator. 250 ml of 5 % H_2O_2 was added to the mixture and the extraction was lasted for more 12 h at 45 °C. The pH of the H_2O_2 solution was adjusted to 11.5 with 4 M NaOH before added. After the extraction, the residue was separated out by vacuum filtration and the filtrate was neutralized with 6 M HCl to pH 8.5 for removal of the silicate. The pH of the supernatant was further decreased to 6 with same acid concentration. Three volumes of ethanol was added to the supernatant and the hemicelluloses was precipitated during 24 h at 4 °C. After filtration, hemicellulose was freeze-dried (Martin Christ Gefriertrocknungsanlagen GmbH, ALPHA 2-4 LDplus, Osterode am Harz, Germany) at 0.017 mbar for 24 h (Sun et al., 2000).

3.2.3 Crude hemicellulose purity determination

Purity of the hemicellulose extracts and composition of hazelnut shell, were determined by High-Performance Liquid Chromatography (HPLC) method. For this purpose, HPLC system (Shimadzu Corporation, Kyoto, Japan) equipped with Aminex HPX 87H (300 x 7.8 mm); (Bio-Rad Laboratories Inc., Hercules, CA,

USA) HPLC column was used. Standard curve for glucose, xylose and arabinose was constructed by using 0.5, 1.0, 2.0 and 4.0 g/L concentrations.

Dried sample (1 g) was hydrolyzed with 72 % H_2SO_4 (10ml) for 1 hour at room temperature. Then, 140 ml distilled water was added and autoclaved for 1 hour at 120 °C. The residue was removed by vacuum filtration. To precipitate the sulphate anions, 1 g of $Ba(OH)_2*8H_2O$ was added to 20 ml of the supernatant. The solution mixed for 1 min and centrifuged for 5 min at 9,279 x g. The supernatant was diluted with 4 mM H_2SO_4 at 1:3 ratio. HPLC column working conditions with 4 mM H_2SO_4 as an eluent were 0.6 ml/min at 54 °C for 25 min (Gáspár et al., 2007; Varga et al., 2005; Yılmaz Celebioglu et al., 2012).

3.2.4 Determination of Moisture Content

Fresh and dried apricots were kept at 105 °C for 24 h at the oven (Simsek Laborteknik, ST120, Ankara, Turkey) until the constant weight reached. For weight measurements, electronic balance (RADWAG Wagi Elektroniczne, Radom, Poland) with 0.001 g precision was used. The moisture content (wet basis) was calculated with the formula given below:

$$Moisture\ content, wb\ (\%) = \frac{Initial\ weight - Final\ weight}{Initial\ weight} * 100 \qquad (13)$$

3.2.5 Coating material preparation

The coating material was prepared by mixture of dried hemicellulose and distilled water to form different concentrations (1.0, 2.0 and 3.0 g/100 ml). Then, 0.2 ml Tween 80 was added for 100 ml solution. The solution was homogenized with an ultrasonic disintegrator (MSE Soniprep 150, London, UK) for 5 min at 5 amplitude

microns. Afterwards, the solution was mixed with a magnetic stirrer for 30 min. However, chitosan solution was prepared with 1 % acetic acid instead of distilled water due to difficulties with dissolution (No et al., 2006; Van & Hanh, 2013).

3.2.6 Color measurement

The color of apricots were measured before and after drying by The Color Reader-10 (Konica Minolta, Inc., Osaka, Japan). The L*, a* and b* values were obtained and used for the calculation of color parameters listed below:

The total color change (ΔE):

$$\Delta E = \left[\left(L_i^* - L_f^*\right)^2 + \left(a_i^* - a_f^*\right)^2 + \left(b_i^* - b_f^*\right)^2\right]^{0.5} \quad (14)$$

$$\text{Chroma} = \left(a^{*2} + b^{*2}\right)^{0.5} \quad (15)$$

$$\text{Hue Angle} = [\arctan(b^*/a^*)][180/\pi] \quad (16)$$

$$\text{Browning index (BI)} = \frac{100(x - 0.31)}{0.17} \text{ where } x = \frac{a^* + 1.75L^*}{5.645L^* + a^* - 3.012b^*} \quad (17)$$

$$\Delta b = b_f^* - b_i^* \quad (18)$$

where L_i^*, a_i^*, b_i^* were the initial color values of fresh apricot and L_f^*, a_f^*, b_f^* were the values of color parameters after drying (Ihns et al., 2011; Mohammadi et al., 2008). For all color data, average of five measurements were used for high precision.

3.2.7 Apricot Drying

First of all, L*, a* and b* values were measured by The Color Reader-10 before drying of apricots. Later, the apricots were coated by dipping to the coating material (hemicellulose and chitosan) and aligned to the trays with uncoated apricots.

Subsequently, the coated apricots were dried for 300 min according to the experimental design. After drying, the L*, a* and b* values were also measured. Final moisture content was also calculated for every drying experiment in two replicates.

3.2.7.1 Mathematical Modelling

3.2.7.1.1 Moisture Loss

Weight loss data were recorded by the tray dryer. By these data, the dry basis moisture content (kg water/kg bone dry solid) was calculated. Moisture ratio was calculated by the equation below;

$$MR = \frac{X - X_{eq}}{X_0 - X_{eq}} \quad (19)$$

where X= moisture content (kg water/ kg bds) at time t,

X_{eq}= Equilibrium moisture content (kg water/ kg bds) and

X_0=initial moisture content (kg water/ kg bds)

3.2.7.1.2 Equilibrium Moisture Content

Equilibrium moisture content was determined by using two different models.

The first model was by Henderson and Pabis (1961);

$$\frac{X - X_{eq}}{X_0 - X_{eq}} = ae^{-kt} \quad (20)$$

By some configuration, the equation became as follows;

$$X = X_{eq} + a_1 e^{-kt} \quad (21)$$

Nonlinear regression was taken between X and time to calculate the constant, X_{eq}. SigmaPlot for Windows Version 11.0 (Systat Software GmbH, Erkrath, Germany) was used for the exponential decay, nonlinear regression.

The second model used was by Henderson (1974);

$$\frac{X - X_{eq}}{X_0 - X_{eq}} = ae^{-kt} + be^{-k_1 t} \quad (22)$$

In the same manner, the X_{eq} was also calculated from the nonlinear regression of the equation below;

$$X = X_{eq} + a_1 e^{-kt} + b_1 e^{-k_1 t} \quad (23)$$

3.2.7.1.3 Drying curve models

Four different models were used to find the best model for apricot drying (Table 3.1).

Table 3.1 Drying curve models

Model equation	Name	Reference
MR=exp(-kt)	Newton	(Liu & Bakker-Arkema, 1997)
MR=a*exp(-kt)	Henderson and Pabis	(Chhinnan, 1984)
MR=a*exp(-kt)+c	Logarithmic	(Ademiluyi & Abowei, 2013; Yaldiz et al., 2001)
MR= exp(-k*t^n)	Page	(Page, 1949)

3.2.8 Microbiological Analyses

Apricots (10 g) were placed into stomacher bags and stomached with 90 ml of 0.1 % peptone water for 2 min. Serial dilutions ranging from 10^{-1} to 10^{-6} were prepared. Total bacterial count was determined by pour plate method and Plate Count Agar (PCA) was used as the growth medium. PCA plates were incubated at 28 °C for 48 h (Türkyılmaz et al., 2012). Potato Dextrose Agar (PDA) was used as the nutrient medium for yeast and mold growth. The growth was observed after 7 days at 30 °C incubation of PDA plates (Sağırlı et al., 2008). All analyses were done in triplicate (Karabulut et al., 2007; Khattak et al., 2014).

3.2.9 Statistical Analyses

The design of experiments was performed using Minitab® 16.1.1 software (Minitab Inc., State Collage, PA, USA). For extraction part of the study, Response Surface Methodology (RSM) with Box-Behnken design was constructed by 3 parameters (alkaline concentration, temperature and time) with 3 levels (40, 50, 60 °C; 10, 15, 20 %; 4, 8, 12 h). The response was the purity of the dried crude hemicellulose as measured by HPLC method. The experimental design of the drying conditions was also carried out by Box-Behnken RSM design. Coating material concentrations (1, 2 and 3 %, w/v), air velocities (0.5, 1 and 1.5 m/s) and air temperatures (60, 70 and 80 °C) were tested. Apricot color and final moisture content were measured after drying as responses.

Results were checked whether normal or not. If not, data were normalized by Box-Cox method. The two experimental designs were optimized by the response optimizer tool of the Minitab® 16.1.1. 95 % confidence level was used in all of the statistical calculations.

Drying models were compared by coefficient of determination (R^2), root mean square error (RMSE), mean bias error (MBE) and reduced chi-square (χ^2). These parameters were calculated with the following formulas;

$$RMSE = \left[\frac{1}{N}\sum_{n=1}^{N}(MR_{pre,i} - MR_{exp,i})^2\right]^{0.5} \quad (24)$$

$$MBE = \frac{1}{N}\sum_{n=1}^{N}\left(MR_{pre,i} - MR_{exp,i}\right) \quad (25)$$

$$\chi^2 = \frac{\sum_{i=1}^{N}(MR_{exp,i} - MR_{pre,i})^2}{N-n} \quad (26)$$

where $MR_{pre,i}$ was used for the predicted MR of the i^{th} element, $MR_{exp,i}$ represented the experimental value of the MR of the i^{th} element, N stands for the observation number and n is the number of parameters in the model (Toğrul & Pehlivan, 2003).

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Crude hemicellulose purity determination

The purity of crude hemicellulose samples were determined by HPLC. The HPLC standard curves for glucose and arabinose are given in Figures B.1-B.2 and for xylose in Figure 4.1.

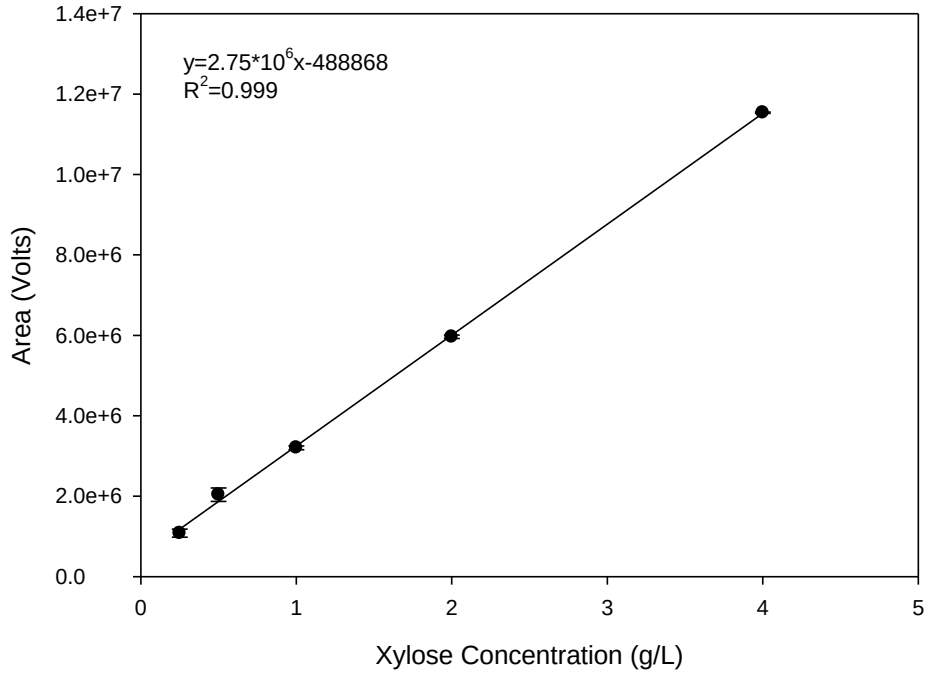


Figure 4.1 Standard curve for xylose determination

In all standard curves, y stands for the area (volts) and x is the concentration (g/L) of the sugar. The purity of the hemicellulose extract was calculated from the multiplication of concentration with dilution factors.

A sample HPLC chromatogram of hemicellulose extract and standard curve of xylose are also given in Figure 4.2. Peaks were observed for glucose between 10th and 11th minutes; for xylose between 11th and 12.5th minutes and for arabinose between 12.5th and 13.5th minutes. These values are relatively close with the literature (Yılmaz Celebioglu et al., 2012).

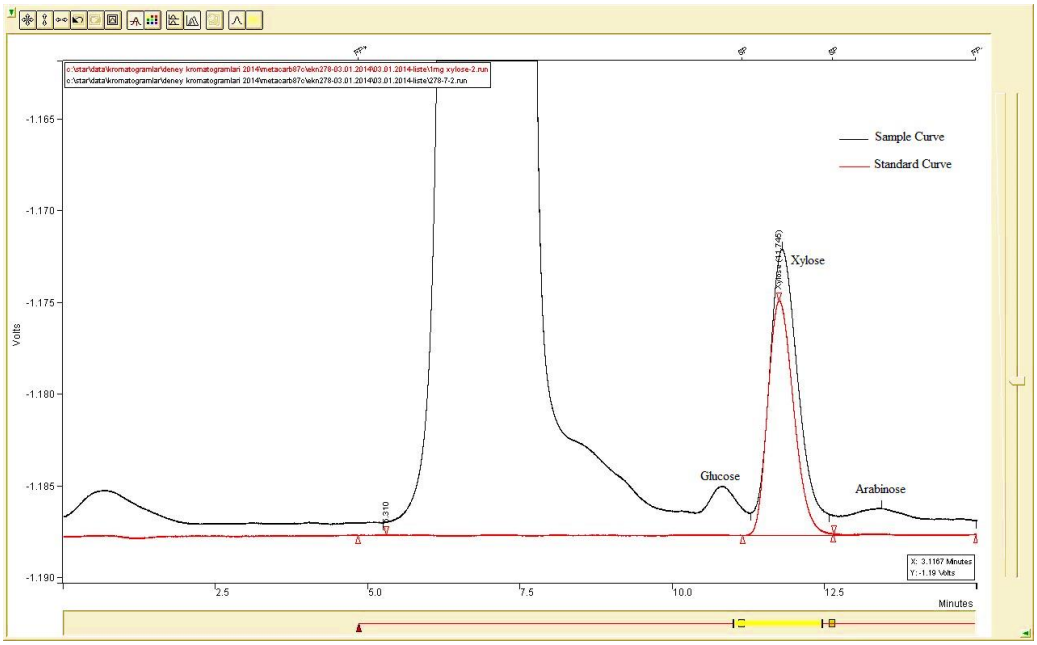


Figure 4.2 A sample of HPLC chromatogram of extract and xylose standard

4.2 Selection of Hemicellulose Extraction Method

Hemicellulose was extracted by several methods. The color and purity of the extracts were of major concern because of their use as a coating material. Direct alkaline method was eliminated due to the brown color of the extract (Yılmaz Celebioglu et al., 2012). Therefore, alkaline hydrogen peroxide extraction methods were tested.

The brown color of the extracts was prevented due to hydrogen peroxide. Three hydrogen peroxide methods were compared in terms of their hemicellulose purity. Purity values were found as 19.30 %, 15.5 % and 25.36 % according to Doner & Hick (1997), Peng et al. (2012) and Sun et al. (2000), respectively. Thus, optimization experiments were carried out according to the method of Sun et al. (2000) which gave the highest hemicellulose purity.

4.3 Optimization of Extraction Conditions

Extraction conditions were optimized by Box-Behnken response surface method for varying temperature (40, 50 and 60 °C), alkaline concentration (10, 15 and 20 %) and extraction time (4, 8 and 12 h). Box-Behnken design with 3 factors and 3 levels for RSM and experimental results are shown in randomized order in Table 4.1.

Table 4.1 Response surface design and experimental results obtained by alkaline extraction of hemicellulose from hazelnut shells

Run Order	Concentration (%)	Temperature (°C)	Time (h)	Hemicellulose Purity (%)
1	15	60	4	56.25 ± 0.006
2	20	50	4	40.95 ± 0.028
3	20	60	8	45.90 ± 0.003
4	15	40	12	34.65 ± 0.003
5	20	50	12	33.31 ± 0.009
6	15	50	8	54.70 ± 0.922
7	10	40	8	46.35 ± 0.003
8	15	60	12	27.45 ± 0.003
9	15	40	4	56.71 ± 0.010
10	10	50	12	38.70 ± 0.003
11	15	50	8	54.68 ± 0.957
12	20	40	8	47.70 ± 0.003
13	10	60	8	57.15 ± 0.003
14	10	50	4	62.10 ± 0.006
15	15	50	8	52.20 ± 0.056

The experimental results given in Table 4.1 was normalized by Box-Cox approximation with $\lambda=2$ and the normalized data, Anderson-Darling $p=0.086$, were used for the statistical analysis. Statistical analysis (Table 4.2) was conducted with 95 % confidence interval and the significant ($P<0.05$) variables were found. Detailed ANOVA calculations is given in the Table B.1. By excluding the insignificant terms ($p>0.05$), the quadratic model for the hemicellulose purity becomes as represented in the Eq. 28 with R-Sq of 92.65% and lack of fit of 0.1. Lastly, by the help of the response optimizer tool of Minitab® 16.1.1, the optimum conditions of the extraction was found as 10 % (w/v) NaOH at 60 °C for 4 h with 0.98 composite desirability and 64.24 % (w/w) hemicellulose purity as the response (Table B.2). However, temperature change was found to be insignificant thus extraction temperature was selected as 40 °C due to energy saving. Actually, this was an expected result because extraction was continued after the H_2O_2 addition and kept for 12 h at 45 °C as indicated in the method. Vena et al. (2013) deduced that the temperature between 40 °C and 90 °C had a minor effect on the alkaline extraction of hemicellulose from woods (Eucalyptus grandis). Another work of eucalyptus wood was concluded that extraction temperatures (70, 84 and 90 °C) had little effect on the hemicellulose extraction while the alkaline concentration and time had greater impact on the extraction efficiency (Longue Júnior et al., 2010). However, alkaline extraction of the annual plants (sugar beet pulp and corn) were significantly affected by extraction temperature (30, 40 and 50 °C) (Yılmaz Celebioglu et al., 2012). Hemicellulose extraction from wheat straw and sweet sorghum bagasse were also dependent on the extraction temperature (Cunningham et al., 1986).

Table 4.2 ANOVA results[a, b] and estimated regression coefficients for the uncoded hemicellulose purity model

Term	Coefficients	P
Regression		0.000
Linear		0.000
Square		0.000
Interaction		0.001
Lack-of-Fit		0.100
Constant	-0.7101	0.000
Block	-4.64E-05	0.993
Concentration	0.0353	0.000
Temperature	0.0324	0.471
Time	0.0175	0.000
Concentration * Concentration	-0.001	0.039
Temperature * Temperature	-2.02E-04	0.089
Time * Time	-0.0039	0.000
Concentration * Temperature	-6.432E-04	0.008
Concentration * Time	0.0022	0.001
Temperature * Time	-2.48E-04	0.373

[a]Result is significant when $P < 0.05$. [b]R^2 =92.65 %, R^2_{pred} =79.62 % and R^2_{adj} =88.78 %.

The quadratic model for the hemicellulose purity was then written as:

$$Y = -0.7101 + 0.0353X_1 + 0.0175X_3 - 0.001X_1^2 - 0.0039X_3^2 - 6.432E - 04X_1X_2 + 0.0022X_1X_3 \quad (27)$$

where Y: the response ((hemicellulose purity, %)^2), X_1: Alkaline concentration (%), X_2: Temperature (°C) and X_3:Time (h).

Analysis of the experimental data through surface plots of hemicellulose extraction factor introduced that increase in temperature of the extraction slightly increased the hemicellulose purity but reduction in the extraction time resulted in more pure extracts (Figure 4.3) at constant alkaline concentration of 15 %. Figure 4.4 shows that hemicellulose purity was increased with decreasing the alkaline concentration and extraction time. Thus, the lower ends of the extraction time (4 h) and alkaline concentration (10 %) led to increase in the hemicellulose purity at a constant temperature of 50 °C (Figure 4.4). Figure 4.5 revealed that the hemicellulose purity was maximized at high temperature (60 °C) and low alkaline concentrations (10 %) when extraction time was 8 h. Therefore, more concentrated alkaline solutions caused a decrease in the purity of hemicellulose extract by degradation of other molecules. This conclusion was supported by the literature (Yılmaz Celebioglu et al., 2012). Extraction of hemicellulose was also reached to an optimum point at 4 h and thus no further extraction was needed.

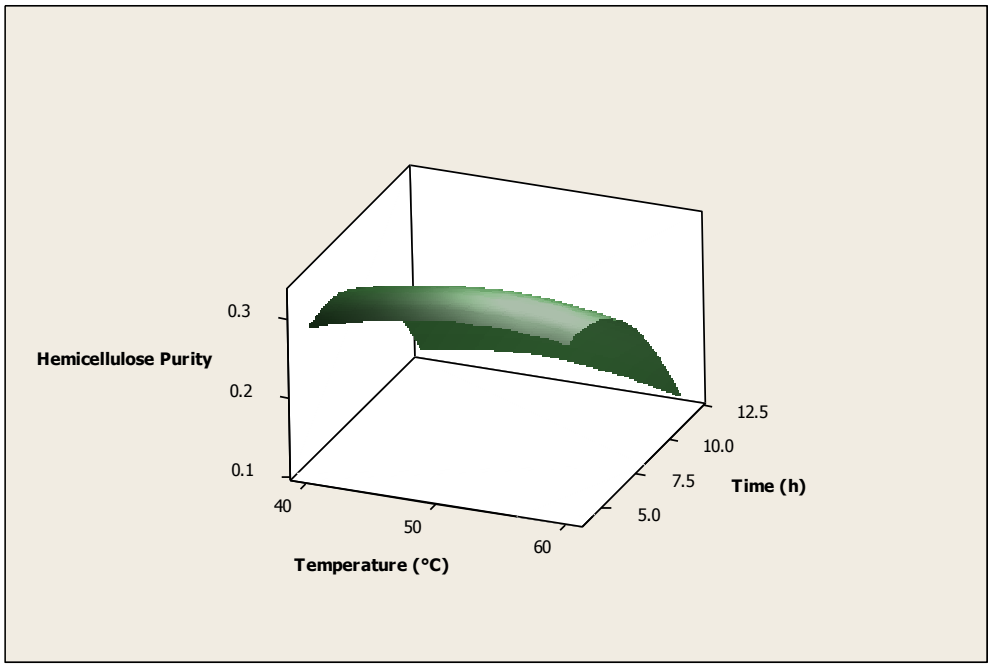


Figure 4.3 Surface plot of Hemicellulose Purity vs Time (h); Temperature (°C) for a fixed concentration of 15 %

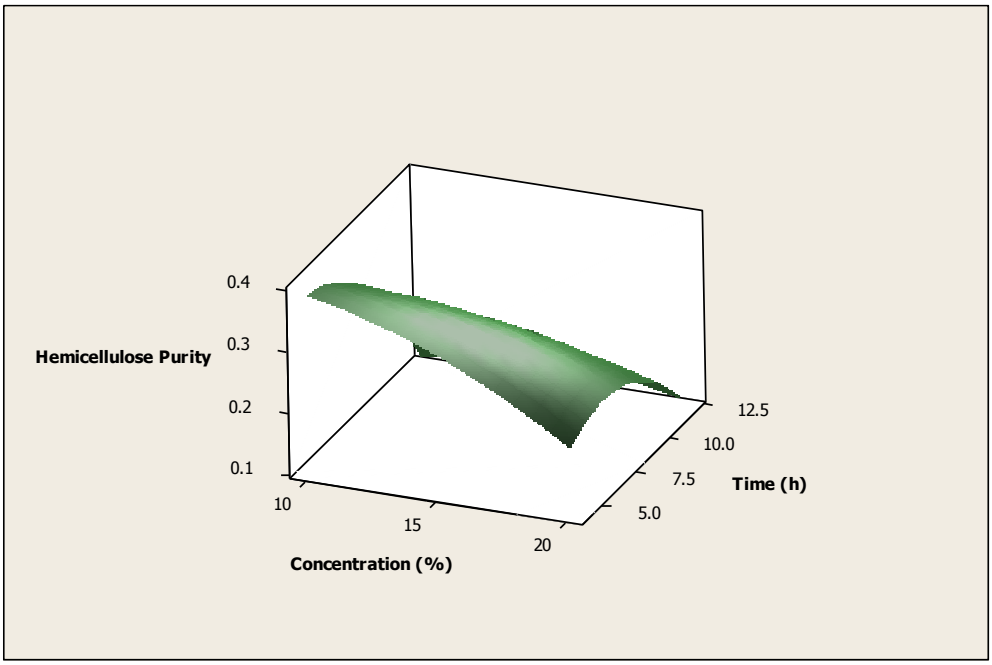


Figure 4.4 Surface plot of Hemicellulose Purity vs Time (h); Concentration (%) for a fixed temperature of 50 °C

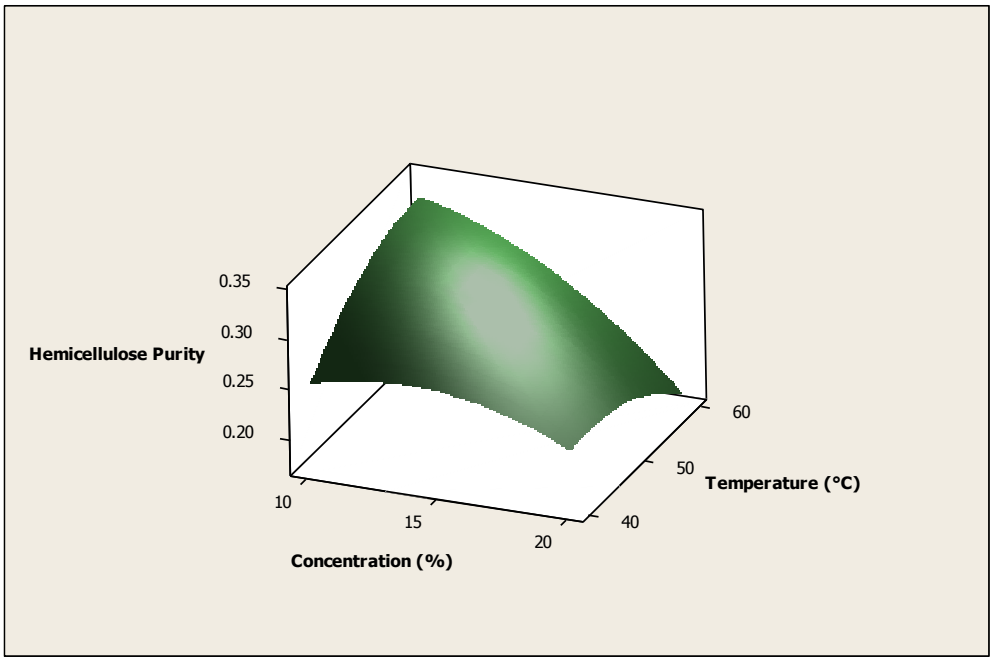


Figure 4.5 Surface plot of Hemicellulose Purity vs Temperature (°C); Concentration (%) for a fixed time of 8 h

Figure 4.6 shows the response of the two factors, time and temperature, at constant alkaline concentration of 15 % by contour plots and it was observed that extraction temperature did not affect hemicellulose purity as the extraction time. Thus, the highest hemicellulose purity was observed at 4 h and 40 °C. Figure 4.7 represents effects of extraction time and alkaline concentration. A parallel pathway was noted for both factors and that was both decrease in time and concentration increased the purity. Hemicellulose purity above 59.16 % is seen in the Figure 4.7 at lower values of time and alkaline concentration, 7 h and 13 %, respectively. Maximum value of the response line was 55.23 % when alkaline concentration and temperature interaction compared at a constant extraction time of 8 h (Figure 4.8). According to the Figure 4.8, the optimal response range is very narrow due to the extraction time of 8 h.

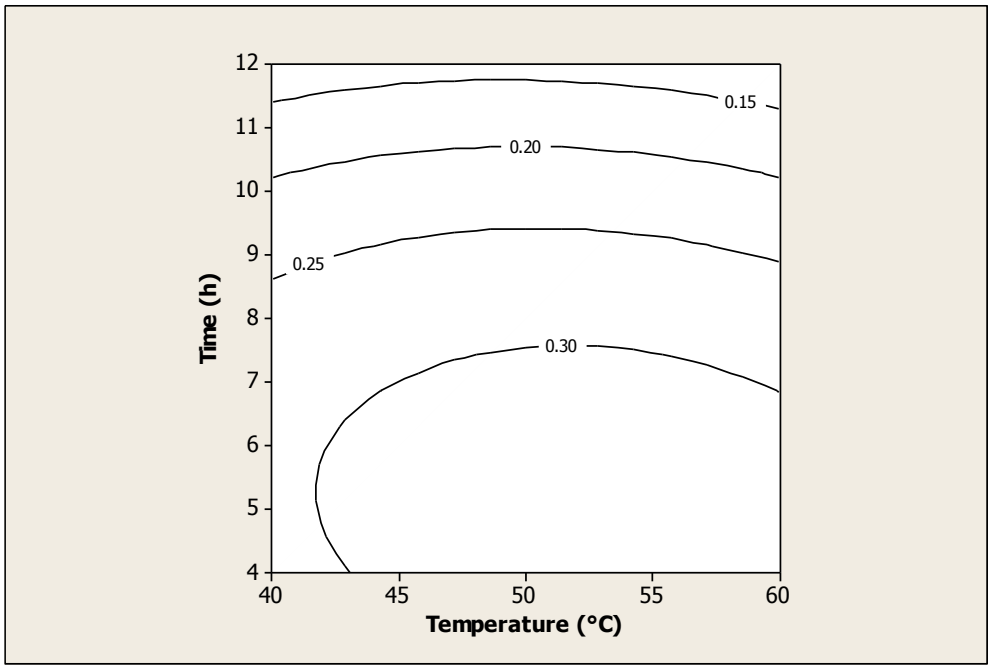


Figure 4.6 Surface response contour plot for effect of time (h) and temperature (°C) on hemicellulose purity at fixed concentration of 15 %

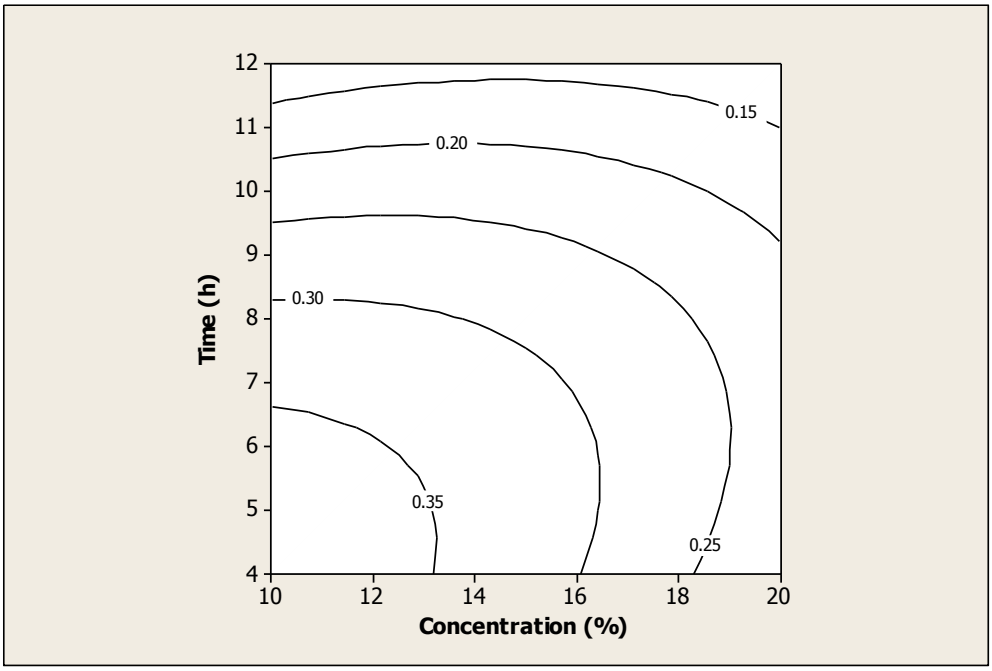


Figure 4.7 Surface response contour plot for effect of time (h) and concentration (%) on hemicellulose purity at fixed temperature of 50 °C

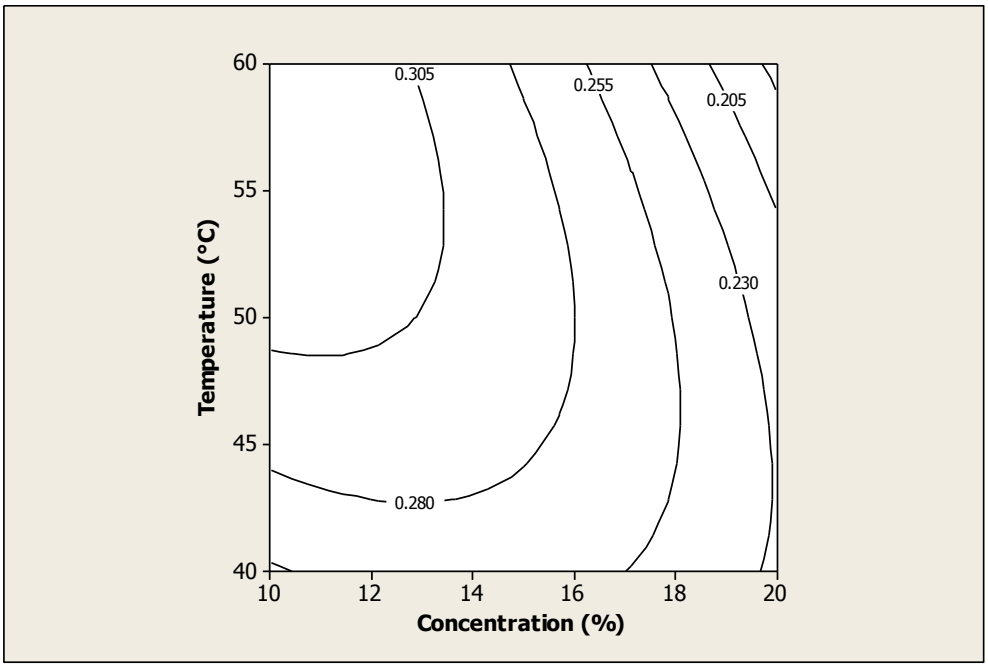


Figure 4.8 Surface response contour plot for effect of temperature (°C) and concentration (%) on hemicellulose purity at fixed time of 8 h

Yields of the hemicellulose extractions were calculated by considering purity values. The yield of the optimum conditions was found as 75.13 %. Yield values of the experimental design (%) are presented in the Table 4.3. The yield of hemicellulose extraction increases insignificantly from 24.58 to 24.86 % when the time increased from 4 to 12 h at 60 °C with 15 % alkaline concentration. However, short extraction time increases the yield at 50 °C with 20 % alkaline extraction. At 10 % NaOH for 8 h extraction, temperature change from 40 to 60 °C does not affect the yield significantly. Moreover, effect of the alkaline concentration can be seen in the Table 4.3 and as the alkaline concentration decreases, the yield increases. For example, two folds increment in alkaline concentration (from 10 % to 20 %) changes yield from 68.94 to 30.29 % at 40 °C and 8 h.

Table 4.3 Hemicellulose extraction yields from the hazelnut shells

Concentration (%)	Temperature (°C)	Time (h)	HC Yield (%)*
15	60	4	24.58 ± 0.79
20	50	4	38.06 ± 0.29
20	60	8	44.47 ± 0.32
15	40	12	28.30 ± 0.30
20	50	12	25.70 ± 0.33
15	50	8	49.83 ± 0.96
10	40	8	68.94 ± 0.01
15	60	12	24.86 ± 0.22
15	40	4	26.98 ± 0.80
10	50	12	37.29 ± 0.27
15	50	8	48.94 ± 0.12
20	40	8	30.29 ± 0.56
10	60	8	73.33 ± 0.12
10	50	4	74.44 ± 0.24
15	50	8	50.69 ± 0.61

*It is the mean of two replicates.

4.4 Color parameters of the dried apricots

Color change in dried apricot was optimized by Box-Behnken RSM design. The three factors with three levels were hemicellulose (HC) concentration (1, 2 and 3 %, w/v), air velocity (0.5, 1 and 1.5 m/s) and air temperature (60, 70 and 80 °C). Total color change, delta b and final moisture content (Final MC) were investigated as responses of apricot drying. Final moisture content was added to the responses because it is an important parameter that affects the color values (Özkan et al., 2003). The experimental design and results are provided in the Table 4.4.

Table 4.4 Response surface experimental design and results of responses

HC Concentration (%)	**Air Velocity** (m/s)	**Air Temperature** (°C)	**Total Color Change**	**Delta b**	**Final MC**
2	1.5	80	24.86	-18.18	52.88
1	1	60	3.58	1.56	66.91
1	1.5	70	26.59	-17.6	66.31
3	1.5	70	22.25	-15.46	66.99
2	1.5	60	5.70	-2.64	74.97
3	1	60	3.29	0.18	63.00
2	1	70	23.04	-16.00	30.91
1	0.5	70	25.00	-13.70	28.68
1	1	80	25.46	-17.84	30.52
2	1	70	22.00	-15.22	30.78
3	0.5	70	25.86	-17.02	24.65
2	0.5	80	38.96	-27.88	14.80
2	0.5	60	20.65	-13.94	44.62
2	1	70	29.80	-22.00	30.88
3	1	80	10.02	-5.36	30.70
2	1.5	80	26.13	-17.52	50.24
1	1	60	3.41	1.44	63.64
1	1.5	70	26.95	-17.78	64.00
3	1.5	70	21.09	-15.3	66.45
2	1.5	60	5.70	-3.94	74.87
3	1	60	3.45	3.22	61.82
2	1	70	24.84	-15.64	30.74
1	0.5	70	27.00	-13.32	27.46
1	1	80	24.55	-17.18	30.96
2	1	70	31.52	-17.06	30.00
3	0.5	70	23.99	-17.26	23.95

Table 4.4 (continued)

2	0.5	80	36.18	-26.21	14.06
2	0.5	60	22.19	-12.94	42.89
2	1	70	24.89	-14.86	30.52
3	1	80	12.83	-5.28	30.20

The final moisture content data was normalized by using linearization approximation of natural logarithm. ANOVA results found for the three responses are given in Tables 4.5-7.

Table 4.5 ANOVA results[a, b] and estimated regression coefficients for the uncoded Final MC model

Term	**Coefficients**	**P**
Regression		0.000
Linear		0.000
Square		0.000
Interaction		0.000
Lack-of-Fit		0.120
Constant	12.3009	0.000
Block	0.0141	0.000
HC Concentration	-1.0079	0.000

Table 4.5 (continued)

Air Velocity	-2.5674	0.000
Air Temperature	-0.2953	0.000
HC Concentration * HC Concentration	0.2062	0.000
Air Velocity * Air Velocity	0.3842	0.000
Air Temperature * Air Temperature	0.0016	0.000
HC Concentration * Air Velocity	0.0820	0.000
HC Concentration * Air Temperature	0.0012	0.047
Air Velocity * Air Temperature	0.0365	0.000

[a]Result is significant when $P < 0.05$. [b]R^2=99.93 %.

All factors (HC concentration, air velocity and air temperature); were found significantly effective ($p<0.05$) on final moisture content (Table 4.5). Figure C.1-C.2 show that air velocity had greater effect on final moisture ratio than air temperature. Model coefficients were proved this consideration. Togrul & Pehlivan (2003) also obtained air flow dominance over air temperature during apricot drying.

Table 4.6 ANOVA results[a, b] and estimated regression coefficients for the uncoded Total Color Change model

Term	Coefficients	P
Regression		0.000
Linear		0.000
Square		0.000
Interaction		0.000
Lack-of-Fit		0.649
Constant	-490.15	0.000
Block	-0.25	0.713
HC Concentration	48.87	0.016
Air Velocity	-58.50	0.000
Air Temperature	13.55	0.000
HC Concentration * HC Concentration	-6.45	0.000
Air Velocity * Air Velocity	21.10	0.001
Air Temperature * Air Temperature	-0.09	0.000
HC Concentration * Air Velocity	-2.02	0.458
HC Concentration * Air Temperature	-0.34	0.021
Air Velocity * Air Temperature	0.18	0.502

[a]Result is significant when $P < 0.05$. [b]R^2=90.68 %.

Total color change (Table 4.6) was significantly affected by HC concentration, air velocity and air temperature ($p<0.05$). Interactions between HC concentration and air velocity; air velocity and air temperature were found insignificant on the total color change.

Table 4.7 ANOVA results[a, b] and estimated regression coefficients for the uncoded Delta b model

Term	Coefficients	P
Regression		0.000
Linear		0.000
Square		0.000
Interaction		0.000
Lack-of-Fit		0.359
Constant	375.77	0.000
Block	-0.38	0.532
HC Concentration	-45.30	0.109
Air Velocity	40.16	0.019
Air Temperature	-9.91	0.000
HC Concentration * HC Concentration	5.68	0.000
Air Velocity * Air Velocity	-19.26	0.001
Air Temperature * Air Temperature	0.06	0.000
HC Concentration * Air Velocity	2.97	0.217
HC Concentration * Air Temperature	0.30	0.018
Air Velocity * Air Temperature	-0.05	0.839

[a]Result is significant when $P < 0.05$. [b]R^2=88.96 %.

As shown in the Table 4.7, different HC concentrations were observed to have insignificant ($p>0.05$) effects on delta b. However, air temperature and velocity affected the delta b value significantly.

According to the surface plots of final moisture content given in Figure C.1.a-C.1.c, as air velocity decreased, the final moisture content also decreased but there was an inverse relationship between temperature and final moisture content. The HC concentration did not sharply change the final moisture content. Moreover, surface plots of total color change (Figure C.2.a-C.2c) revealed that mid-values of the parameters other than air velocity triggered the total color change value which means higher degree of browning. Surface plots of delta b showed that the boundary conditions of air temperature (60 and 80 °C) and HC concentration (1 and 3 %) increased the delta b values but mid-value of air velocity (1 m/s) increased the delta b (Figure C.3.a-C.3.c). Reduction in delta b means bluer colors and the opposite gives yellower colors (Brasil et al., 2012). Contour plots of the responses (final moisture content, total color change and delta b) are also given in Figure C.2, C.4 and C.6 because contour plots better visualize the interactions of the factors and maximal response values.

Table 4.8 Models, Rsqr and lack-of-fit of the responses

Models for responses using data in uncoded units	**R^2**	**Lack-of-Fit**
$\mathbf{Y_1}$= 12.3 - X_1 - 2.57X_2 - 0.29X_3 + 0.21X_1^2 + 0.38X_2^2 + 0.0016X_3^2 + 0.082X_1X_2 + 0.0012 X_1 X_3 + 0.0365X_2 X_3	0.9993	0.120
$\mathbf{Y_2}$=-490 + 48.87X_1 - 58.50X_2 + 13.55X_3 - 6.45X_1^2 + 21.1X_2^2 - 0.09X_3^2 - 0.34X_1 X_3	0.9068	0.649
$\mathbf{Y_3}$=375.77 + 40.16X_2 - 9.91X_3 + 5.68X_1^2 - 19.26X_2^2 + 0.06X_3^2 + 0.03X_1 X_3	0.8896	0.359

Fitted models ($p>0.05$) are given in the Table 4.8 with high R^2 values. A value of $R^2>0.75$ gives a strong correlation (Moffroid, 1993). In the Table 3.8, responses are shown as Y_1: ln (Final MC), Y_2 : Total color change and Y_3 : Delta b. X_1, X_2 and X_3 stand for hemicellulose concentration, air velocity and air temperature, respectively.

Multiple response optimization was investigated by response optimizer tool of the Minitab® 16.1.1 statistical software. Target values of color parameters were selected according to the dried apricots with sulfuring pretreatment. The final moisture content was also determined by considering conventional dried apricots as 25 % (Institution, 2002). The optimum conditions of hemicellulose coating prior to apricot drying were found as 1 m/s of air velocity, 80 ℃ of air temperature and 3 % hemicellulose concentration with a composite desirability of 0.972. Predicted values are presented in the Table 4.9. The predicted final moisture content was 24.9 %.

Table 4.9 Response optimization

Parameters	**Predicted Responses**	**Desirability**	**Experimental Results**
Ln(Final MC)	-1.3896	0.993	-1.347
Total color change	14.757	1.000	15.206
Delta b	-8.699	0.926	-8.335

L*, a* and b* values of apricots before drying are given in Table 4.10 and Table 4.11 after drying at 80 °C with 1 m/s air velocity for various coating conditions. The red, green and blue (RGB) model conversions of the L*, a* and b* values are also presented in the tables (Logical Color Technology, 2013). The RGB outputs were obtained by an observer in daylight 2° (1931).

Table 4.10 L*, a*, b* and RGB values of apricots before drying

Coating Material	L*	a*	b*	RGB
3 % HC	60.96±1.1	6.14±0.3	35.76±0.1	
1.5 % Chitosan	61.94±0.1	11.91±1.0	37.61±1.3	
Uncoated	63.28±0.2	8.59±0.6	38.42±1.2	
0.2 % Sodium Sulfite	59.02±0.5	7.65±0.5	36.18±0.1	

Table 4.11 L*, a*, b* and RGB values of apricots after drying

Coating Material	L*	a*	b*	RGB
3 % HC	43.11±0.6	16.09±0.5	23.5±0.1	
1.5 % Chitosan	42.92±0.6	9.44±0.2	18.8±0.7	
Uncoated	39.18±1.2	9.44±0.3	16.12±1.4	
0.2 % Sodium Sulfite	46.68±0.3	10.98±0.5	28.57±0.1	

By pairwise t-test comparison, hemicellulose coating gave significantly better color values than the uncoated dried apricots ($p<0.05$). However, there was no significant difference between chitosan and uncoated apricots ($p>0.05$). The sulfured apricots provided significantly better color values than the hemicellulose coating and other coatings. These results can also be realized with eyes as the color variations are above the just noticeable difference (JND). Mahy et al. (1994) deduced the JND of ΔE^* as 2.3. For example, ΔE^* values of dried apricots for HC coating were lower than uncoated dried apricots (Figure 4.9). Chroma change (ΔC^*, color intensity) also decreased for these two dried apricots. The lightness change (ΔL^*) was in a decreasing order for uncoated, chitosan, hemicellulose and sodium sulfite coated apricots. The yellowest color of dried apricot was obtained by sulfuring and followed by hemicellulose coating.

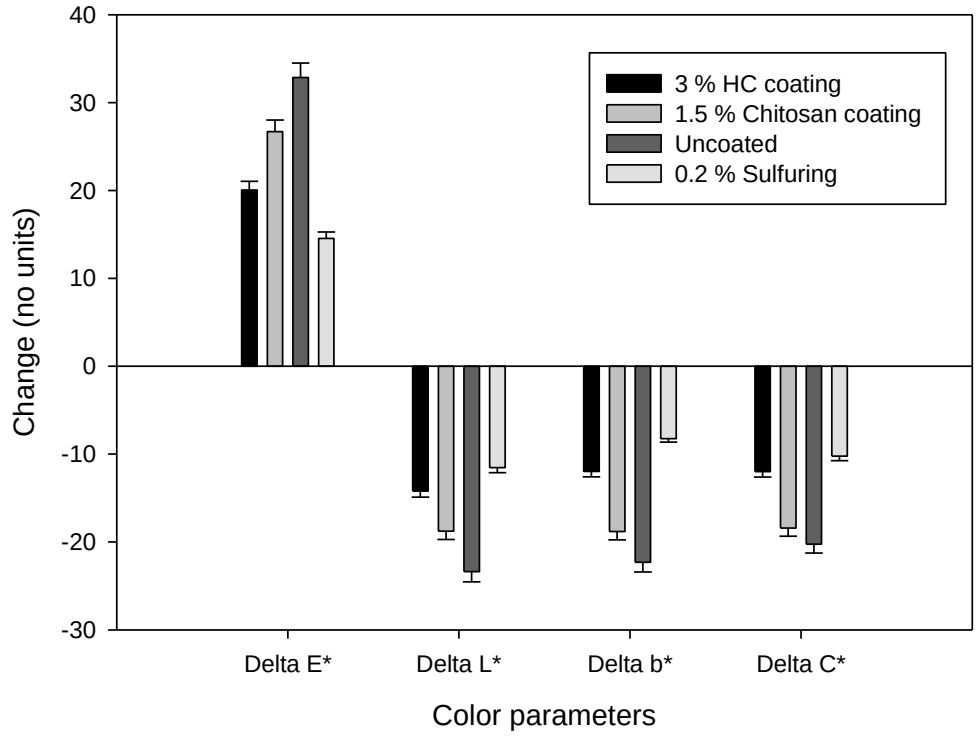


Figure 4.9 Color parameters of drying at 80 °C with 1 m/s air velocity

L*, a* and b* values of sulphureted dried apricots at 80 ℃ and 1 m/s air velocity was reported by Karabulut et al. (2007) as 45.8, 12.5 and 34.2, respectively. These data support L*, a* and b* values in the Table 4.11.

Moreover, browning index and hue angle of the hemicellulose coated apricots are evaluated in Figure 4.10. Hue angle which indicates 0° for red and 90° for yellow and browning index decreased when compared with before drying values. The same pattern of the hue angle and browning index according to temperature change was also reported by Ihns et al. (2011) for apricot drying.

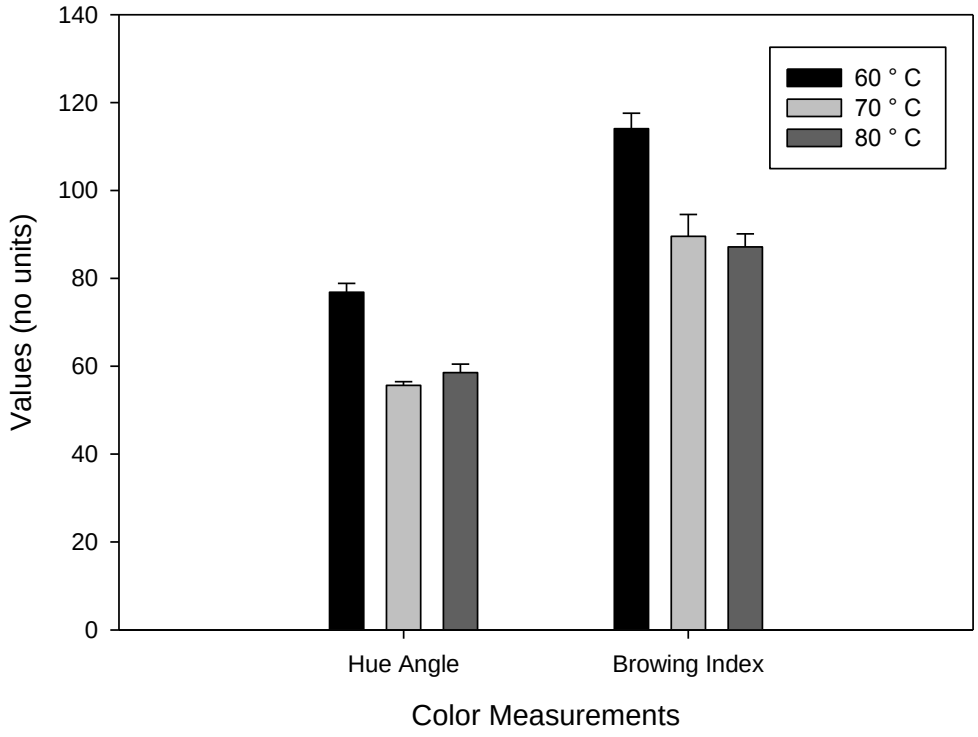


Figure 4.10 Hue angle and browning index for 2 % HC coating with 1 m/s at different air temperatures

Browning reactions of the apricot during drying caused color change. Browning decreased the β-carotene content of dried apricot (Karabulut et al., 2007). Therefore, it is expected that hemicellulose coating decreases the degradation of β-carotene due to delay in the browning reactions.

4.5 Drying of apricots

There was not a constant rate drying period for all coating types during apricot drying (Figure 4.11, 4.12). Two falling rate periods were observed during drying with various temperature and air velocity.

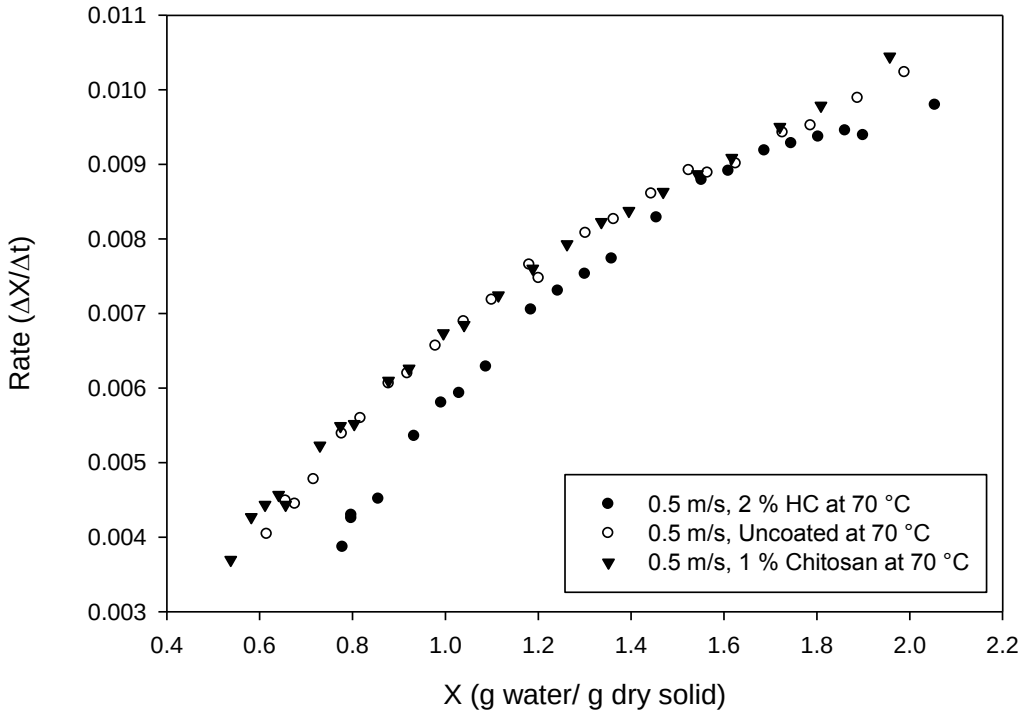


Figure 4.11 Drying rate of different coatings and uncoated apricots at 70 °C and 0.5 m/s.

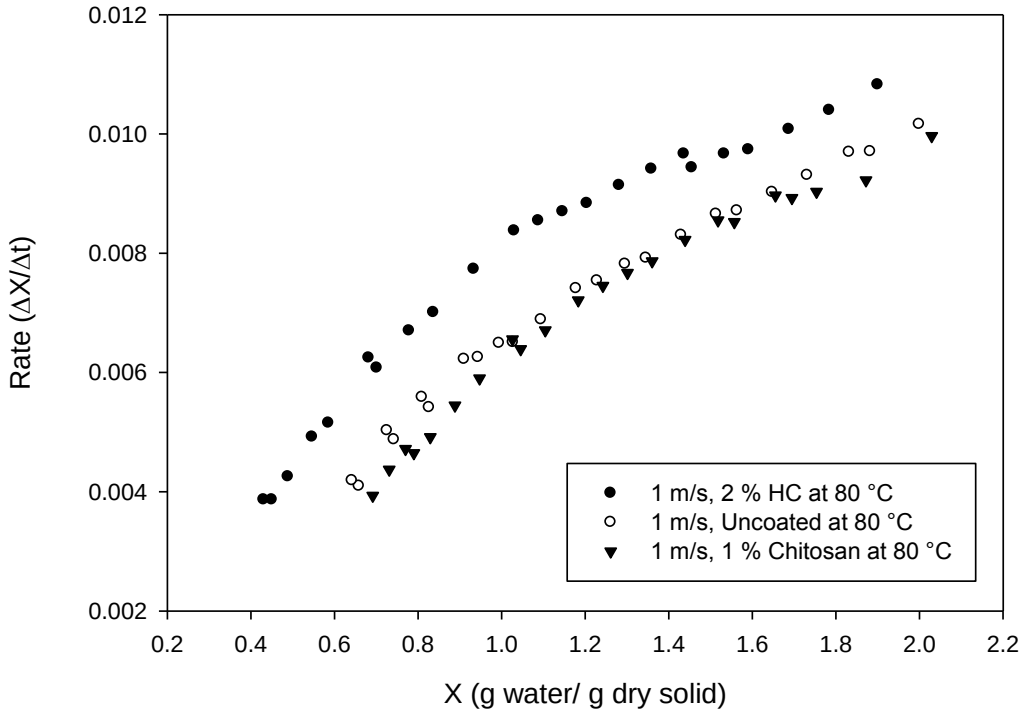


Figure 4.12 Drying rate of different coatings and uncoated apricots at 80 °C and 1 m/s.

4.5.1 Equilibrium moisture content

Equilibrium moisture content was determined by using two models namely, Henderson and Pabis (1961) and Henderson (1974) (Soydan Karabacak et al., 2014). Values of coefficient of determination and SEE ranged between 0.9974 and 0.9838; 0.0488 and 0.0161, respectively for the model of Henderson and Pabis (1961). By Henderson (1974) model, SEE changed from 0.0386 to 0.0174 and R^2 ranged between 0.9973 and 0.9891 (Table D.1). Therefore, Henderson (1974) was selected for further calculations due to lower upper limit of SEE and higher lower

limit of R^2. It was also selected by Ghatrehsamani et al. (2012) for apricot drying. Equilibrium moisture content calculated by two methods are also given in Table D.1.

4.5.2 Mathematical models

4.5.2.1 Drying Curve modeling for 2 % hemicellulose coated apricots

The mathematical models were investigated for the best moisture ratio determination with respect to time. Four models were studied for every temperature of drying. Different models with their constants and statistical results are provided for drying of apricots coated with 2 % HC solution at 60 °C and 1 m/s air velocity in Table 4.12. The best fitted model was selected as the Logarithmic model due to highest R^2 and RMSE values (Figure 4.13).

Table 4.12 Statistical results of different models for 2 % hemicellulose coated apricots at 60 °C

Model	Constants	Rsqr	RMSE
Newton	k=0.003	0.951	0.045149
Page	k=0.0006 n=1.3197	0.9922	0.018048
Henderson and Pabis	k=0.0037 a=1.1178	0.9929	0.011627
Logarithmic	c = 1.89E-11 a = 1.1178 k = 0.0037	0.9931	0.011629

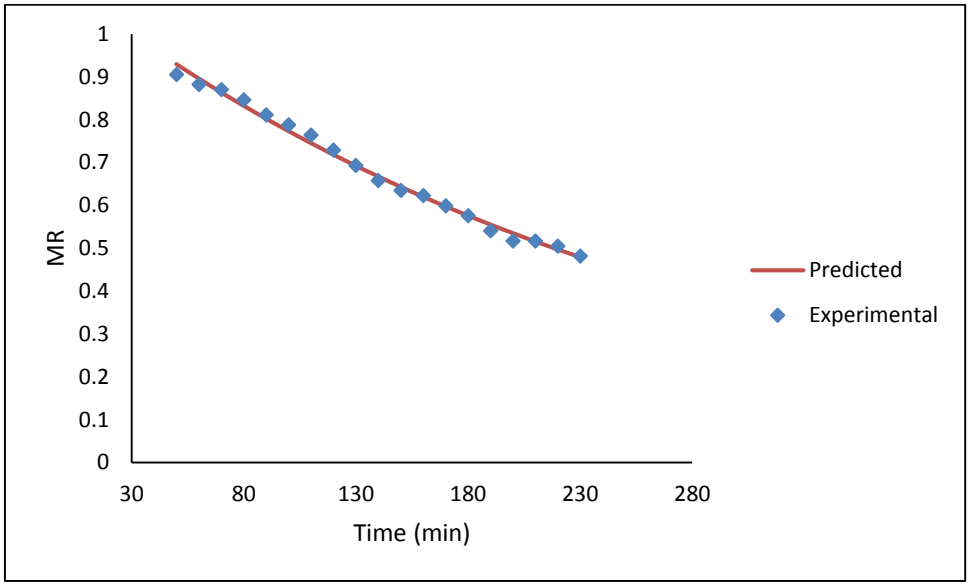


Figure 4.13 Approximation to MR data at 60 °C and 1 m/s with logarithmic model

Henderson and Pabis model was not used for further calculations because its constants and statistical evaluation was very close to the logarithmic model. Logarithmic model was chosen for drying at 70 °C with 2 % hemicellulose coating as the best fitted. Logarithmic model was also selected by several studies (Mirzaee et al., 2010; Toğrul & Pehlivan, 2003).

Table 4.13 Statistical results of different models for 2 % hemicellulose coated apricots at 70 °C with 1 m/s air velocity

Model	Constants	Rsqr	RMSE
Newton	k=0.0049	0.993	0.025720845
Page	k=0.0033 n=1.074	0.996	0.018768304
Logarithmic	c = 6.09E-12 a = 1.0252 k = 0.005	0.996	0.009651005

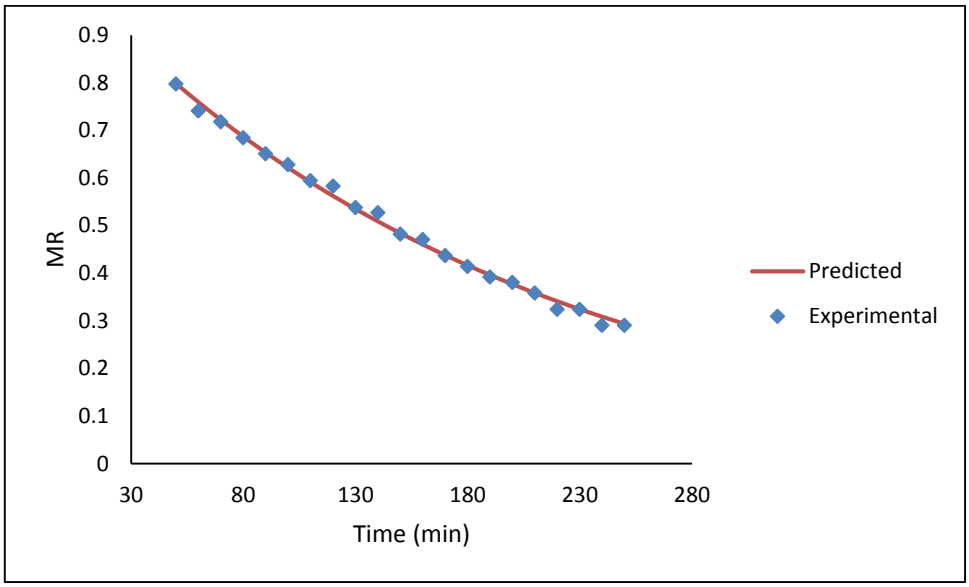


Figure 4.14 Approximation to MR data at 70 °C and 1 m/s with logarithmic model

In the figure above, the correlation of the model with experimental data can be seen for drying of 2 % hemicellulose coated apricot at 70 °C with 1 m/s air velocity (r = 0.998).

According to the R^2 values in Table 4.14, Page model was selected as the best fitted model for the drying at 80 °C with air velocity of 1 m/s (Igual et al., 2012). Moreover, model curve and the experimental data for drying of 2 % hemicellulose coated apricots were represented in the Figure 4.15 with r = 0.997.

Table 4.14 Statistical results of different models for 2 % hemicellulose coated apricots at 80 °C with 1 m/s air velocity

Model	Constants	Rsqr	RMSE
Newton	k=0.0074	0.929	0.1627
Page	k=0.0007 n=1.4542	0.9948	0.0328
Logarithmic	c = 3.93E-12 a = 1.254 k = 0.0085	0.9772	0.0314

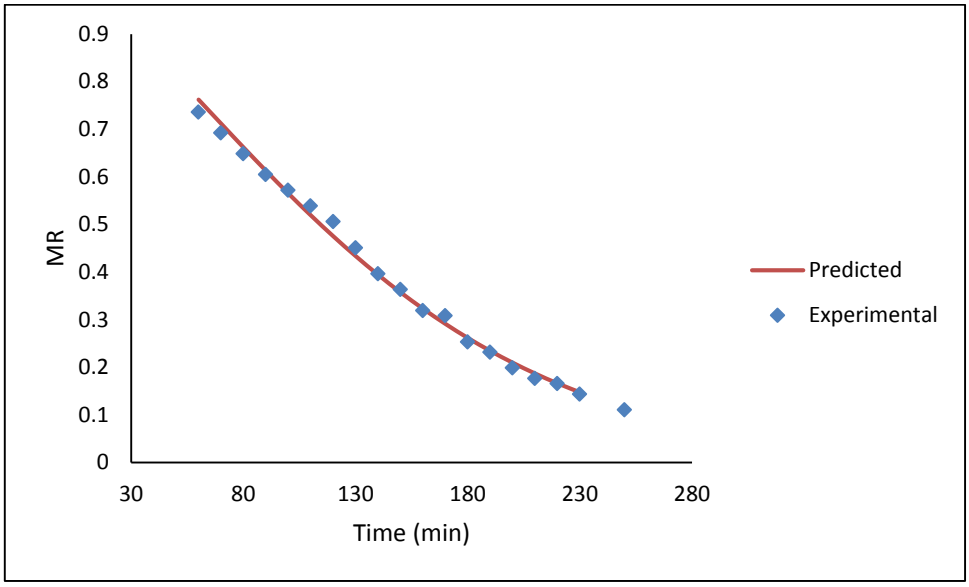


Figure 4.15 Approximation to MR data at 80 °C and 1 m/s with Page model

As drying temperature increased the drying constant (k) which also known as drying rate constant (Chen et al., 1997) also increased from 0.0037 to 0.0085 min^{-1} as seen in Figure 4.16. According to Togrul & Pehlivan (2003), change in temperature from 60 to 85 °C resulted in an increase of k value from 0.0029 to 0.0035 (min^{-1}) at air velocity of 0.5 m/s.

Logarithmic model coefficients and statistical analyses of different coating materials at various temperature and air velocities are presented in the Table D.2.

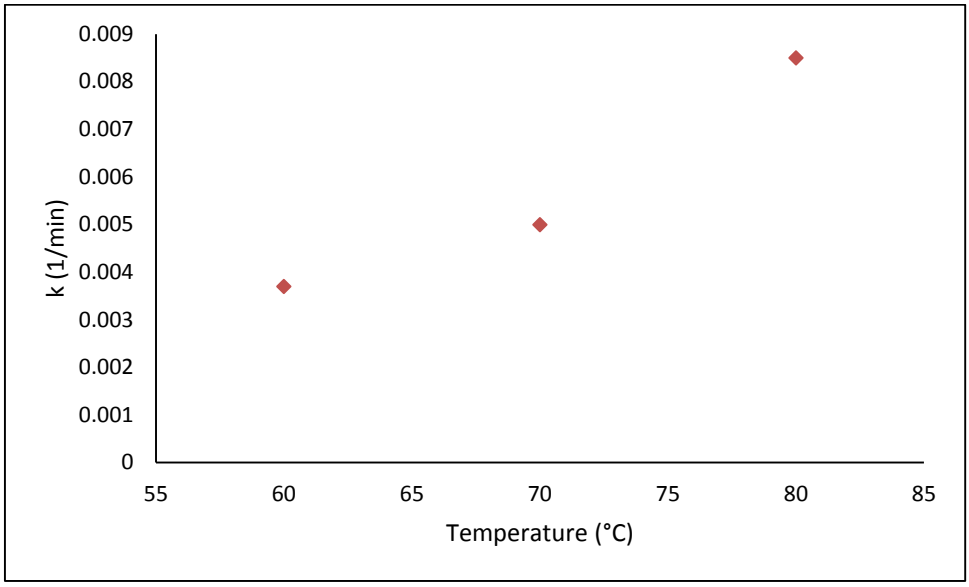


Figure 4.16 Drying constant at different temperatures for drying 2 % hemicellulose coated apricots with air velocity of 1 m/s

Drying constant increased when air velocity decreased at 70 °C (Table D.3). Reduction in air velocity from 1.5 to 0.5 m/s increased the constant ‘’k’’ value from 0.0051 to 0.0071 (min^{-1}). The same result was also obtained in the literature for apricot drying in the study of Togrul & Pehlivan (2003).

4.5.2.2 Effective diffusion coefficients, drying time and activation energy

Effective diffusion coefficient was calculated by equation 10. For different air temperatures and air velocities, the effective diffusion coefficients are given in Table D.3.

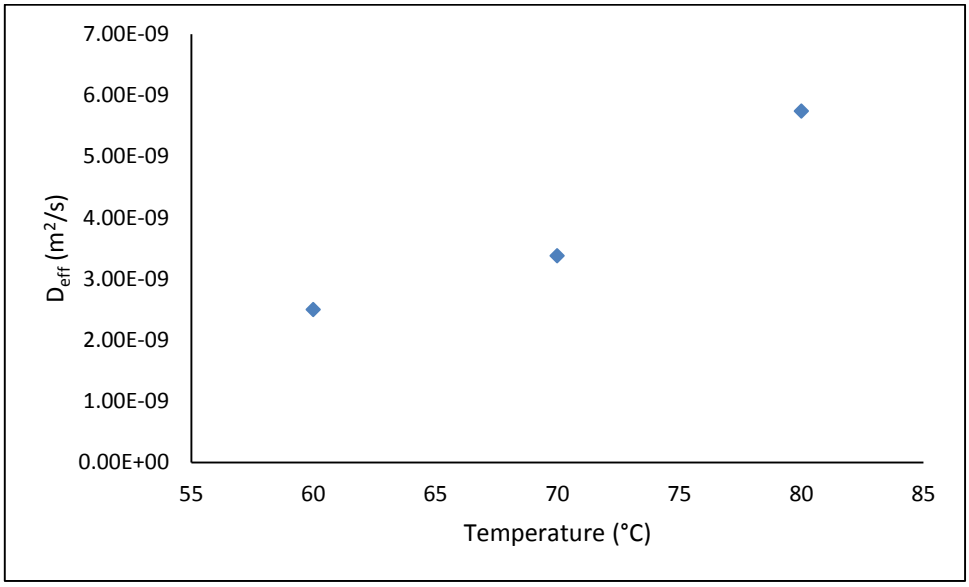


Figure 4.17 Effective diffusion coefficient at different temperatures for drying 2 % hemicellulose coated apricots with air velocity of 1 m/s

Figure 4.17 shows that effective diffusion coefficients increased as the temperature increased and the values in the table were also similar with the uncoated apricot drying studied by Mirzaee et al. (2009) and Togrul & Pehlivan (2003). Fourier number assumption was corrected for the drying times higher than 163 min at 60 °C and 33.3 min at 80 °C with 1 m/s air velocity.

Drying time predictions for 2 % hemicellulose coated apricots were calculated as 19.9 h at 60 °C, 14.8 h at 70 °C and 8.7 h at 80 °C by using effective diffusion coefficients at air velocity of 1 m/s. Ihns et al. (2011) estimated the drying times as 16.5 h at 60 °C, 7.45 h at 80 °C and 4.58 at 100 °C for Moorpark apricot drying with 0.2 m/s air velocity. The reduction in the drying times is due to low air velocity.

Activation energy was also computed by the slope of linear regression of ln (D_{eff}) and $1/T_a$ given in the Table D.3. Activation energy was found as 40.52 kJ/mol with R^2 of 0.967 and in good agreement with reported values. Activation energy of

apricot during drying was determined as 33.78 kJ/mol for the temperature range between 40 and 80 °C and air velocity of 1 m/s (Mirzaee et al., 2009). Bon et al. (2007) reported activation energies of apricots during drying between 32.8 and 46.3 kJ/mol for temperature change from 50 to 90 °C. According to another study, energy of activation figured out between 25 and 40 kJ/mol for apricots during drying (Abdelhaq & Labuza, 1987).

4.5.3 Coating effects on apricot drying and rehydration

Moisture ratio of apricot drying with various treatments are given in Figure 4.18. Hemicellulose coating increased the drying rate more than the other pretreatments. However, moisture ratio pattern of hemicellulose coating was not different from the others.

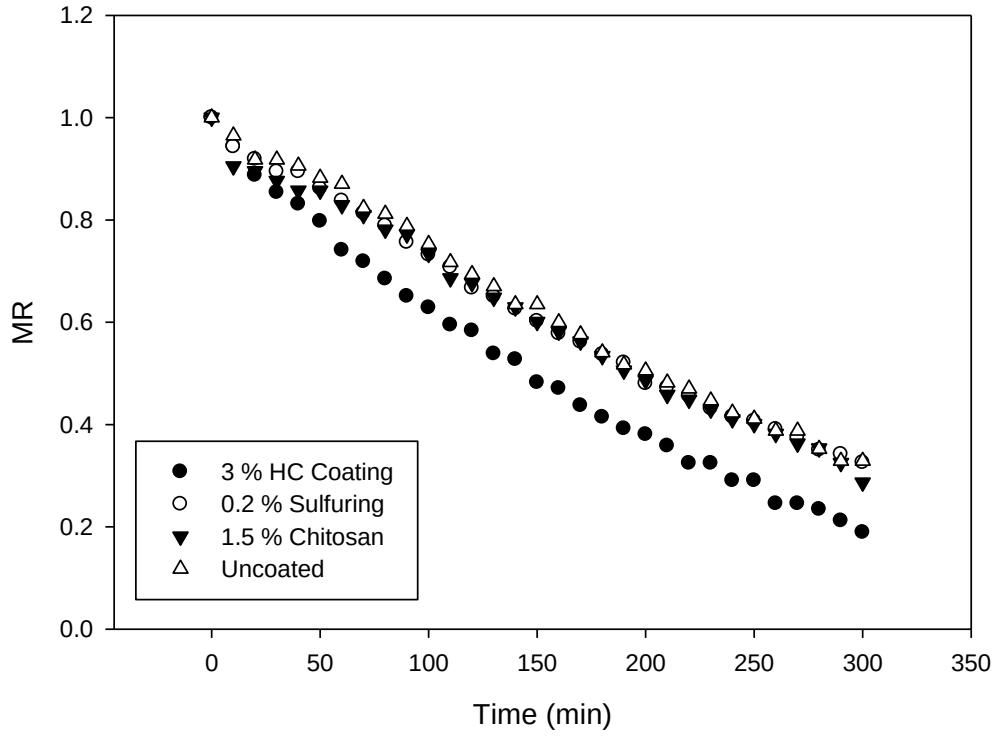


Figure 4.18 Moisture ratio of different coating during drying apricot at 70 °C with air velocity of 1 m/s

Rehydration rates of different coating materials applied to apricot are represented in Figure 4.19. The difference between the curves was insignificant to eliminate any coating material. However, the fastest rehydration was observed in uncoated apricots.

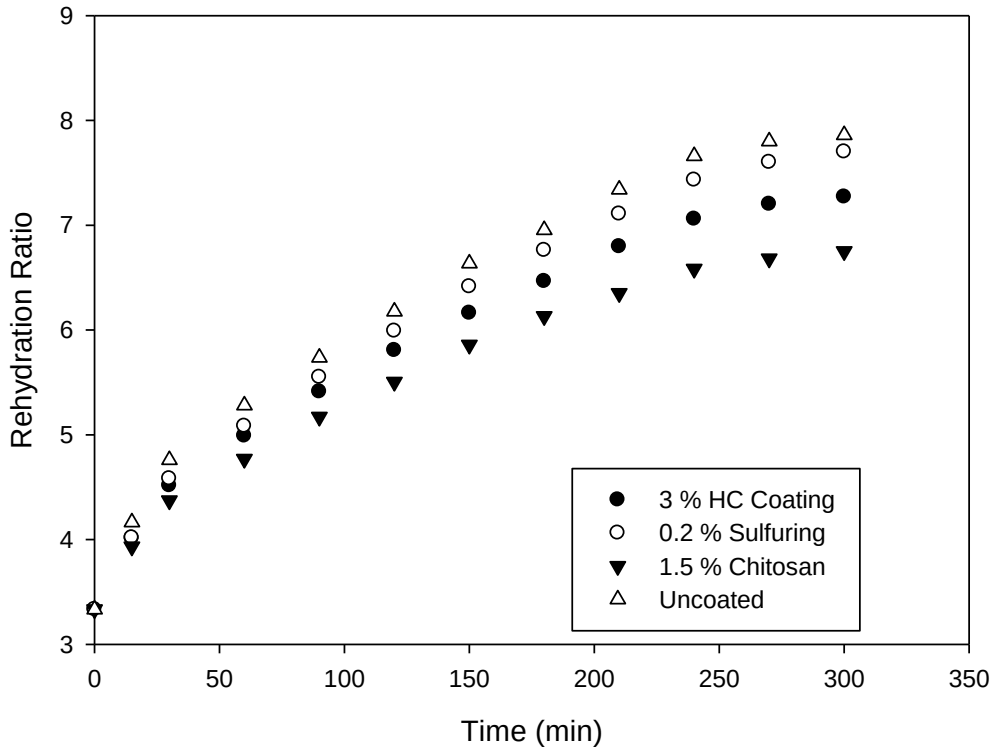


Figure 4.19 Rehydration of dried apricot at 80 °C and 1m/s

Rehydration rates were calculated by the equation follows (Jiao et al., 2014):

$$RR = RR_{eq}\,(1 - e^{-k_r t}) \qquad (29)$$

where RR: rehydration ratio, RR_{eq}: equilibrium rehydration ratio and k_r: rehydration rate (min^{-1}). The regression results are given in Table 4.15. The rehydration rates changed from 0.010 to 0.012 (min^{-1}).

Table 4.15 Rehydration rates of dried apricots at 80 °C and 1 m/s

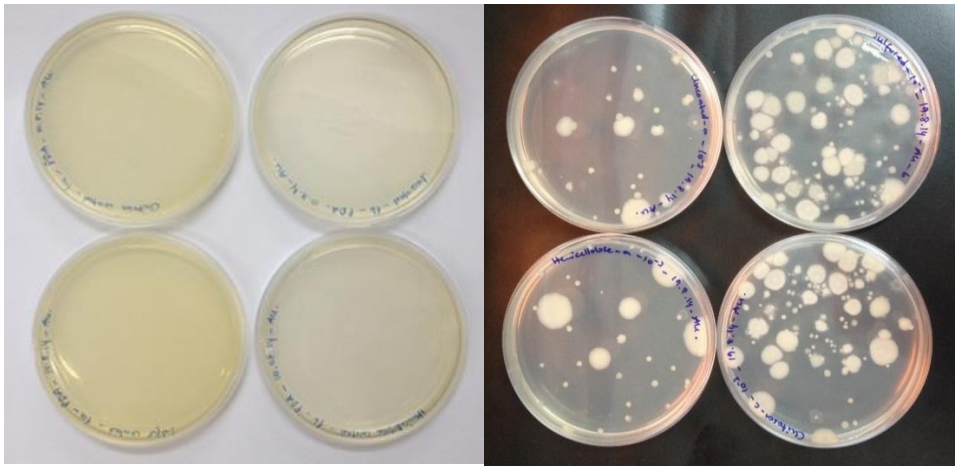
Coating type of dried apricot	Rehydration Rate (min^{-1})	Rsqr	SEE
3 % HC Coating	0.011 ± 0.0003^{a}	0.9923	0.0334
0.2 % Sulfuring	0.010 ± 0.0003^{b}	0.9942	0.0338
1.5 % Chitosan	0.012 ± 0.0003^{c}	0.9932	0.0244
Uncoated	$0.010 \pm 0.0004^{a, b}$	0.9914	0.0368

Rehydration rates were compared by Tukey method (Table D.4) of Minitab 16.1.1 and it was observed that there was no significant difference between the hemicellulose coated and uncoated dried apricots. Similarly, sulfuring did not affect the rehydration rate significantly in uncoated dried apricots. However, chitosan coating increased slightly the rehydration rate of dried apricots and this increase was found significant compared to uncoated apricots.

4.6 Microbial counts

No growth of yeast and mold was observed in the inoculated plates of PDA for different coating types (Figure 4.20a). However, number of total mesophilic bacteria (Figure 4.20b) detected was 3.3×10^2 cfu/g which is below the hazard limit ($<10^5$ cfu/g) (Livestock, 2011). Growth of mesophilic bacteria can be due to the water entrapped in the apricots during drying which provides required water activity

(> 0.9) for growth (Sperber & Doyle, 2010). The number of total mesophilic aerobic bacteria was also counted as 1.8 x 10^2 by Türkyılmaz et al. (2012) for dried apricots.



(a) (b)

Figure 4.20 Microbial growth after 15 days storage at room temperature: a) Total yeast and mold b) Total mesophilic bacteria

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

This study was composed of two main parts, namely, hemicellulose extraction and apricot drying with hemicellulose coating.

Firstly, hazelnut shells were investigated as the source of hemicellulose due to economic and environmental benefits. Alkaline hydrogen peroxide extraction was selected as the best extraction method. Optimum extraction conditions were found as 10 % NaOH at 40 °C for 4 h with 0.98 composite desirability (d) and highest hemicellulose purity (response of the extraction) as 64.24 % (w/w) by Box-Behnken response surface methodology.

Secondly, apricots were dried in a tray dryer with various drying conditions and coating materials. During apricot drying, color parameters (ΔE* and Δb*) and moisture content were investigated. Optimum conditions giving the best color and final moisture content combination were found as 1 m/s of air velocity, 80 °C of air temperature, and 3 % (w/v) hemicellulose coating prior to apricot drying (d=0.972). Responses predicted by the models were 14.8 of ΔE*, -8.7 of Δb* and 24.9 % final moisture content. Comparison of dried apricots with respect to color parameters revealed that hemicellulose coated apricots were significantly better than uncoated and chitosan coated apricots. However, sulfuring gave significantly better color values than hemicellulose coating and other coatings at tested conditions.

Moreover, apricot drying kinetics was evaluated by four models: Newton, Page, Henderson and Pabis and Logarithmic model. Logarithmic model described best the drying model for 2 % hemicellulose coated apricots at 60 °C (0.9931) and 70 °C (0.996). The best approximation to 2 % hemicellulose coated apricots drying at 80 °C was given with Page model (0.9948).

Effective diffusion coefficient values ranged at 2.499-5.742 x 10^{-9} in an increasing order with increasing air temperature. The temperature dependency of effective diffusion coefficient was described by Arrhenius type equation and activation energy of apricot during drying was calculated as 40.52 kJ/mol. Rehydration rate of hemicellulose coated dried apricots was higher than uncoated dried apricots, 0.011 and 0.010 (min^{-1}) , respectively.

To conclude, hazelnut shell is an effective feedstock for the hemicellulose extraction and hemicellulose coating has the required properties to be used prior to apricot drying and to enhance the dried apricot quality.

For future studies, changes in nutritive value of hemicellulose coated apricots during drying and effects of hemicellulose coating during storage should be conducted. Hemicellulose coating can also be investigated for other fruits and vegetables.

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APPENDIX A

CHEMICALS AND SUPPLIER INFORMATION

Table A.1 Chemicals and supplier information

Chemical	Supplier
Sodium hydroxide	Merck
Hydrochloric acid	Merck
Hydrogen peroxide	Merck
Sodium sulfite	Merck
Ethanol	Merck
Chitosan	Sigma Aldrich
Toluene	Merck
Barium hydroxide octahydrate	Merck
Sulfuric acid	Merck
Sodium chlorite	Merck
Tween 80	Merck
Xylose (HPLC grade)	Merck
Arabinose (HPLC grade)	Merck
Glucose (HPLC grade)	Merck
Mannose (HPLC grade)	Merck
Acetic acid	Merck

APPENDIX B

HEMICELLULOSE PURITY OPTIMIZATION

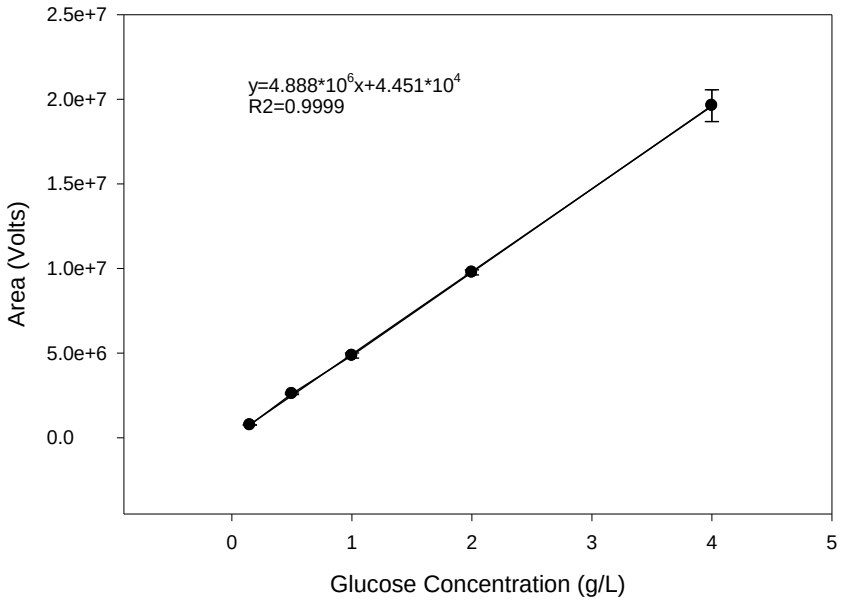

Figure B.1 Standard curve for glucose determination

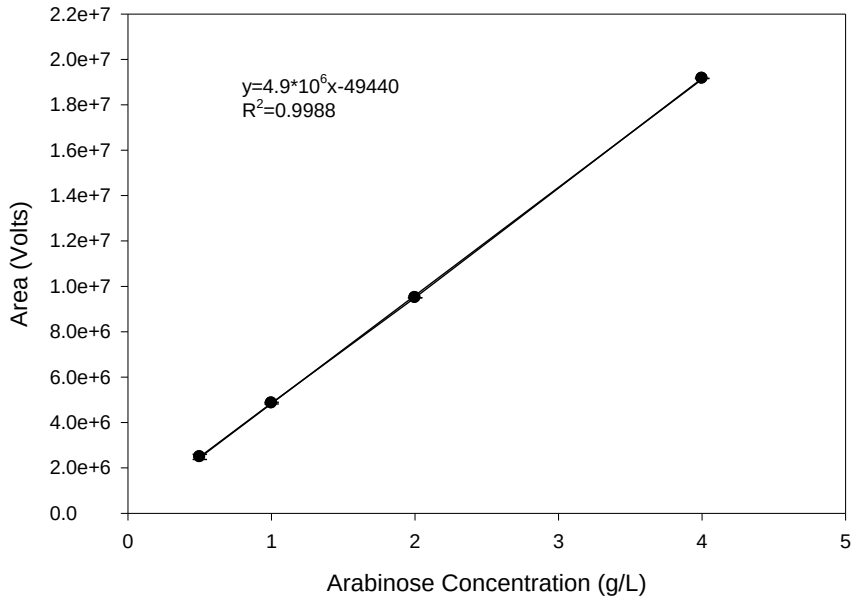

Figure B.2 Standard curve for arabinose determination

Table B.1 ANOVA table of hemicellulose purity

The analysis was done using coded units.

Estimated Regression Coefficients for Hemicellulose Purity

Term	Coef	SE Coef	T	P
Constant	0.290254	0.012534	23.158	0.000
Block	-0.000046	0.005605	-0.008	0.993
Concentration (%)	-0.045010	0.007675	-5.864	0.000
Temperature (°C)	0.005639	0.007675	0.735	0.471
Time (h)	-0.091908	0.007675	-11.975	0.000
Concentration (%)*Concentration (%)	-0.025076	0.011298	-2.220	0.039
Temperature (°C)*Temperature (°C)	-0.020242	0.011298	-1.792	0.089
Time (h)*Time (h)	-0.061646	0.011298	-5.457	0.000
Concentration (%)*Temperature (°C)	-0.032158	0.010854	-2.963	0.008
Concentration (%)*Time (h)	0.044784	0.010854	4.126	0.001
Temperature (°C)*Time (h)	-0.009902	0.010854	-0.912	0.373

S = 0.0307009 PRESS = 0.0496635
R-Sq = 92.65% R-Sq(pred) = 79.62% R-Sq(adj) = 88.78%

Analysis of Variance for Hemicellulose Purity

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Blocks	1	0.000000	0.000000	0.000000	0.00	0.993
Regression	9	0.225788	0.225788	0.025088	26.62	0.000
Linear	3	0.168078	0.168078	0.056026	59.44	0.000
Concentration (%)	1	0.032414	0.032414	0.032414	34.39	0.000
Temperature (°C)	1	0.000509	0.000509	0.000509	0.54	0.471
Time (h)	1	0.135154	0.135154	0.135154	143.39	0.000
Square	3	0.032608	0.032608	0.010869	11.53	0.000
Concentration (%)*Concentration (%)	1	0.002760	0.004644	0.004644	4.93	0.039
Temperature (°C)*Temperature (°C)	1	0.001785	0.003026	0.003026	3.21	0.089
Time (h)*Time (h)	1	0.028063	0.028063	0.028063	29.77	0.000
Interaction	3	0.025102	0.025102	0.008367	8.88	0.001
Concentration (%)*Temperature (°C)	1	0.008273	0.008273	0.008273	8.78	0.008
Concentration (%)*Time (h)	1	0.016045	0.016045	0.016045	17.02	0.001
Temperature (°C)*Time (h)	1	0.000784	0.000784	0.000784	0.83	0.373
Residual Error	19	0.017908	0.017908	0.000943		
Lack-of-Fit	15	0.016755	0.016755	0.001117	3.87	0.100
Pure Error	4	0.001154	0.001154	0.000288		
Total	29	0.243697				

Estimated Regression Coefficients for Hemicellulose Purity using data in uncoded units

Term	Coef
Constant	-0.710100
Block	-4.63684E-05
Concentration (%)	0.0353342
Temperature (°C)	0.0324336
Time (h)	0.0174582
Concentration (%)*Concentration (%)	-0.00100304
Temperature (°C)*Temperature (°C)	-2.02419E-04
Time (h)*Time (h)	-0.00385289
Concentration (%)*Temperature (°C)	-6.43168E-04
Concentration (%)*Time (h)	0.00223920
Temperature (°C)*Time (h)	-2.47541E-04

Table B.2 Response optimization of hemicellulose purity

```
Parameters

              Goal     Lower  Target   Upper  Weight  Import
Hemicellulos  Maximum   0.07  0.4225  0.4225       1       1


Starting Point

Concentratio   =   10
Temperature    =   40
Time (h)       =    4


Local Solution

Concentratio   =   10
Temperature    =   60
Time (h)       =    4


Predicted Responses

Hemicellulos   =   0.412691  ,   desirability =   0.972173


Composite Desirability = 0.972173


Global Solution

Concentratio   =   10
Temperature    =   60
Time (h)       =    4


Predicted Responses

Hemicellulos   =   0.412691  ,   desirability =   0.972173


Composite Desirability = 0.972173
```

APPENDIX C

OPTIMIZATION PLOTS OF DRYING CONDITIONS

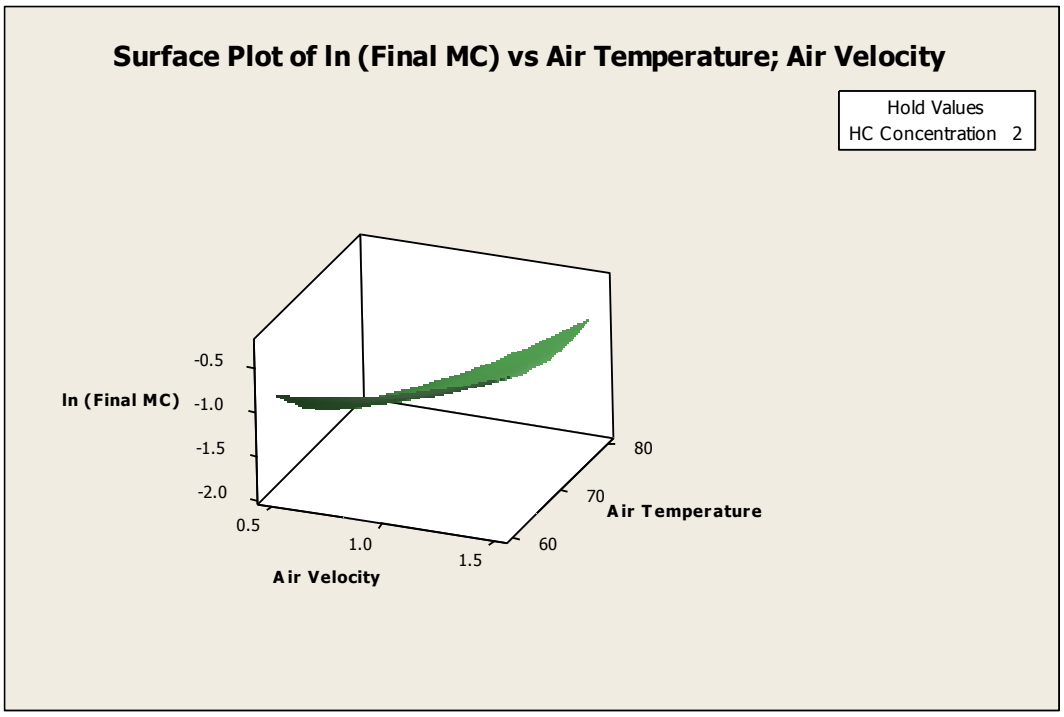

Figure C.1.a Surface plot of final moisture content vs. air temperature; air velocity

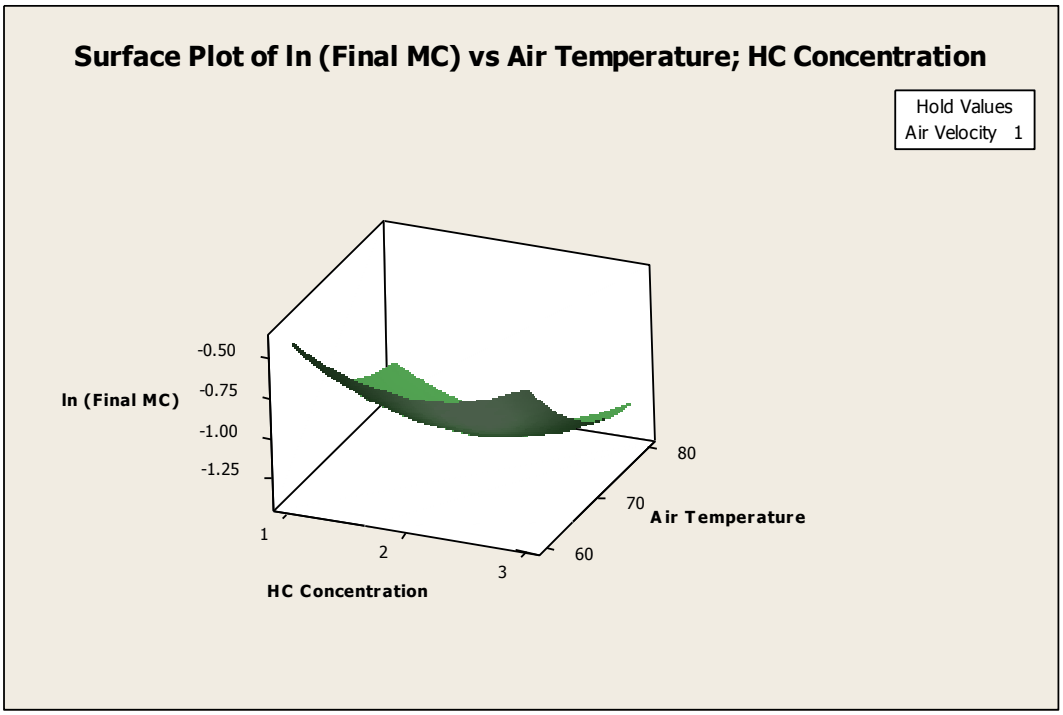

Figure C.1.b Surface plots of final moisture content vs. air temperature; HC concentration

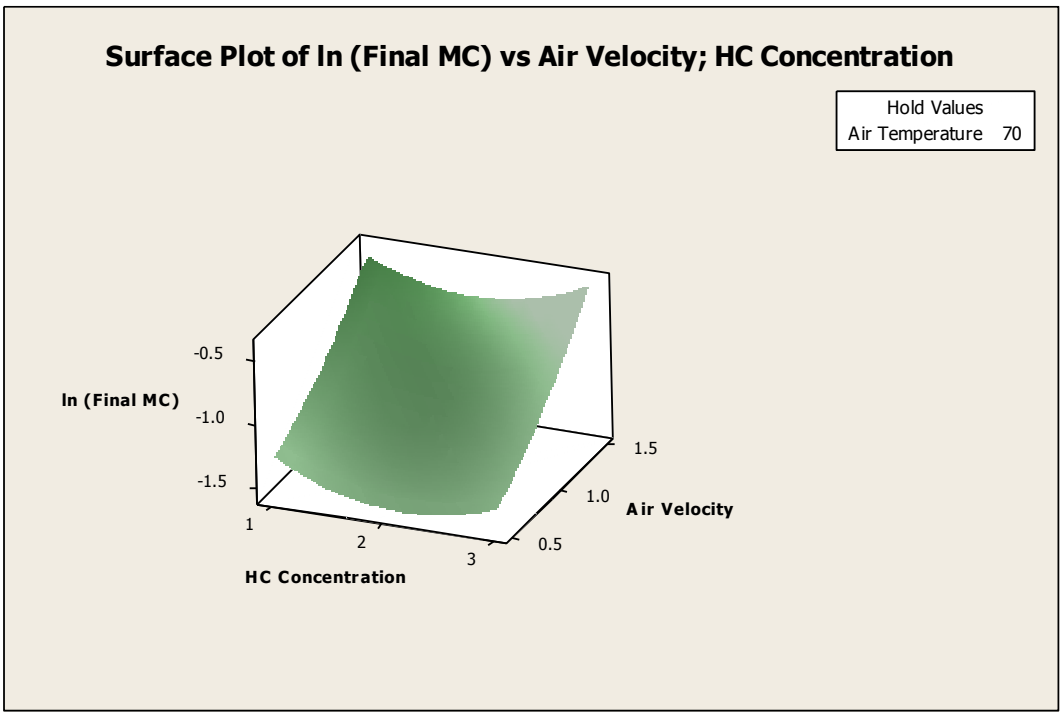

Figure C.1.c Surface plots of final moisture content vs. air velocity; HC concentration

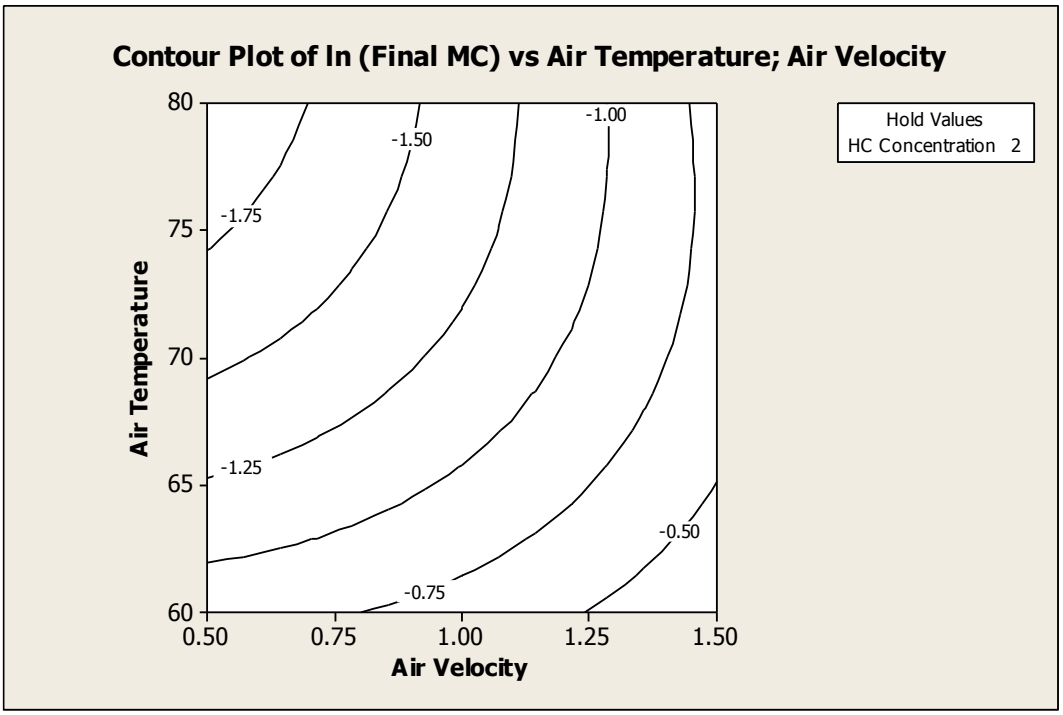

Figure C.2.a Contour plot of final moisture content vs. air temperature; air velocity

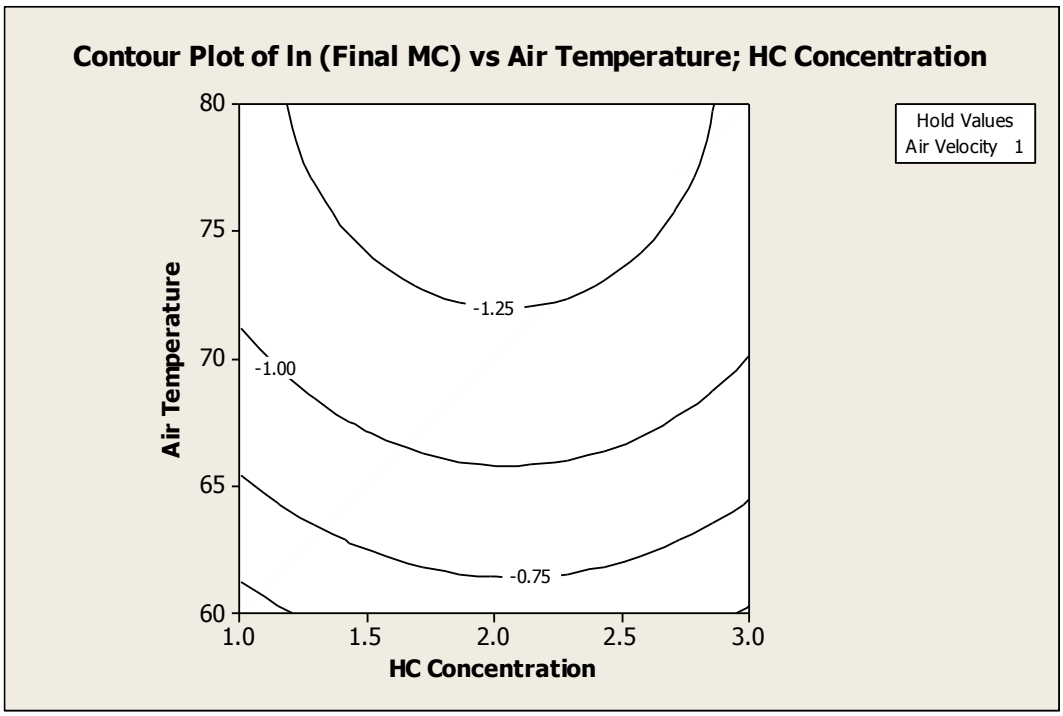

Figure C.2.b Contour plot of final moisture content vs. air temperature; HC concentration

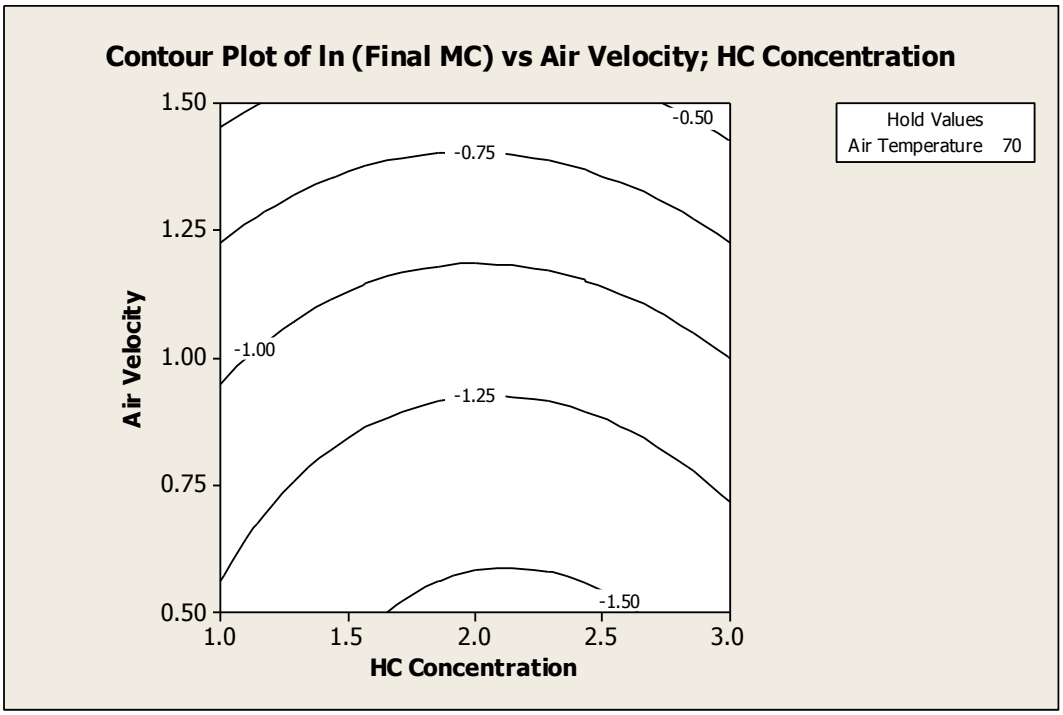

Figure C.2.c Contour plot of final moisture content vs. air velocity; HC concentration

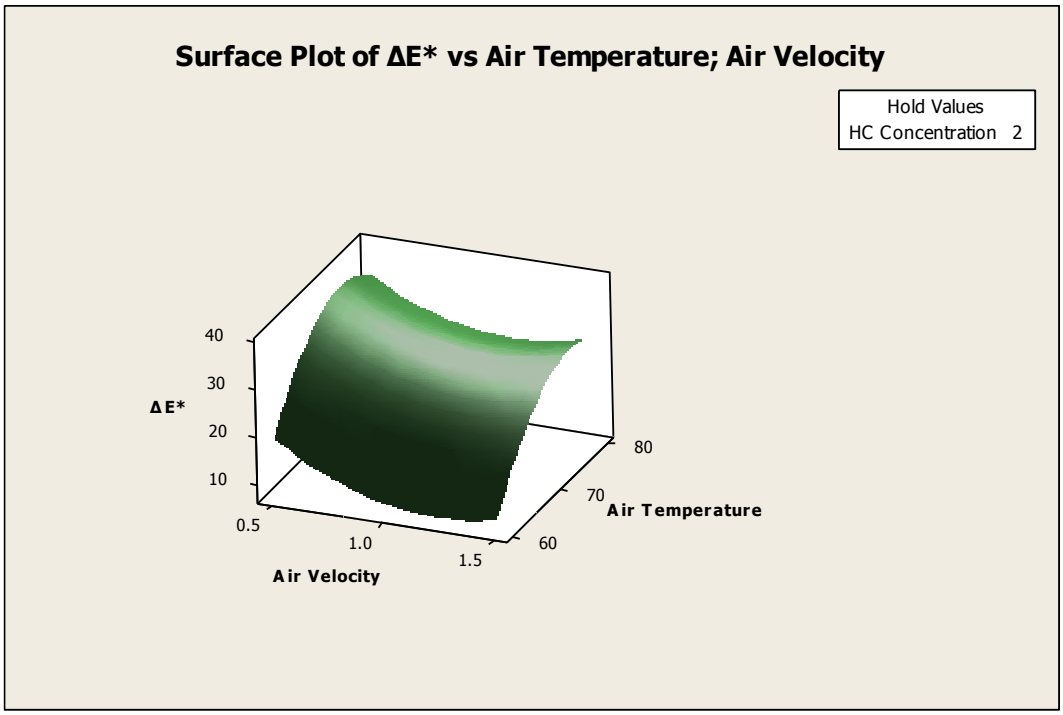

Figure C.3.a Surface plots of total color change (ΔE*) vs. air temperature; air velocity

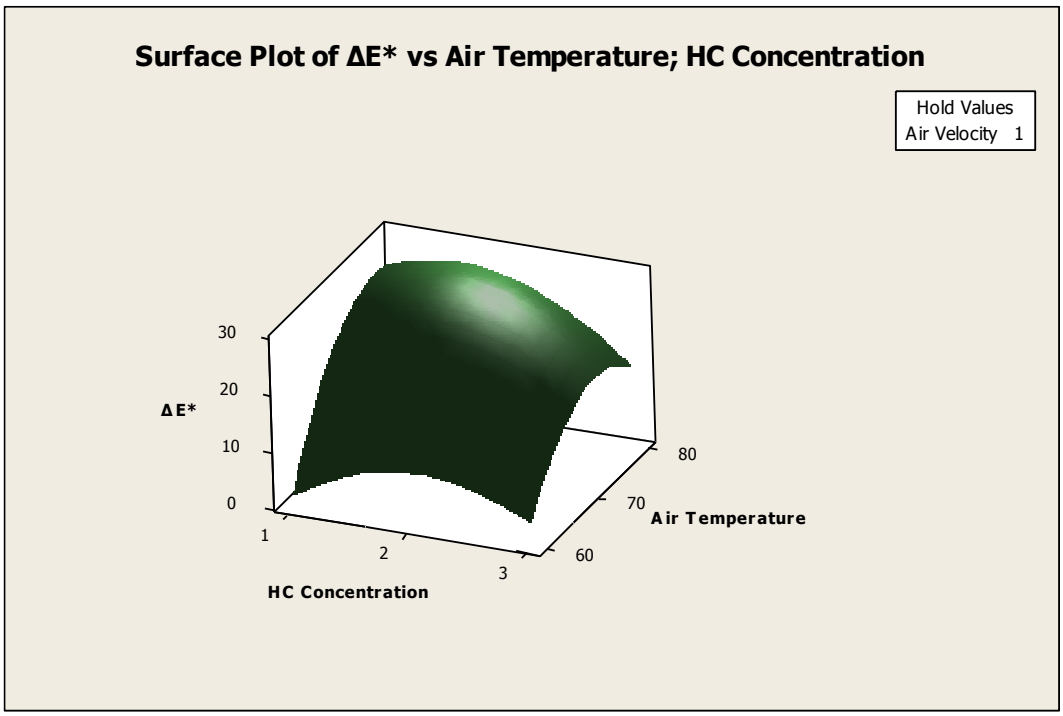

Figure C.3.b Surface plots of total color change (ΔE*) vs. air temperature; HC concentration

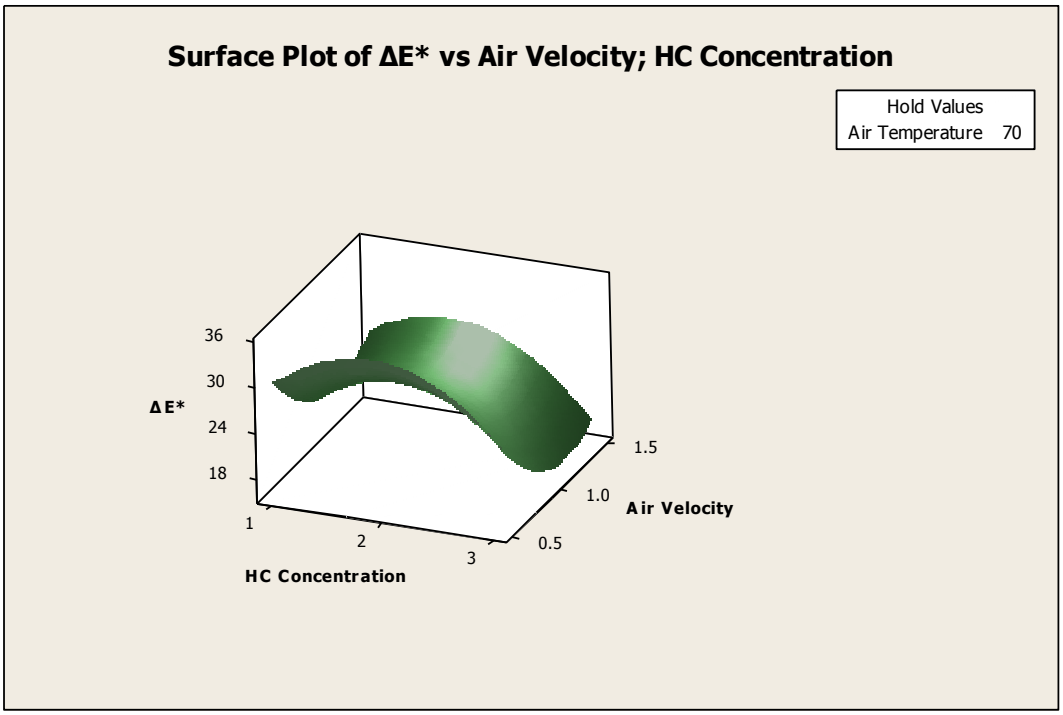

Figure C.3.c Surface plots of total color change (ΔE*) vs. air velocity; HC concentration

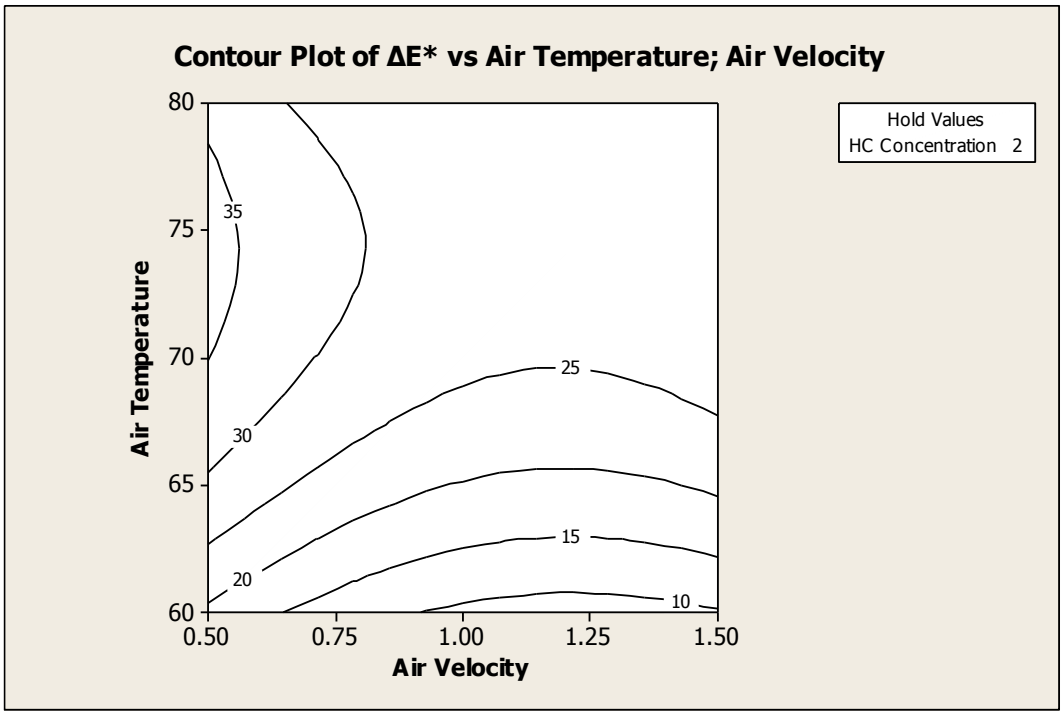

Figure C.4.a Contour plots of total color change (ΔE*) vs. air temperature; air velocity

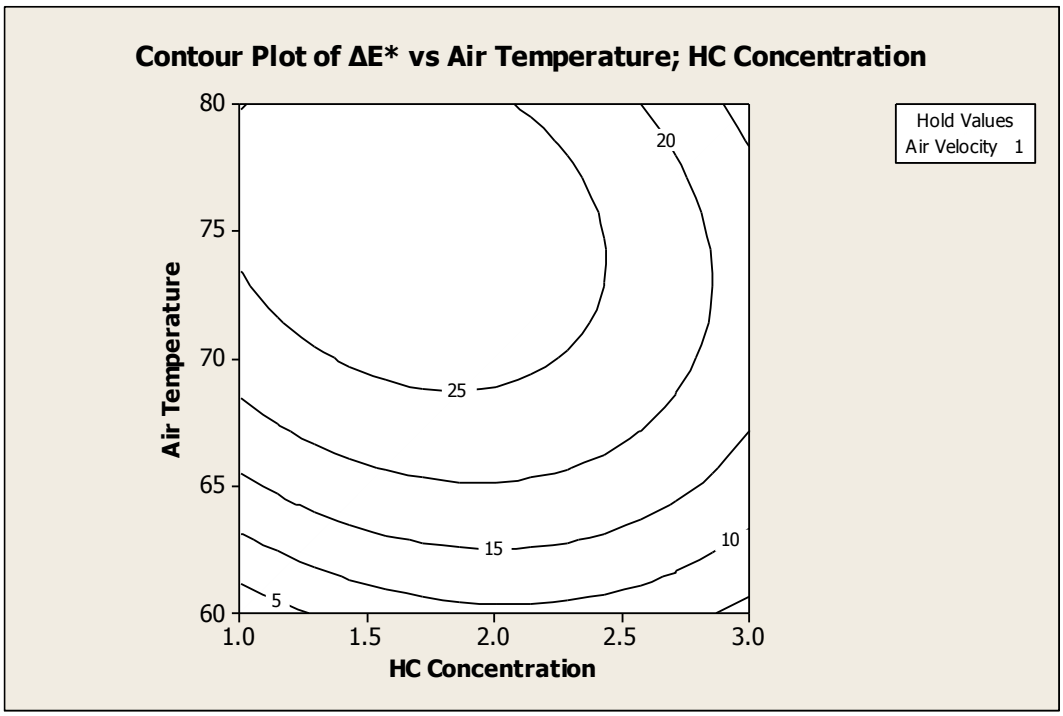

Figure C.4.b Contour plots of total color change (ΔE*) vs. air temperature; HC concentration

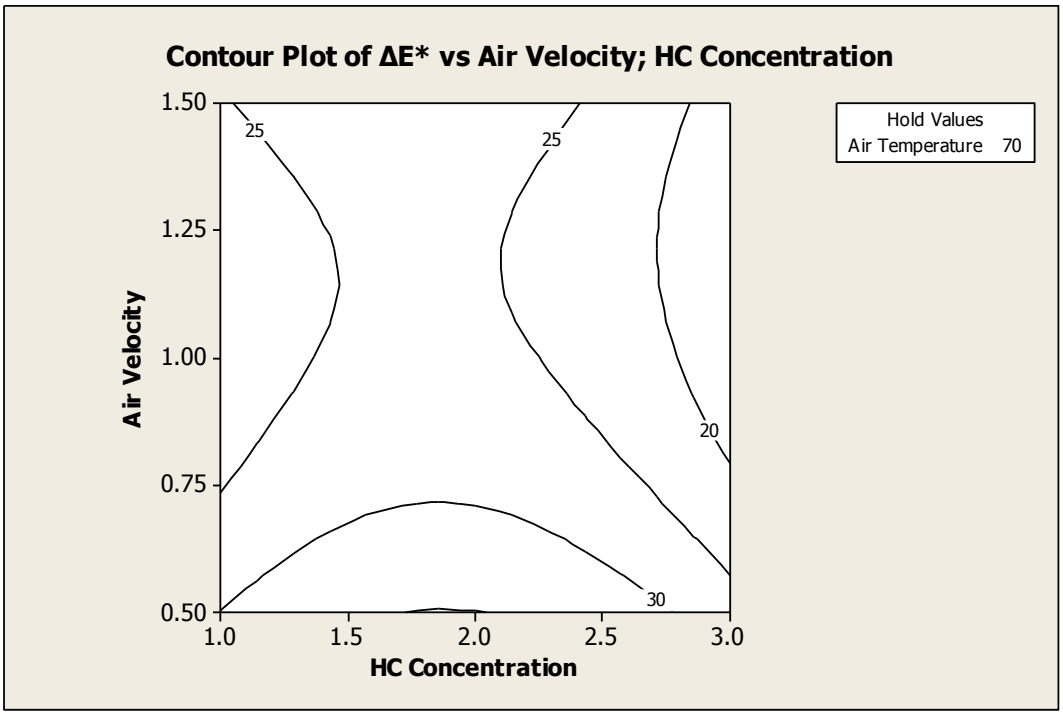

Figure C.4.c Contour plots of total color change (ΔE*) vs. air velocity; HC concentration

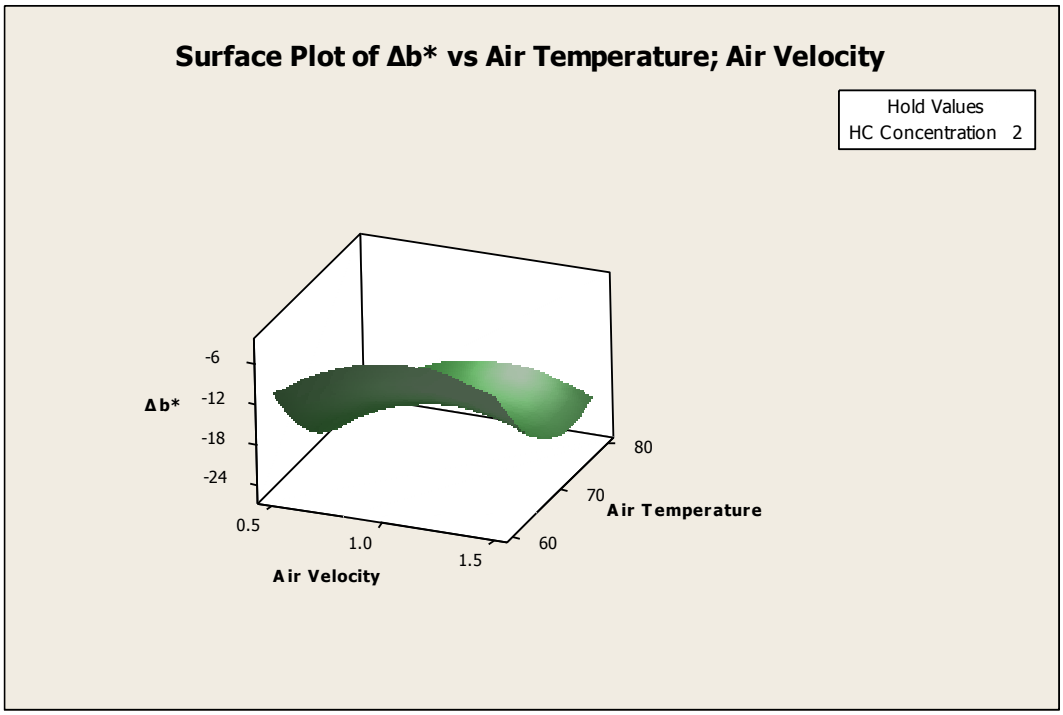

Figure C.5.a Surface plots of delta b (Δb*) vs. air temperature; air velocity

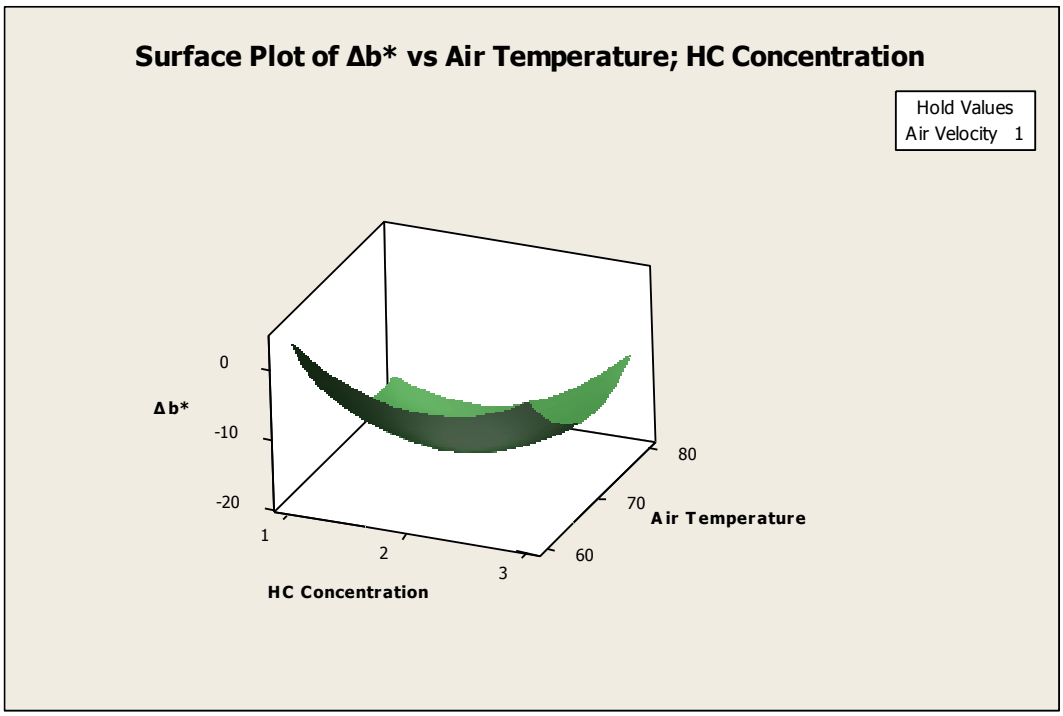

Figure C.5.b Surface plots of delta b (Δb*) vs. air temperature; HC concentration

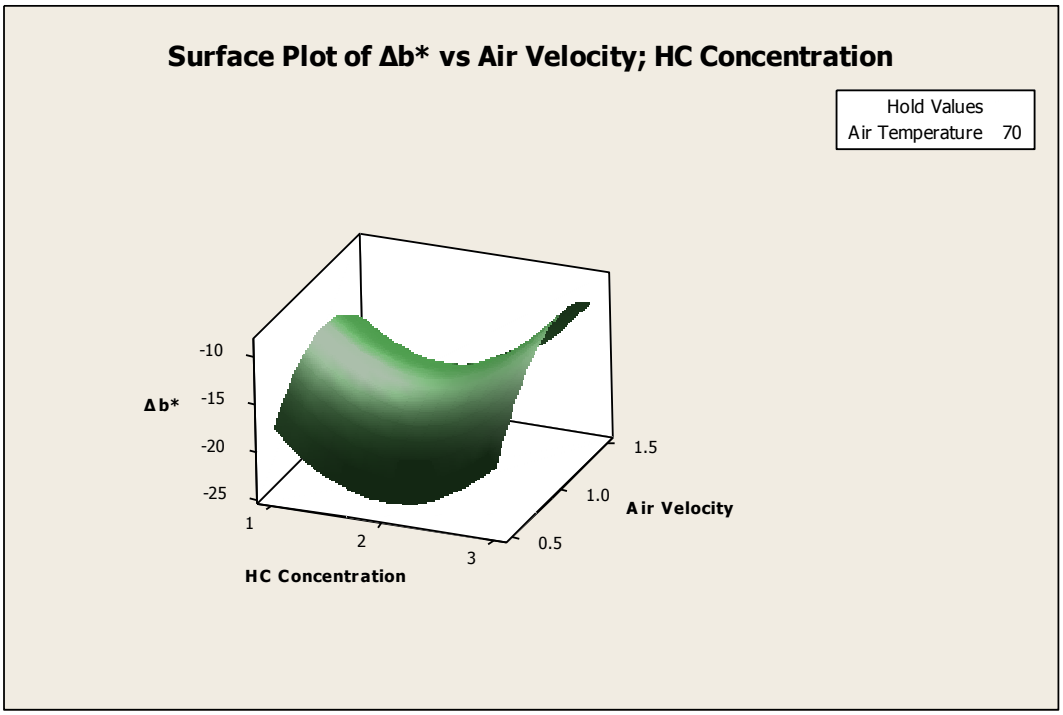

Figure C.5.c Surface plots of delta b (Δb*) vs. air velocity; HC concentration

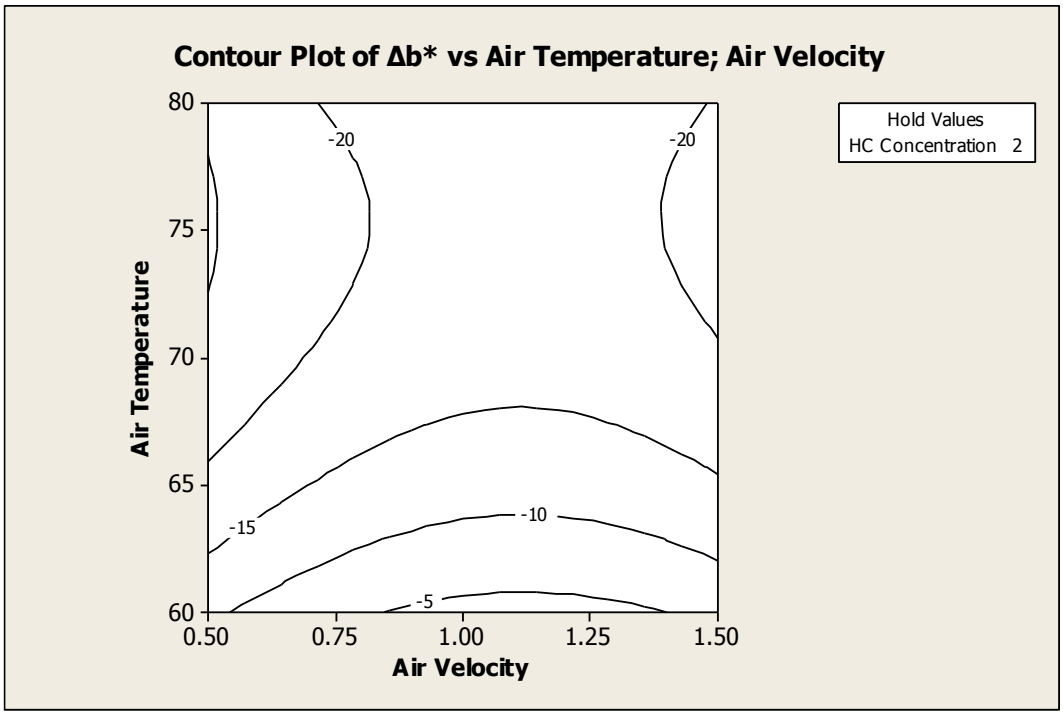

Figure C.6.a Contour plots of delta b (Δb*) vs. air temperature; air velocity

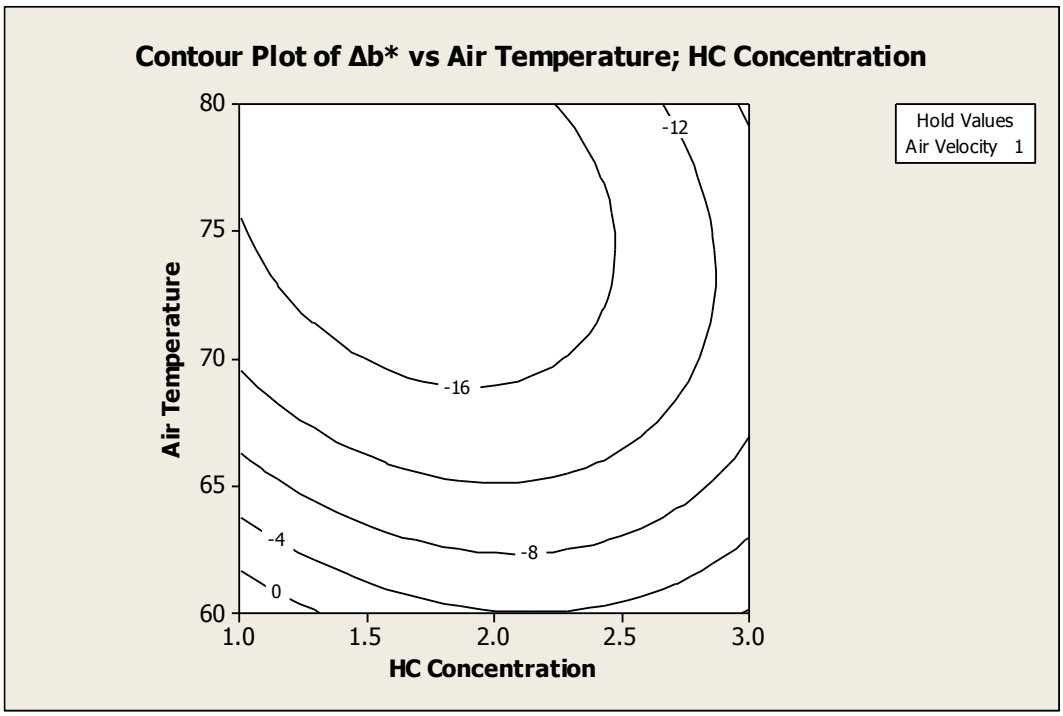

Figure C.6.b Contour plots of delta b (Δb*) vs. air temperature; HC concentration

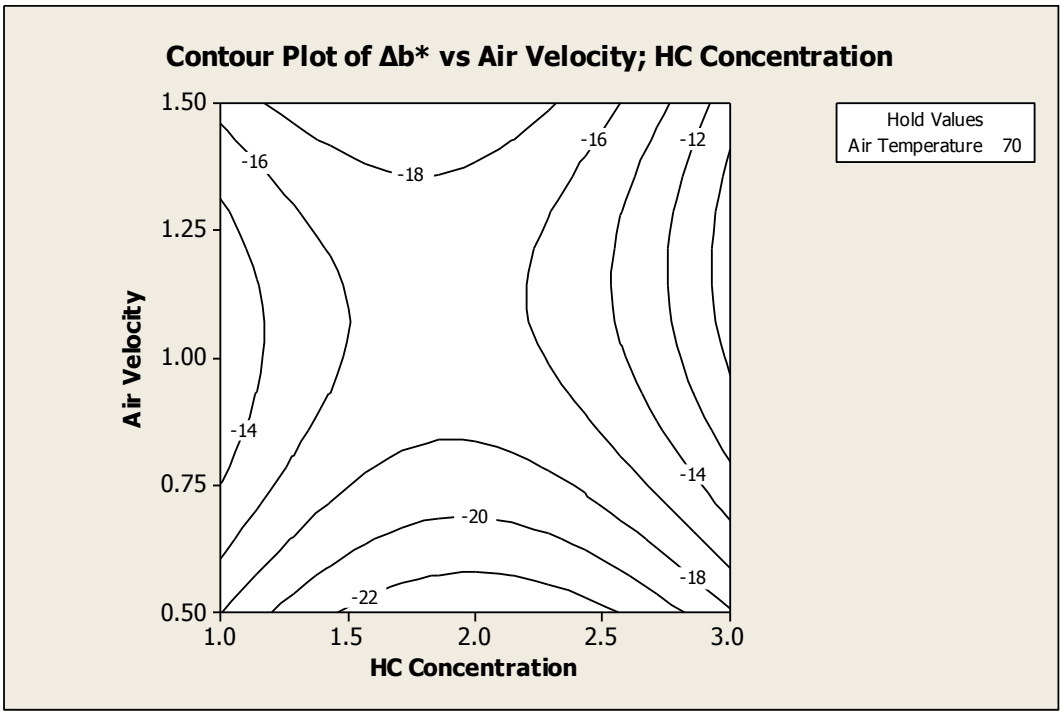

Figure C.6.c Contour plots of delta b (Δb*) vs. air velocity; HC concentration

APPENDIX D

MODELS OF DRYING KINETICS AND REHYDRATION DATA

Table D.1 Equilibrium moisture contents of different coatings and drying conditions

	Model 1 **f=y0+a*exp(-b*x)**			**Model 2** **f=y0+a*exp(-b*x)+c*exp(-d*x)**		
	Xeq	Rsqr	SEE	Xeq	Rsqr	SEE
0.5 m/s, 1 % Chitosan at 70 °C	2.61E-11	0.9973	0.0269	2.81E-11	0.9973	0.0279
1 m/s, 1 % Chitosan at 70 °C	2.26E-09	0.9941	0.0264	1.17E-09	0.9946	0.0304
1.5 m/s, 1 % Chitosan at 70 °C	4.70E-10	0.9933	0.032	5.79E-10	0.9933	0.0333
0.5 m/s, 2 % HC at 70 °C	6.54E-11	0.9931	0.0488	5.33E-11	0.9969	0.033
1 m/s, 2 % HC at 70 °C	7.77E-11	0.9946	0.0303	1.89E-10	0.9945	0.0318
1.5 m/s, 2 % HC at 70 °C	7.39E-11	0.9942	0.029	2.69E-11	0.9942	0.0302
1 m/s, 2 % HC at 60 °C	1.17E-09	0.9914	0.0344	3.09E-11	0.9933	0.0379
1 m/s, 2 % HC at 80 °C	3.95E-11	0.9838	0.0336	5.33E-11	0.9969	0.033
0.5 m/s, Uncoated at 70 °C	1.98E-11	0.9942	0.0405	1.15E-10	0.9942	0.0383
1 m/s, Uncoated at 70 °C	2.23E-10	0.9937	0.0319	1.04E-09	0.9937	0.0332
1.5 m/s, Uncoated at 70 °C	3.77E-10	0.9954	0.0245	1.76E-11	0.9941	0.0255
1 m/s, Uncoated at 60 °C	0.4291	0.9974	0.0315	0.3212	0.9891	0.0339
1 m/s, Uncoated at 80 °C	3.30E-11	0.997	0.0275	2.18E-11	0.997	0.0286
1 m/s, 1 % Chitosan at 60 °C	7.82E-11	0.997	0.0161	5.52E-11	0.997	0.0174
1 m/s, 1 % Chitosan at 80 °C	5.63E-11	0.9939	0.037	7.38E-11	0.9939	0.0386

Table D.2 Statistical analyses and constants of logarithmic model

	Rsqr	SEE	c	a	k	Chi Square	MBE	RMSE
0.5 m/s, 1 % Chitosan at 70 °C	0.9965	0.0112	2.32E-12	1.0906	0.0076	0.00011	0.00058	0.0103
1 m/s, 1 % Chitosan at 70 °C	0.9951	0.0108	2.29E-09	1.063	0.0039	0.00011	0.00016	0.0100
1.5 m/s, 1 % Chitosan at 70 °C	0.9938	0.0122	4.37E-12	1.0096	0.0044	0.00014	0.00025	0.0113
0.5 m/s, 2 % HC at 70 °C	0.9948	0.0154	5.03E-12	1.2279	0.0071	0.00022	0.00061	0.0143
1 m/s, 2 % HC at 70 °C	0.996	0.0104	6.09E-12	1.0252	0.005	0.00010	0.00024	0.0096
1.5 m/s, 2 % HC at 70 °C	0.9866	0.0185	6.05E-12	0.9711	0.0051	0.00032	0.00059	0.0171
1 m/s, 2 % HC at 60 °C	0.9929	0.0127	1.89E-11	1.1178	0.0037	0.00015	7.89E-05	0.0116
1 m/s, 2 % HC at 70 °C	0.996	0.0104	6.09E-12	1.0252	0.005	0.00010	0.00024	0.0096
1 m/s, 2 % HC at 80 °C	0.9772	0.0339	3.93E-12	1.254	0.0085	0.00109	0.00300	0.0314
0.5 m/s, Uncoated at 70 °C	0.9935	0.0161	4.83E-12	1.145	0.0073	0.00024	0.00106	0.0149
1 m/s, Uncoated at 70 °C	0.9959	0.0103	1.77E-11	1.0956	0.0039	9.9E-05	0.00015	0.0095
1.5 m/s, Uncoated at 70 °C	0.9962	0.008	1.79E-11	1.0005	0.0031	6.1E-05	9.05E-05	0.0074
1 m/s, Uncoated at 60 °C	0.9952	0.0098	1.79E-11	0.9704	0.004	9.1E-05	8.57E-05	0.0091
1 m/s, Uncoated at 70 °C	0.9959	0.0103	1.77E-11	1.0956	0.0039	9.9E-05	0.00015	0.0095
1 m/s, Uncoated at 80 °C	0.9955	0.0129	3.12E-12	1.0994	0.0069	0.00015	0.00071	0.0119
1 m/s, 1 % Chitosan at 60 °C	0.9894	0.0118	2.66E-11	0.9835	0.0026	0.00013	2.86E-05	0.0109
1 m/s, 1 % Chitosan at 70 °C	0.9951	0.0108	2.29E-09	1.063	0.0039	0.00011	0.000162	0.0100
1 m/s, 1 % Chitosan at 80 °C	0.9953	0.0135	5.72E-12	1.1352	0.0068	0.00017	0.000638	0.0124

Table D.3 Effective diffusion coefficients of 2 % hemicellulose coated apricots during drying

Drying Conditions	Final Moisture Content (db)	D_{eff} (m^2/s)
0.5 m/s at 70 °C	0.5853	4.79587E-09
1 m/s at 70 °C	0.6667	3.37737E-09
1.5 m/s at 70 °C	0.6240	3.44492E-09
1 m/s at 60 °C	1.6562	2.49926E-09
1 m/s at 80 °C	0.2760	5.74154E-09

Table D.4 The results of One-way ANOVA and comparison of different coating materials on rehydration by Tukey method

```
Source  DF         SS         MS      F      P
Factor   3  0.0000039  0.0000013  64.67  0.001
Error    4  0.0000001  0.0000000
Total    7  0.0000040

S = 0.0001414   R-Sq = 97.98%   R-Sq(adj) = 96.46%



Level            N      Mean     StDev
2 % HC Coating   2  0.010600  0.000141
0.2 % Sulfuring  2  0.009800  0.000141
1.5 % Chitosan   2  0.011700  0.000141
Uncoated         2  0.010300  0.000141

                 Individual 95% CIs For Mean Based on
                 Pooled StDev
Level            ----+---------+---------+---------+-----
2 % HC Coating              (---*---)
0.2 % Sulfuring  (---*---)
1.5 % Chitosan                           (---*---)
Uncoated               (---*---)
                 ----+---------+---------+---------+-----
                   0.00980   0.01050   0.01120   0.01190

Pooled StDev = 0.000141
```

Grouping Information Using Tukey Method

	N	Mean	Grouping
1.5 % Chitosan	2	0.0117000	A
2 % HC Coating	2	0.0106000	B
Uncoated	2	0.0103000	B C
0.2 % Sulfuring	2	0.0098000	C

Means that do not share a letter are significantly different.