# 博士論文

# Analysis of Drying Mechanism and Quality Retention Mechanism during Drying of Fruits and Vegetables

果実および野菜の乾燥における乾燥挙動と品質保持挙動の解析

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#### Abstracts

Drying is one of the food preservation method that have been most widely used for grains, crops and foods in all varieties. Usually, drying is carried out at low humidity values in order to reduce the drying time. However, such rapid drying often causes the unwanted quality degradation such as irregular shrinkage and significant color changes. Pre-drying treatments such blanching and dipping in sugar solution are needed for vegetable drying in order to avoid damages to tissue structures. In this experiment, as model vegetables potato and carrot were chosen. Trehalose and sucrose were employed as a pretreatment reagent. Isothermal drying experiments were carried out with samples prepared with different pretreatments. A dipping in sugar solution relatively short time (10 minutes) was effective for obtaining high quality of dried foods. Dipping in a sugar solution was found to be the most effective pre-treatment method due to high water loss and low price. The drying rates of sliced lemons were much lower compared with those for sliced potatoes and carrots. A steam blanching increased the drying rate significantly. Drying at relatively low humidity resulted in the dried product with less color changes and shrinkage both on potato and lemon. The combination of blanching and dipping sugar solution was found to be the best appearance based on color and shrinkage.

Isothermal drying rates and desorption isotherms of lemon juice were measured and compared with the data for a simulated lemon juice, sucrose, maltodextin and citric acid. During isothermal drying experiment, the drying rate of lemon juice are much lower than those for simulated lemon juice, sucrose and maltodextrin. In addition, the drying rate of simulated lemon juice at X=0.3 was approximately have same value with sucrose before fell rapidly when X<0.4. On the other hand, citric acid became crystallized at late stage of drying process. Hence, it is considered that the low drying rate of lemon juice is not affected by citric acid which is the largest component in lemon juice but rather small component such as sugar and other carbohydrates.

Desorption isotherms of lemon juice shows a similar behavior to the literature values (Martinelli *et.*al., 2007) and had presented satisfactory adjustment in GAB equation. In comparison with sugar such as sucrose and maltodextrin, at high water activity ( $a_w$ >0.75), the equilibrium water content X were more than 0.5 kg-water/kg-solid. Citric acid is the main component in lemon juice, and shows similar behavior with lemon juice at high water activity. Citric acid crystallized at low water activity and the water content became constant (X=about 0.1). Therefore, it is considered that equilibrium moisture content of simulated lemon juice shows similar results with literature (Martinelli *et.*al., 2007) at high water activity, whereas at low water activity (lower than 0.5) the equilibrium moisture content value relatively low, may be due to the effect of citric acid.

The adoption of HSL color system based on digital camera was successfully done to analyze color changes on lemon peel. As model fruit, lemon was chosen. Color changes of lemon peel were analysed by using HSL color system developed by Hashimoto from Mie University. Color changes were observed under two different experimental conditions. The color changes were observed during constant temperature hot air drying experiments. The sample of a constant water content was incubated in a sealed container and then the color was analysed as a function of incubation time. Vacuum and freeze drying experiments were used to prepare different water content of sample prior to incubation experiments. Hue value tends to decrease as the browning increase. Unfortunately, there are no significantly behavior affect on the change of the saturation (S) and lightness (L). Hue value decrease with increase in water content. The color degradation became faster when the water content was high. The decreasing of hue value on blanching and dipping and dipping in sucrose solution was effective as pre-treatments resulted in better surface color and prevent shrinkage.

要旨

果実・野菜は水分を多く含み、腐敗しやすく、常温での保存・流通が困難である。 乾燥は、脱水による容量・重量減とともに、長期保存を可能にする、すぐれた食品 加工技術である。加熱操作をともなわない凍結真空乾燥は、熱に弱い物質の乾燥に 利用されるが、コストが高く、一般的な食品乾燥は熱風乾燥装置で実施される。熱 風乾燥においては、脱水とともに、栄養成分、色、香り、形状などさまざまな品質 劣化が生じるので、乾燥挙動とともに、それらの品質保持挙動を定量的に知る必要 がある。色は消費者が製品を判断する非常に重要な品質である。多くの食品におい ては酵素的および非酵素的褐変が生じる。レモン等のフルーツでは、非酵素的褐変 は顕著であり、その抑制は重要な課題となる。乾燥時および乾燥後の褐変を抑制し、 高品質な乾燥製品を製造するためには、乾燥機構と褐変機構を定量化する必要があ る。また、前処理による乾燥速度の促進および褐変の抑制も有望な方法である。

本研究では、はじめに第1章で野菜・果実の乾燥の特徴およびさまざまな前処理 方法とその効果についてレビューしている。

第2章においてスライスした野菜(ジャガイモ)と果実(レモン)をサンプルとした 比較的低温の乾燥における前処理効果を検討した。ブランチングは酵素的褐変を抑 制するのみならず、乾燥速度を促進した。これは細胞壁の水透過速度が速くなるた めと考えられた。またブランチング後に、糖溶液に浸漬すると浸透圧脱水が起きる とともに、乾燥後の収縮が抑制されたが、とりこまれた糖のために乾燥速度が遅く なった。比較的高い湿度の乾燥が高品質製品の製造に有利と報告されているが、本 研究では顕著なメリットは見られなかった。スライスレモンの乾燥は非常に遅く、 砂じょう表面の膜の水分透過が原因と考えられた。糖浸漬サンプルの脱着等温線は、 2成分固体に対するモデルで記述できた。

第3章では、レモンジュースの乾燥速度と脱着等温線について検討した。試料としてレモン果汁およびレモン果汁の構成成分に基づいて乾燥および吸湿挙動を解析するために、レモン構成成分を用いて、その乾燥挙動および乾燥速度を比較・検討した。レモン果汁の脱着等温線は GAB 式で良好にあらわされ、スクロースやマルトデキストリンといった糖と比較すると、高水分活性領域(*a*<sub>w</sub>>0.75)で平衡含水率 *X*が 0.5 以上の高い値を示した。レモン果汁中で最も多い構成成分であるクエン酸について調べたところ、高 *a*<sub>w</sub>値ではレモン果汁の文献値と同様であったが、低 *a*<sub>w</sub>では結晶化し、*a*<sub>w</sub>に関わらず一定の含水率(約 0.1)を示した。このことから、疑似合成レモン果汁ではクエン酸の結晶化の影響が大きいと考えられた。レモン果汁の乾燥速度は糖(マルトデキストリン)と比較すると非常に小さいことが分かった。また、疑似レモン果汁の乾燥速度は *X*>0.2 では、マルトデキストリンとほぼ同じ値であったが、*X*<0.2 で急激に低下した。クエン酸は、乾燥後期で結晶化し、乾燥速度の低下は顕著ではなかった。レモン果汁の低乾燥速度は、最も多い構成成分である

クエン酸が支配しているのではなく、他の糖質および高分子糖質によるものでなな いかと考えられる。

第4章では、レモンピールの乾燥時の褐変について検討した。褐変速度の温度および 含水率依存性について実験で調べたところ、褐変速度は温度とともに増加し、含水率の 低下とともに減少した。したがって、できるだけ低湿度で迅速に乾燥することにより、 褐変の少ない乾燥レモンピールが製造できることが明らかとなった。レモンパウダーに ついても同様な傾向が確認された。

# CONTENTS

CHAPTER 1 General Introduction	1
CHAPTER 2 Drying of sliced vegetables and fruits at relatively high humidities for producing high quality products	4
2.1 Introduction	
2.2 Material and method	
2.2.1 Material	
2.2.2 Methods	
2.2.2.1 Preparation of sample	
2.2.2.2 Determination of water loss and solid gain during pre-treatments	
2.2.2.3 Isothermal drying experiments	
2.2.2.4 Determination of desorption isotherm	
2.3 Results and Discussion	
2.3.1 The effect of osmotic dehydration	
2.3.2 The effect of pre-treatments on isothermal drying	
2.3.3 Effect of pre-treatments on desorption isotherms	
2.3.4 Effect of pre-treatments on appearance of final dried potato	
2.3.5 Effect of relative humidities on drying of sliced lemons	
2.4 Conclusion 14	4
CHAPTER 3 Drying rates and desorption isotherm of lemon juice 1	5
3.1 Introduction	5
3.2. Materials and Methods	6
3.2.1 Materials	6
3.2.2 Methods	6
3.2.2.1 Preparation sample for isothermal drying	6
3.2.2.2 Desorption isotherm	
3.2.2.3 Drying experiment	7
3.3 Results and Discussion	7
3.4 Conclusion	0
CHAPTER 4 Quality evaluation of dried lemon peel by HSL color analysis	1
4.1 Introduction	1
4.2 Materials and method	
4.2.1 Materials	
4.2.2.Methods	
4.2.2.1 Preparation of sample	
4.2.2.2 Drying experiment	
4.2.2.3 Drying experiment prior to incubating process	
4.2.2.4 Isothermal incubation experiments	
4.2.2.5 Measurement of color changes	
4.2.2.6 Color analysis	

4.2.2.7 Determination of desorption isotherm	24
4.3 Results and discussion	
4.3.1 The effect of pre-treatment on desorption isotherm	
4.3.2 The effect of pre-treatments on isothermal drying	
4.3.3 The effect of pre-treatments on color changes during isothermal drying	
4.3.3.4. The effect of pre-treatments on appearance of lemon peel during	
isothermal drying	27
4.3.3.5. The effect of pre-treatments on color changes and on appearance of lemon peel	
after FD and VD	28
4.4 Conclusions	32
CHAPTER 5 General Conclusion	33
List of Nomenclature	34
List of References	35
List of Publication	39
Acknowledgement	40

# CHAPTER I GENERAL INTRODUCTION

The critical quality of food is attributed to color, flavor, texture and nutritional value. From fruit and vegetables, color is derived from their natural pigments. During storage and advanced processing, color degradation and browning are caused by enzymatic and non enzymatic reactions. As non enzymatic chemical reactions, sugar related reaction, the Maillard reaction and caramelization and oxidation reaction of ascorbic acid and lipids caused by food browning.

As an evaluation method for the food color quality, colorimeter is one of conventional instruments which usually read in RGB, XYZ and L\*a\*b\* color space. Unfortunately, they are unsuitable for all food materials, especially for the surface color and color uniformity measurements since they only provide an average value. This method can be difficult and takes longer time to collect data from many locations to obtain color distribution. Alternatively, computer vision technology adopted as a nondestructive method. In this method, the color measurements have been conducted using digital camera that can easily acquire the surface information and the color distribution (Table 1). Application of HSL color system based on digital camera has been successfully performed for analyzing color changes. Transformation of digital camera image from RGB color system to HSL color system can perceive because these color change measurements have a similar way with human interaction and perception (Motonaga et.al, 2004; Hashimoto et.al, 2006; Levkowitz et.al, 1993).

Product	Remarks	References
"Aki	- The HSL color system used for color analysis	Motonaga et.al,
Queen" grape	- Quantity of light, uneven lighting and uneven surface	2004
	does not affect to the hue and saturation value	
	- Hue value used as the maturation index that	
	corresponded from yellow to red	
Pizza	- Application of digital camera, computer and graphic	Yam and
	software can be used to measure and analyze color	Papadakis,
	change on the surface.	2004
Sugar maple	- Quantify leaf color (red and green) as an indicator of	Murakami et.al,
leaves	plant nutrition	2005
Tomato	- Surface color change can be monitored by using a	Hashimoto
	digital camera with Fieldserver	<i>et.al</i> , 2006
	- The effect of outdoor light could be eliminated by	
	applying color calibration to the image in the field	
	condition	

Table 1-1. Review of non-destructive method of color analysis in color system

Drying is one of the most cost-effective methods for food preservation of all food varieties which involves water vapor removal from the solid by application of heat. Heat transferred from the surrounding air to the food product. (Table 2).

Table 1-2. Review of hot air drying methods on agricultural products

Product	Remarks	References	5
Potato	- High temperature of drying resulted in high moisture	Leeratanar	ak
	diffusivity, high drying rate and shorten drying time	et.al, 2006	
	- Quality degradation in color and texture because of high		
	temperature of drying		
Potato and	- The drying rate increased with increasing of drying	Aktas	et.al,
carrot	temperature	2007	
	- The different thickness of potato did not alter the drying		
	rate at the end of the drying process		
Orange	The drying rate increased with increasing of drying	Garau,	et.al,
	temperature	2006	
Aonla (Indian	Redness (a) value increased while drying, yellowness (b)	Gupta	et.al
gooseberry)	and lightness (L) value decreased while drying. The color of	(2011)	
	dried product was turning darker.		
Basil leaves	The drying rate increased with increasing of relative	Taheri-	
	humidity	Garavand	et.al
		(2011)	
Bamboo	- Shrinkage occurred because of temperature effect while	Zheng	et.al
	drying	(2013)	
	- Yellowness (b) value increased during drying, while		
	redness (a) and lightness (L) value decreased during drying		

The combination between drying and pre-treatment prior to drying are known to be effective to enhance the product quality. Pre-treatment such as blanching and the addition of sugar are needed to increase the drying rate and to avoid color degradation and damages to tissue structure (Table 3).

Pre- treatment	Drying method	Product	Remarks	References
Blanching	Hot air	Aonla	Hot water blanching prevents color degradation	Gupta <i>et.al</i> (2011)
Blanching	Hot air	Potato	Blanching increased the rate of water vapor removal resulted in better color retention, less shrinkage and less hardness on dried product.	Leeratanarak et.al (2006)
Blanching and dipping in glycerol solution	Hot air	Potato chips	A combination of pre-treatments resulted in slower drying rate due to the presence of sugar	Pimpaporn et.al (2007)
Blanching and dipping in sucrose solution	Freeze	Citrus fruit	• Loosen the water during osmotic dehydration leading to the collapse, decreased turgor pressure, deformation of the cell walls and even to plasmolysis	Katsiferis <i>et.al</i> (2008)
Blanching and dipping in sucrose, trehalose	Hot air drying	Potato and carrot	<ul> <li>Osmotic dehydration decreased initial water content</li> <li>The combination of blanching and dipping in a sugar solution resulted in less browning color and shrinkage either for potato and carrot.</li> </ul>	Aktas <i>et.al</i> (2007)

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This research mainly focuses on studying of drying behavior of vegetables and fruits and their quality changes during drying at several temperatures (303-333K). Effects of relative humidity and pre-treatments using sliced potatoes, sliced lemon and lemon peel as a model on drying behavior also conducts. Isothermal drying rates and desorption isotherms of lemon juice also measure and compare with data of simulated lemon juice, citric acid and other sugars. HSL color analysis using a digital camera and computer software employs for experimental investigation of lemon peel during drying.

## **CHAPTER 2**

## DRYING OF SLICED VEGETABLES AND FRUITS AT RELATIVELY HIGH HUMIDITIES FOR PRODUCING HIGH QUALITY PRODUCTS

#### 2.1 Introduction

Drying is one of the food preservation method that have been most widely used for grains, crops and foods in all varieties. Several factors affect the transfer of water (drying rate), such as temperature, humidity, air velocity, vapour pressure between material and drying air, water diffusion coefficient in the material, thickness and surface properties exposed for drying (El-Aouar *et al.*, 2003).

Usually, drying is carried out at low humidity values in order to reduce the drying time. However, such rapid drying often causes the unwanted quality degradation such as irregular shrinkage and significant color changes. Several Japanese companies applied low temperature and high humidity drying for sliced fruits and vegetables in order to maintain the quality of dried products.

Osmotic dehydration is well known as a simple and inexpensive process. This method is effective even at ambient temperature and preserves the colour, flavour and texture of food, and used as a pre-treatment to improve the nutritional, sensorial and functional properties of food and also reduce the overall energy requirement for drying process (Khin *et al.*, 2006).

In the osmotic dehydration, cell damages sometimes happen by water transfer. However some sugars effectively cause the osmotic dehydration and protect the cell structure. The additions of sucrose, trehalose, maltodextrin, maltosyl-trehalose prevent the cell damage by the drying to avoid the shrinkage and color changes (Aktas *et al.*,2007, Fujii *et al*, 2011).

Steam and hot water blanching prior to drying also inactivates enzymes that lead to quality degradations. Blanching also facilitates starch gelatinization and water removal which influence the drying rate and quality of the dried products (Moreno-Perez *et al.*, 1996).

In this study, effects of blanching and soaking in a sugar solution as pre-treatments on the drying of sliced vegetables were studied at low and high humidity conditions. The solid gain (SG), water loss (WL) and weight reduction (WR) during the pre-treatment were examined. The desorption isotherms and drying kinetics were determined by isothermal desorption and drying experiments.

#### 2.2 Material and method

#### 2.2.1 Material

Sucrose, maltosyl-trehalose syrup (contains 52% of maltosyltrehalose ;  $C_{24}H_{42}O_{21}$ , mol.wt 666, Hallodex, Hayashibara, Japan) and maltodextrin#2 (Dextrose equivalent 11±1, Pinedex #2, Matsutani Kagaku Kogyo,Japan) were used. Potatoes were purchased from the local market.

#### 2.2.2 Methods

#### 2.2.2.1 Preparation of sample

Fresh potatoes were cleaned and cut into samples in a 1 mm thickness using an adjustable slicer. Thickness was measured using a Digital Linear Gauge DG-911 (Ono Sokki, Japan). The sliced samples were cut into a round shape in 20 mm diameter using a round shape cookie cutter. The sample was placed on a net dish and covered with aluminium foil and blanched with a steam for 3 minutes. The temperature of steam is about 372K. Under this condition the sample was not cooked.

As a sugar solution, sucrose, maltosyl-trehalose and maltodextrin of 20 wt% were used. Blanched samples were dipped in a sugar solution for 10 minutes.

2.2.2.2 Determination of water loss and solid gain during pre-treatments

Blanched samples were dipped in a sucrose, maltosyl-trehalose or maltodextrin solution for 10 minutes at room temperature.

The solid mass of the sample  $(W_s)$  was measured by drying the sample at 378K for 4 hours.

SG, WL and WR were calculated from the following equations (Antonia and Murr, 2002, Eren and Kaymak-Ertekin, 2007),

SG = 
$$\frac{(W_s - W_{s0})}{M_0} x 100$$
 (2-1)

WL = 
$$\frac{(M_{\theta} - W_{S\theta}) - (M_T - W_S)}{M_{\theta}} x 100$$
 (2-2)

 $WR = WL - SG \tag{2-3}$ 

 $W_{\rm S}$  and  $W_{\rm S0}$  is the solid mass at time *t* and the initial time,  $W_{\rm W}$  and  $W_{\rm W0}$  is the water mass at time t and the initial time, respectively.  $M_{\rm T}$  is mass of the sample after dipped in a solution, and  $M_0$  is the initial mass (water and solid) of the fresh sample (prior to blanching).

All the experiments were performed in triplicates, and the average values were calculated.

#### 2.2.2.3 Isothermal drying experiments

Isothermal drying experiments were performed in a constant air temperature box. This drying equipment has two fans, which circulate the air in the box well, a fan control unit, a heater, a temperature control unit and digital balance. The relative humidity (RH) was adjusted by silica gels (RH<1%) for low humidity drying or a NaCl saturated solution (RH=75%) for high humidity drying. The air temperature and relative humidity were monitored by the thermometer and hygrometer in the box. The sample was placed on a spiral wire dish covered with a silicon tube. This dish placed on a wire net cage, which was attached to an aluminium dish. The aluminium dish eliminates unwanted vibrations of the wire net cage by the hot air stream. The dish was hanged to an electronic balance placed on the drying box.

#### 2.2.2.4 Determination of desorption isotherm

Samples were stored in an airtight plastic container in the presence of salt solutions of known  $a_w$  values at 303K. Then the samples weighed every 24 hours until the weight loss became less than 2%.

The desorption isotherm data were fitted by a three parameter Guggenheim-Anderson -de Boer (GAB) model (Blahovec, 2004; Rahman, 1995; Van den Berg, 1984 ).

$$X = \frac{CKa_{\rm w}W_{\rm m}}{(1 - Ka_{\rm w})(1 - Ka_{\rm w} + CKa_{\rm w})}$$
(2-4)

 $W_{\rm m}$  implies the water content equivalent to monolayer coverage. C and K are constants related to the binding energies.

Two models were applied to describe the desorption isotherms.

[Model 1] This model assumes that the water content X at a given  $a_w$  is the weighted-average of single component one (Lang and Steinberg (1980))

$$X_{\text{sugar+potato}} = X_{\text{sugar}} \times W_{\text{sugar}} + X_{\text{potato}} \times W_{\text{potato}}$$

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at a given a_w
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(2-5)

Where  $W_{sugar}$  and  $W_{potato}$  is the mass fraction of sugar and potato,  $X_{sugar}$ ,  $X_{potato}$  and  $X_{sugar+potato}$  is the equilibrium water content of sugar, potato, sugar-potato mixture, respectively.

[Model 2] This model is based on the Ross method (Ross, 1975; Rahman 1995), which was originally developed for intermediate moisture foods.

 $a_{\rm w \ sugar+potato} = a_{\rm w \ sugar} \times a_{\rm w \ potato}$ at a given X (2-6)

#### 2.3 Results and Discussion

#### 2.3.1 The effect of osmotic dehydration

In the osmotic dehydration by sugar, water diffuses from outer layer of potato. This increases the surface osmotic pressure. When the osmotic pressure reaches  $1.95 \times 10^5$  Pa (Rastogi, 2004), the cell membrane of potato ruptures and shrinks. The cell becomes porous and loses water. At the same time, the cell gains solid components from the solution (Phisut, 2012). The osmotic dehydration is used primarily for partial dehydration of cellular products containing a large amount of water.

The solid gain (SG), water loss (WL) and weight reduction (WR) data for potato samples dipped into three sugar solution are shown in Fig.2-1. SG, WL and WR of maltosyl-trehalose samples were higher than sucrose and maltodextrin samples. Although the molecular weight of maltosyl-trehalose is higher than sucrose, maltosyl-trehalose was absorbed. High solid gain in the case of maltosyl-trehalose is not clear.

Maltosyl-trehalose is a non-reducing tetrasaccharide, in which maltose is linked to trehalose. It does not crystallize during drying and has very low Maillard reactivity.



Fig. 2-1. Water loss, solid gain and weight reduction of potato samples during pre-treatment with sugar solution

2.3.2 The effect of pre-treatments on isothermal drying

Fujii *et al* (2011) has reported that a soaking of sliced potatoes in a maltosyl-trehalose solution for 10 minutes is a very effective pre-treatment method for the drying of sliced potatoes. Blanching increased the drying rate and inactivated the enzyme activity that leads to quality degradation, such as browning and shrinkage. Blanching simultaneously may change the physical properties of cells and enhance water transfer (Phisut, 2012).

Isothermal drying experimental data for potato samples prepared with different pretreatments at low and high humidity conditions are shown in Figs.2-2 and 2-3, respectively. The initial water content values of all pre-treatment samples were lower than the values for the non-treated samples due to the osmotic dehydration (Fig.2-2). The lowest initial moisture content was found for samples soaked in a maltosyl-trehalose solution. The drying time was reduced due to this lower initial water content compared with non-treatment samples. The final water content of the sample treated with sucrose was slightly higher than the others. The final water content of the sample soaked in a maltosyl-trehalose solution and that in a maltodextrin solution were almost similar.

Osmotic dehydration effect lowered the initial moisture content. However, the presence of sugars in potato led to a low drying rates at the late stage of drying. The drying rate was lower for sucrose-treated samples compared with maltodextrin and maltosyl-trehalose treated samples.



Fig. 2-2. Drying curves of potato with or without pre-treatments at low humidity, 303K

The drying time at high humidity was longer than low humidity (Fig.2-3). The drying curves of samples pretreated with sucrose, maltosyl-trehalose and maltodextrin solutions are almost similar. The final water content of sucrose samples was slightly higher than maltosyl-trehalose and maltodextrin samples.



Fig. 2-3. Drying curves of potato with or without pre-treatments at high humidity, 303K

The drying rate depends on the relative humidity and the equilibrium water content. Taheri-Garavand *et al*, (2000) reported that drying rate of basil leaves increased with a decrease in the relative humidity. However, the effect of relative humidity on the drying is much lower than air-temperature (Saeed *et al*, 2008 and Krokida *et al*, 2003)

## 2.3.3 Effect of pre-treatments on desorption isotherms

Desorption isotherm data of potato samples prepared with different pre-treatments are shown in Fig. 2-4. At  $a_w$  above 0.1, the equilibrium water contents of samples soaked in a sucrose solution were higher than non-treated and blanched samples.



Fig. 2-4. Desorption isotherm of potato with or without pre-treatments

Figure 2-5 shows the desorption isotherms of potato and sucrose solution. The desorption isotherms of sucrose and nontreated potato show typical food isotherm shape, which can be described well by the GAB equation, Eq.(2-4). Two models, Model 1 (Lang and Steinberg (1980)) and Model 2 (Ross, 1975; Rahman, 1995) were applied to describe the desorption isotherms. Model 1 was applicable to the data and can reasonably describe the isotherm well when  $a_w>0.3$ . On the other hand, Model 2 is not able to describe the isotherm of potato and sucrose solution.



Fig. 2-5. Desorption isotherm of potato and sucrose solution

2.3.4 Effect of pre-treatments on appearance of final dried potato

The appearance of final dried potato with different pre-treatments at low humidity and high humidity are shown in Fig. 2-6 and 2-7. Generally, shrinkage occurred in all treatments. In the early stage of drying at low humidity, the samples kept their original geometry although shrinkage is considerable. About thirty minutes later, shrinkage proceeded more rapidly. Shrinkage was not significant at the final stage of drying. Non-pre-treated samples showed shrinkage in all surface and were rolled upward. Their color became darker. Blanched samples did not shrink irregularly and the color change was not significant. It was found that blanching can maintain color but can not prevent shrinkage. All sugar treatments after blanching resulted in better color quality. Shrinkage was not remarkable for the sucrose treated sample. Overall, maltosyl-trehalose sample was found to be the best appearance based on shrinkage and color.

Soaking in a maltosyl-trehalose solution can maintain the cell tissue structure so that the color of the sample is much clear and less transparent. Combination of blanching and soaking in a sugar solution resulted in less color changes during drying process and inactivated the enzyme activity that causes quality degradation. Aktas, *et al* (2006) reported that the pre-treatments using sucrose and trehalose solution for carrot and potato provided better properties in terms of the appearence. Non-enzymatic browning may occur because of the interaction of protein (amino acids) with reducing sugars (aldehyde or ketone) at high temperatures during drying. By using non-reducing sugars such as trehalose, the nonenzymatic bowning can be prevented.



Fig. 2-6. Photograph of slices potato after drying at low humidity 303K: (a) non-treatment,(b) blanched, (c) dipped in sucrose solution, (d) dipped in maltodextrin, (e) dipped in maltosyl-trehalose



Fig. 2-7. Photograph of slices potato after drying at high humidity, 303K: (a) non-treatment,(b) blanched, (c) dipped in sucrose solution, (d) dipped in maltodextrin, (e) dipped in maltosyl-trehalose

Compared with low humidity drying, high humidity drying caused more shrinkage in the middle stage of the drying process. This may be due to slow mass transfer of water in potato. Further research is needed to find out the appropriate humidity for potato drying in order to obtain the better appearance and the quality of the final dried product.

2.3.5 Effect of relative humidities on drying of sliced lemons

Sliced lemons in 3mm thickness were dried at low and high humidity conditions for 1500 minutes (Fig.2-8). The drying at high humidity resulted in less shrinkage and better color retention (Figs.2-9 and 2-10).

However, the drying rates were much lower compared with those for sliced potato samples. At this condition a very long drying time is needed to obtain the dried product having safe  $a_w$  values at high humidity. A one minute steam blanching pre-treatment increased the drying rate compared with non-treatment samples. This may be one of the options for reducing the drying time at high humidity.



Fig. 2-8. Drying curve of sliced lemons at low and high humidity conditions (air temperature, 313K)



Fig. 2-9. Photographs of non-treatment lemon (A) before drying low humidity, (B) after drying low humidity (313K), (C) before drying high humidity, (D) after drying high humidity (313K)



Fig. 2-10. Photographs of lemon (A) non-treatment before drying high humidity, (B) nontreatment after drying high humidity (313K), (C) blanched lemon before drying high humidity, (D) blanched lemon after high humidity (313K)

2.4 Conclusion

Combined effects of steam blanching and soaking in a sugar solution as pretreatments on drying of sliced vegetables and fruits at low and high humidity conditions were studied.

Soaking in a sugar solution caused the mass transfer due to osmotic dehydration. In terms of solid gain, water loss and water regain, soaking in a maltosyl-trehalose solution was found to be the most effective pre-treatment method.

The desorption isotherms of potato and sucrose solution were well described by a model which assumes that the water content at a given water activity  $a_w$  is the weighted-average of single component one when  $a_w>0.3$ . On the other hand, a modified Ross method was not able to describe the isotherm of potato and sucrose solution.

The drying rates of sliced lemons were much lower compared with those for sliced potatoes and carrots. A steam blanching increased the drying rate significantly.

Although the drying rate decreased, the drying at relatively high humidity conditions may provide better product quality for sliced vegetables and fruits.

#### **CHAPTER 3**

## DRYING RATES AND DESORPTION ISOTHERMS OF LEMON JUICE

## 3.1 Introduction

Various fruit juices are used for drinks, and ingredients of confectionaries and other foods. Lemon is one of the most commonly consumed fruits for drinks, cooking and confectionaries (Morton, 1987). Because of the high water contents, fruits such as lemon have a rather short shelf life.

Drying is a well-known method for stabilizing food materials. Once the water content is reduced to a certain level, dried (dehydrated) materials become very stable primarily because of the low water activity ( $a_w$ ) values. Glassy-state is also an important factor for producing stable products.

Slow drying of sliced lemons was reported (Chen *et.al.*, 2005, Hawa *et.al.*, 2012). However, the drying rates of lemon juice have not been investigated fully. We have reported the drying rates (and the diffusion coefficients) of various carbohydrates by using the modified regular regime method (Yamamoto, 2001, 2004, 2006; Yamamoto *et.al.*, 2002; Kawata *et.al*, 2012., Fujii *et.al.*, 2013). We also found that drying rates of amorphous carbohydrate solutions change in the presence of crystalline materials (salts) (Kawata *et.al.*, 2012). Therefore, it is interesting to analyze drying rates of lemon juice in terms of sugar and citric acid contents in order to know the slow drying of lemon products.

The purpose of this study is to examine the drying rate and the desorption isotherms of lemon juice. Our method developed for the regular regime drying curves (Yamamoto, 2001, 2004, 2006; Yamamoto *et.al.*, 2002; Kawata *et.al*, 2012.) was applied to the isothermal drying experimental curves of an agar-gelled lemon juice slab shaped sample. A simulated mixture of lemon juice was also used as a sample. The obtained data were compared with the values for other sugars or carbohydrates. Lemon juice powder is very hygroscopic and difficult to handle without additives (Martinelli *et.al.*, 2007). Therefore, desorption isotherms were also measured and compared with the isotherms of other sugars and carbohydrates, a simulated lemon juice and a citric acid.

#### 3.2. Materials and Methods

#### 3.2.1 Materials

As a fresh lemon juice sample, a commercial product POKKA LEMON (POKKA SAPPORO Food & Beverage, Nagoya, Japan), was used. For comparison, a simulated lemon juice solution (18wt% citric acid, 0.9wt% fructose, 2.1% glucose, 0.3% sucrose, 0.1% ascorbic acid) was used. Maltodextrin (dextrose equivalent DE=11, Pinedex #2, Matsutani Chemical Industry, Itami, Japan) was also employed. All chemicals were of analytical grade.

#### 3.2.2 Methods

#### 3.2.2.1 Sample preparation for isothermal drying

A sample solution (10-40 wt %) was heated with agar-agar (1 wt%) until a homogeneous solution was obtained. For lemon juice and simulated lemon juice sample, agar was heated separately until a homogenous solution was obtained before mixed with heated lemon juice solution. The solution was then injected into an aluminum dish to prepare slab shaped samples (diameter = 50 mm, depth = 1-5 mm) carbohydrates (Yamamoto, 2001, 2004, 2006; Yamamoto *et.al.*, 2002; Kawata *et.al*, 2012). The solid weight of the sample  $W_s$  was determined by drying at 378K for 4 to 5 hours in a drying oven or a known water concentration of solid powders.

## 3.2.2.2 Desorption isotherm

Samples were stored in an airtight plastic box in the presence of saturated salt solutions of known water activity ( $a_w$ ) values. The samples were weighed periodically. It is not easy to confirm the equilibrium of these samples as the physical properties (i.e., crystallization, rubber-glass transition, etc.) change with time. So we decided to terminate the experiment when the weight loss became less than 2% per 12 hours (the total duration time was usually two to three days).

Single component desorption isotherm data were fitted by a three parameter Guggenheim-Anderson -de Boer (GAB) model (Van den Berg, 1984; Blahovec, 2004; Rahman, 1995).

$$X = \frac{CKa_{\rm w}W_{\rm m}}{(1 - Ka_{\rm w})(1 - Ka_{\rm w} + CKa_{\rm w})}$$
(3.1)

 $X = (W - W_s)/W_s$  is the average water content [kg-water/kg-dry solid], where W is the total weight of the sample.  $W_m$  implies the water content equivalent to a mono-layer coverage. C and K are constants related to the binding energies. GAB equation is known to describe food

sorption isotherms in the range of  $a_w$ =0-0.9 (Yamamoto, 2004, 2006; Kawata, 2012, Van den Berg, 1984; Blahovec, 2004; Rahman, 1995). Experiments were repeated twice and the average of *X* was drawn in the figure with the error bar.

## 3.2.2.3 Drying experiment

Isothermal drying experiments were performed in a constant-air temperature box (Yamamoto, 2001, 2004, 2006; Yamamoto *et.al.*, 2002; Kawata *et.al*, 2012). Silica gels were placed in the box to reduce the relative humidity (RH). A Testo 608-H2 (Newman Lane, UK) monitor was installed in the drying box, which can monitor RH from 2 to 98% (accuracy  $\pm 2\%$ ). RH was maintained below 2% during experiments. The air temperature was controlled so that the sample temperature is maintained at an assigned temperature. The air temperature in the drying box was somewhat higher than the assigned value at the beginning of the experiment, and then, lowered gradually with the progress of the drying. The sample disk was weighed by using a digital balance whereas the temperature of the sample was measured by inserting a thermocouple to the sample. The weight and temperature  $T_A(T_A-T_d \approx 1-2^{\circ}C)$  when the average water content *X* became less than 1.0 for sucrose and maltodextrin. For samples of high initial water contents (simulated lemon juice and lemon juice) the condition  $T_A-T_d \approx 1-2^{\circ}C$  was attained when *X*< 0.5. Distinct constant drying rate periods were not observed. Experiments were repeated twice.

#### 3.3 Results and Discussion

Figure 3-1 shows typical experimental drying curves of lemon juice and simulated fruit juice. For comparison, the data for maltodextrin, sucrose and citric acid are shown. In order to understand the drying rate quantitatively the drying rate F defined by Eq.(3.2) was calculated and plotted against the average water content, X (Yamamoto, 2001, 2004, 2006; Yamamoto *et.al.*, 2002; Kawata *et.al*, 2012)

$$F' = -\frac{dX}{d\tau'} = -\frac{dX}{dt/(d_s R_s)^2} = -(d_s R_s)^2 \frac{dX}{dt} = -(W_s / A)^2 \frac{dX}{dt}$$
(3.2)

In the above equation,  $d_s$  is the solid pure density,  $R_s$  is the thickness of the completely dried sample,  $W_s$  is the solid weight and A is the drying area.  $\tau' = t/(d_s R_s)^2 = t/(W_s/A)^2$  is the normalized time based on the shrinking coordinate system (Yamamoto, 2001, Yamamoto *et.al*, 2002, Yamamoto, 2004, Yamamoto, 2006), where t :drying time [s],  $d_s$  : pure solid density [kg/m<sup>3</sup>],  $R_s$ : thickness of slab [m],  $W_s$ :solid weight in the absence of water [kg] and A:drying area [m<sup>2</sup>].



Fig. 11. Drying curves as a function of normalized time at 303K.

*t*: drying time [s], *d*<sub>s</sub> :pure solid density [kg/m<sup>3</sup>], *R*<sub>s</sub>:thickness of slab [m], *W*<sub>s</sub>: solid weight in the absence of water [kg], *A*:drying area [m<sup>2</sup>]. Curves are fitted curves using the following three-parameter equation, *X*=exp [(*b*+*ac* $\tau$ )/(1+*ac* $\tau$ )] *a* : parameter in reduced diffusion coefficient, b:ln *X*<sub>0</sub>, c:ln *X*<sub>e</sub> (Yamamoto, 2001, Yamamoto *et.al*, 2002, Yamamoto, 2004, Yamamoto, 2006, Fujii, *et.al*, 2013, Gianfrancesco, 2010, Gianfrancesso, 2012). For maltodextrin and sucrose only fitted curves are shown for the sake of clarity. The data can be found in our previous publications (Yamamoto, 2006, Fujii, *et.al*, 2013, 2004, Yamamoto, 2006, Fujii, *et.al*, 2013)

Isothermal drying rates of lemon juice, sugars and citric acid were calculated from the drying curves based on Eq.(3-2) are shown in Fig.3-2. The drying rates for lemon juice are much lower than those for maltodextrin. However, the drying rates for the simulated lemon juice were much higher and similar to the values for sucrose in the range 0.4 < X < 1. The drying rates for citric acid at low water content (X < 0.2) were similar to maltodextrin (0.3 < X < 1).



Fig. 12. Drying rates based on the normalized time as a function of water content

Desorption isotherms are shown in Fig.3-3. Lemon juice is quite hygroscopic compared with other sugars as equilibrium water contents (EWCs) at higher  $a_w$  values are quite high. Accordingly lemon powders tend to form agglomerated particles (caking) easily (Martinelli *et.al*, 2007). The EWCs for simulated lemon juice, lemon juice and citric acid were similar at high  $a_w$  values ( $a_w$ >0.76). However, the EWCs for citric acid decreased to ca. 0.15 at  $a_w$ =0.52. Similar trends were observed for simulated lemon juice. This is likely due to crystallization of citric acid. We have examined the desorption isotherms and the drying rates of amorphous sugars containing salts (crystalline materials) (Kawata *et.al*, 2012). When the salt concentration is high in the mixture, similar data were obtained (Kawata *et.al*, 2012). Namely, crystals do not retain water except for crystallization water whereas EWCs of amorphous sugars are high.

For amorphous sugar or carbohydrate solutions the drying rates (and the diffusion coefficients) decreases with an increase in the molecular mass of carbohydrates (Yamamoto, 2001, 2004, 2006; Yamamoto *et.al.*, 2002; Kawata *et.al*, 2012, Fujii, *et.al*, 2013, Gianfrancesco, 2010, 2012). The molecular mass of the simulated lemon juice is much smaller than that of maltodextrin. Other components contained in lemon juice may contribute to the lower drying rates. Pectin may be one possible reason of the low drying rates of lemon juice. In our previous study, effects of gelling agents on drying rates of sugars were investigated (Yamamoto *et.al*, 2002, Yamamoto, 2004). Agar and alginate gels did not affect the drying rates whereas pectin and gelatin lowered the drying rates markedly due to

formation of dense surface skins (Yamamoto *et.al*, 2002, Yamamoto, 2004). Effects of crystalline materials (citric acid in this study) on drying rates of carbohydrate solutions are complicated (Kawata *et.al*, 2012, Gianfrancesso, 2010). Further studies are needed to clarify low drying rates of lemon juice.



Fig. 13. Desorption isotherms at 303K For the sake of simplicity, the data for sucrose and maltodextrin are shown only by the fitted GAB equations (Yamamoto, 2004, Yamamoto, 2006, Kawata *et.al*, 2012)

#### 3.4 Conclusion

The drying rates of lemon juice at 303K were much lower than the values for the simulated lemon juice and maltodextrin, especially at low water content regions. The equilibrium water contents determined from the desorption isotherms of lemon juice were much higher than those for other sugars, and similar to the values for the simulated lemon juice and citric acid. High equilibrium water contents of lemon juice were likely due to citric acid. Further study is needed to understand slow drying rates of lemon juice.

#### **CHAPTER 4**

## QUALITY EVALUATION OF DRIED LEMON PEEL BY HSL COLOR ANALYSIS

## 4.1 Introduction

Lemon, one of citrus variety, has been a very popular fruit throughout the world. Lemon is a rich source of vitamin, mineral, dietary fiber, low sugar and non-cholesterol content. Lemon can be processed into various products. Lemon peel is used as garnish for food and drinks, dried candy, raw material of lemon powder and pectin. Juice sacs in lemon are used to make concentrated lemon juice and soft drinks.

The critical quality of food is attributed to color, flavor, texture and nutritional value. In fruit and vegetables, color is derived from their natural pigments. The primary pigments consisted of flavonoids (yellow), chlorophylls (green), carotenoids (yellow, orange and red), anthocyanins (red, blue), and betalains (red), gradually change during maturation and ripening process. During storage and additional processing, color degradation, browning is caused by enzymatic and non-enzymatic reaction. As non-enzymatic chemical reactions, sugar related reaction, the Maillard reaction and caramelization and oxidation reaction of ascorbic acid and lipids resulted in food browning (Barret *et.al*, 2010).

As an alternative to chemical analysis, computer based digital camera image analysis can be used for the evaluation of color changes as a non-destructive method. The color analysis using a digital camera is quite useful as it easily acquires the surface information and the color distribution. Application of a HSL color system based on digital camera has been successfully performed. When an image is acquired, the HSL color system will separate this information into three color components (hue, H and saturation, S) and illumination component (lightness, L). Quantity of light as well as uneven lighting or uneven surface shape does not affect to the H and S. Transformation of digital camera image from RGB color system to HSL color system can be perceived because this color change measurements have similar way with human interaction and perception (Motonaga *et.al*, 2004; Hashimoto *et.al*, 2006; Levkowitz *et.al*, 1993).

The shelf life of lemon product is shortened by the time-dependent development of off-flavors, browning, change of colors, and deterioration of nutrients, caused by the oxidative reactions of chemical and nutrient components in the food systems. Consequently,

the food is becoming unattractive to consumers. The combination of drying with pretreatment prior to drying is known to be effective for improving the product quality. Predrying treatment such as blanching and osmotic dehydration is needed for lemon drying in order to avoid shrinkage and color changes.

Blanching in hot water usually applied for fruit and vegetables to increase drying rate and prevent browning (Leeratanarak *et.al*, 2006). Blanching helps the inactivation of enzymes such as polyphenoloxidases (PPO) that cause browning, and phenolase, catalase and peroxidase that are responsible for off-flavors development. Unfortunately blanching cannot prevent shrinkage of final products. Previous research have shown that addition of sugar such as sucrose, trehalose, maltodextrin, maltosyl-trehalose prior to drying are needed for fruit and vegetables in order to avoid browning and damages to tissue structure (Aktas *et.al*, 2006; 2007; Hawa *et.al*, 2011).

In this study, effects of blanching and soaking in a sucrose solution as pre-treatments on the drying of lemon peel were studied. The desorption isotherms of lemon powder, lemon peel and lemon juice were determined by isothermal desorption experiments. Color changes of lemon peel were analysed by using HSL color system developed by Hashimoto. Color changes were observed under two different experimental conditions. The color changes were observed during constant temperature hot air drying experiments. The sample of a constant water content was incubated in a sealed container and then the color was analysed as a function of incubation time. Vacuum and freeze drying experiments were used to prepare different water content of sample prior to incubation experiments. The final appearance such as shrinkage and color changes on dried product were also analyzed.

## 4.2 Materials and method

## 4.2.1 Materials

Lemon (brand Sunkist 4053, USA) were purchased from the local market. Lemon powder (contain trehalose) and lemon juice ("Pokka Lemon 100") were supplied from Pokka Sapporo (Nagoya, Japan). Non-treatment lemon powder were prepared from freeze dried lemon peel by grinding with a blender and sieving through a 500µm-mesh. All other chemicals were of analytical grade.

#### 4.2.2.Methods

#### 4.2.2.1 Preparation of sample

Fresh lemons were washed, separated from their pulps and cut into 2.5 cm length and 0.5 cm width. The sample was placed in saucepan and boiling in hot water (372K) for 5 minutes. Under this condition the sample was not fully cooked.

As a sugar solution, a sucrose solution (40 wt%) was used. Blanched samples were dipped in a sugar solution for 10 minutes. The samples were placed in a freezer (233K) for 1 hour prior to freeze drying (FD), while for vacuum drying (VD) the samples were not frozen.

## 4.2.2.2 Drying experiment

Isothermal drying experiments were performed in a constant air temperature box. This drying equipment has two fans, which circulate the air in the box well, a fan control unit, a heater, a temperature control unit and a digital balance. The relative humidity (RH) was adjusted by silica gels (RH<1%). The air temperature and relative humidity were monitored by the thermometer and hygrometer in the box. The sample was placed on a spiral wire dish covered with a silicon tube. This dish placed on a wire net cage, which was attached to an aluminium dish. The aluminium dish eliminates unwanted vibrations of the wire net cage by the hot air stream. The dish was hanged to an electronic balance placed on the drying box. 4.2.2.3 Drying experiment prior to incubating process

In order to adjust water contents of the sample for the incubation experiments freeze or vacuum drying were performed by using a Freeze dryer (Eyela Freeze Dryer, FD-1000, Tokyo Rikakikai, Japan) for 0.5, 1, 2, 3, and 6 hours at  $223\pm1$ K and  $6.5\pm0.5$ Pa. 4.2.2.4 Isothermal incubation experiments

Dried lemon peel samples were contained in an airtight glass container with a silicon stopper, covered with a plastic film and aluminium foil to avoid light. The container was incubated with a hot block bath (TPB-32, Toyo Seisakisho, Japan) at 333K. The solid mass of the sample ( $W_s$ ) was measured by drying the sample at 378K for 4 hours.

#### 4.2.2.5 Measurement of color changes

Color images of the sample were captured by a digital camera as a function of time during both hot air drying and incubation experiments. All the experiments were performed in triplicate.

#### 4.2.2.6 Color analysis

The experimental setup consisted of a digital camera with 7.1x optical wide zoom lens (Ricoh R10, Ricoh, Tokyo, Japan) and tripod. The camera was fixed 8 cm from the sample plane. Sample was put on a white drafting paper, so that the image background was white. The sample image were recorded as a JPEG format, and then transferred to a PC for the color image processing.

The images were then analyzed with a *Color Tool* software developed by Hashimoto at Mie University to obtain the H, S and L value. The software requires that the background of image should be removed, the pixel size should be lower than 800x800 and the image should be saved in Tiff format. All this process conducted by using Adobe Photoshop CS. H, S and L average values were calculated from 3 data for one sample.

#### 4.2.2.7 Determination of desorption isotherm

Dried peel, lemon powder and lemon juice samples were stored in an airtight plastic container in the presence of salt solutions of known  $a_w$  values at 303K. Then the samples were weighed every 24 hours until the weight loss became less than 2% per 12 hours (Yamamoto *et.al.*, 2002).

The desorption isotherm data were fitted by a three parameter Guggenheim-Anderson-de Boer (GAB) model (Blahovec, 2004; Rahman, 1995; Van den Berg, 1984).

$$X = \frac{CKa_{\rm w}W_{\rm m}}{(1 - Ka_{\rm w})(1 - Ka_{\rm w} + CKa_{\rm w})}$$
(4-1)

 $W_{\rm m}$  implies the water content equivalent to monolayer coverage. C and K are constants related to the binding energies.

#### 4.3 Results and discussion

#### 4.3.1 The effect of pre-treatment on desorption isotherm

Desorption isotherms (lemon peel, lemon powder and lemon juice) are shown in Fig.4-1.



Fig. 4-1. Desorption isotherm of lemon peel, lemon powder and lemon juice

The desorption isotherms of lemon peel, lemon powder and lemon juice show typical food isotherm shape, which can be described well by the GAB equation.

The equilibrium water content for lemon juice were higher compared with lemon peel and lemon powder for higher water activity regions. Lemon juice is quite hygroscopic compared with other lemon product. As lemon powders are also known to be very hygroscopic and sticky, they tend to form agglomerated particles easily (caking).

## 4.3.2 The effect of pre-treatments on isothermal drying

The isothermal drying curve of lemon peels with and without pre-treatment are shown in Fig.4-2. The initial water content of lemon peel dipped in sucrose was lower than that nontreatment one due to osmotic dehydration process. The drying rates decreased after 3 hours. The final water content of lemon peel dipped in a sucrose solution was slightly higher compared with others.



Fig.4-2. Drying curves of lemon peel with or without pretreatment during hot air drying at 318K

Blanching is known to facilitate water removal as the cell structure is partially weakened, which permits easier migration of water. It may also cause starch gelatinization and inactivate polyphenoloxidases that lead to quality degradations. Further possibilities of blanching effects are the collapse to the cell, the decrease in turgor pressure, deformation of the cell walls and even plasmolysis (Leeratanarak *et.al*, 2006; Katsiferis *et.al*, 2008; Moreno-Perez *et.al*, 1996). However, the presence of sugars in lemon peel resulted in low drying rates at the late stage of drying. This is due to slow drying rates of sucrose solutions (Yamamoto *et.al.*, 2002, Pimpaporn *et.al*, 2007).

## 4.3.3 The effect of pre-treatments on color changes during isothermal drying

The surface color of each lemon peel was transformed from the RGB coordinate system to the HSL coordinate system. H value is defined as a color wheel chart, with redpurple at an angle of 0, yellow at  $\pi/2$ , bluish green at  $\pi$  and blue at  $3\pi/2$  rad. The surface color of lemon peel changes from white-yellow to orange-brown, which corresponds to the change of H value from 45 to 25. H value decreases as the browning score increases. Unfortunately, the samples in this study did not show significant changes of the S and L values.

Fig. 4-3. shows that the hue value tends to decrease with increasing time. At the beginning of drying, the sample color was yellow at peel part and white at flavedo part and then turned darker with the progress of drying. The H values of lemon peel dipped in a

sucrose solution were higher than others. The lowest H value was found for non-treatment samples.



Fig.4-3. Hue changes of lemon peel with or without pre-treatment during hot air drying

The non-enzymatic browning was considered as a major cause of color changes of dried lemon peel, since blanching inactivated enzyme that cause color degradation. Hot water blanching prior to drying reduced *a* value (red color) of potato chips, because of the dissolving of reducing sugar, which are the substrates of non-enzymatic browning, Maillard reaction (Leeratanarak *et.al*, 2006).

Application of blanching and addition of sugar such as sucrose and trehalose resulted in less color changes during drying process compared with only blanching. Non-reducing disaccharides such as sucrose and trehalose may protect tissue structures and reduce structural damages. Sucrose and trehalose are non-reducing sugar and does not react with amino acids or proteins as part of Maillard browning (Aktas *et.al*, 2006; 2007; Hawa *et.al*, 2011).

4.3.3.4. The effect of pre-treatments on appearance of lemon peel during isothermal drying

Table 4-1. shows the appearance of lemon peel during hot air drying. Generally the color turned into orange and light brown at the beginning of drying until 3 hours of drying time and gradually became constant until the end of drying.

Time	Hot air drying, 318K			
[hour]	Non-treatment	Blanching	Dipped in 40% sucrose	
0				
1				
2			~	
3				
4				
5		~		
6				

Table 4-1. Photographs of lemon peel with and without pre-treatment in hot air drying

Color changes for samples blanched and dipped in a sucrose solution were much slower compared with non-treatment samples. Shrinkage occurred in all treatment. Shrinkage occurred in early stage of drying and proceeded more rapidly. Shrinkage was not significant at the final stage of drying. Non-treatment sample showed much more shrinkage compared with pre-treatment samples. Blanching resulted in better color retention but did not prevent shrinkage. Lemon peels dipped in a sucrose solution were found to be the best appearance based on color changes and shrinkage.

4.3.3.5. The effect of pre-treatments on color changes and on appearance of lemon peel after FD and VD

In order to understand the effect of water content on color changes, sample were kept in an incubator for 24 hours. Before placing in the incubator, samples were dried to adjust designated water content values.

Drying time	X [kg-water/kg-solid]					
[hour]	Non-trea	atment	Blan	ching		in 40% rose
	FD	VD	FD	VD	FD	VD
0	3.76	3.76	5.41	5.41	3.67	3.67
0.5	3.17	3.18	4.25	4.45	2.26	1.96
1	2.41	1.49	3.78	1.20	1.72	1.29
3	0.55	0.19	0.42	0.17	0.17	0.16
6	0.13	0.11	0.09	0.09	0.10	0.10
12	0.107	0.09	0.08	0.09	0.07	0.09

Table 4-2. Water contents of lemon peel with and without pre-treatment after drying in FD and VD

Hue changes of sample with and without pre-treatments are shown in Fig. 4-4. The appearance of samples during the incubation experiments are summarized in Table 4-3.





Fig. 4-414. Change in hue value of lemon peel during incubation (333K) for samples prepared by FD and VD (a) non-treatment, (b) blanching, (c) dipped in 40% sucrose.
• non-drying, ▲ 3 hour FD, ■ 12 hour FD, △ 3 hour VD, □ 12 hour VD

Fig. 4-4. shows that H value of lemon peel decreased with increase in water content. At low water content the color of sample was found to be more stable. The decrease in H value for blanched and sucrose treated samples was much lower compared with non-treatment samples.

	Drying Time	Incul	pation time at 333 K [l	nour]
	[hour]	0	12	24
	0			
(a)	3	C. Lawrence	and a state of the state	PARAMONE AND
	12		and the second s	State on a fight of
	0			
(b)	3		111 111 1111-1	AND A DESCRIPTION
	12			and the second se
	0			)
(c)	3		and the second s	a start for
	12		And the state	Contra of Street

Table 4-3. Photographs of lemon peel during incubation at 333K. Prior to incubation, samples were prepared by pre-treatment and FD. (a) non-treatment, (b) blanching, (c) dipped in 40% sucrose

Table 4-3 shows that the color degradation became faster when the water content was high. Low water contents prevented color degradation. Dipping in a sucrose solution resulted in better physical properties of appearance compared with non-treated and blanched sample. However, less shrinkage was found for FD samples compared with VD samples. Shrinkage occurred mostly at the beginning of incubation, especially for samples of high moisture content (Table 4-4). Less shrinkage and browning were observed for samples of low water contents (<0.2 kg-water/kg-solid). Similar trends were also found in other samples.

	Incubation time at 333 K [hour]			
	0	12	24	
FD	CONTRACTOR OF	Conte and the los	- Color and a second	
VD	a state of the sta			

Table 4-4. Photographs of lemon peel during incubation at 333K. Prior to incubation, samples were prepared by dipping in 40% sucrose solution and by FD and VD for 12 hours

The final color appearance was quite similar for both freeze and vacuum drying. To obtain better quality of dried product, vacuum drying and freeze drying are good methods. Especially, freeze drying has many advantages for drying of biological materials such as retention of shape, texture and aroma of the original sample (Barta *et.al*, 2012). However, the running cost of freeze drying is much higher compared with hot-air drying or vacuum drying. Freezing process also affects sample color. When material is frozen, the water will form ice crystal. Fast freezing will produce small ice crystal. The present experiments were conducted under a fast freezing condition (233K, 1 hour). The color of small ice crystal was whiter than that of large ice crystals. Small ice crystals tend to scatter more light so that the sample becomes bright because of their small pores (Ceballos *et.al*, 2012).

## 4.4 Conclusions

Effects of blanching and dipping in a sucrose solution as pre-treatment methods of hot air drying of lemon peel on were studied.

The drying rates of samples dipped in a sucrose solution were much lower compared with those of non-treated and blanched samples due to the presence of sugar.

The desorption isotherms of lemon products show typical food isotherm shape, which can be described well by the GAB equation when  $a_w < 0.92$ .

Application of HSL color analysis on color changes of lemon peel has been successfully carried out. The color changes was faster when the water contents were high. The decrease in H value for sampled dipped in a sucrose solution sample were much lower than that for non-treated samples.

Dipping in a sugar solution after blanching and controlling water content on drying may provide better product qualities of dried lemon peel.

#### **CHAPTER 5**

#### **GENERAL CONCLUSION**

A steam blanching increased the drying rate significantly. Dipping in sugar solution for a relatively short time (10 minutes) was effective for obtaining a high quality of dried foods. The combination of blanching and dipping in a sugar solution was found to be a good pre-treatment method for obtaining the dried samples of good color retention and uniform shrinkage.

The drying rates of lemon juice at 303K were much lower than the values for the simulated lemon juice and maltodextrin, especially at low water content regions. The equilibrium water contents determined from the desorption isotherms of lemon juice were similar to the values for the simulated lemon juice and citric acid.

Digital image acquired by a digital camera was processed to obtain the HSL values for color analysis. The browning was well evaluated by the hue values. The color changes (browning) were faster when the water content and temperature were higher. Blanching followed by dipping in a sugar solution was found to be effective to prevent color changes of dried lemon peel.

## LIST OF NOMENCLATURE

А	Drying area	$m^2$
$a_{\rm W}$	water activity	
C	GAB sorption constant related to monolayer properties	
$d_{\rm s}$	pure solid density	$kg/m^3$ $kg^2(m^4s)$
F'	normalized isothermal drying rate	$kg^2(m^4s)$
K	GAB sorption constant related to multilayer properties	
$M_0$	Initial mass (water+solid) of fresh sample (prior to blanching)	kg
$M_T$	Mass after dipped in sugar solution	kg
Rs	thickness of slab	m
SG	solid gain	0⁄0
t	time	S
WL	water loss	0⁄0
W <sub>m</sub>	water content equivalent to a monolayer coverage	kg-water/ kg-dry solid
WR	weight reduction	0⁄0
Ws	solid weight in the absence of water	kg
$W_{ m sugar}$	mass fraction of sugar to the total solid	kg-water/ kg-dry solid
$W_{ m sugarpotato}$	mass fraction of potato to the total solid	kg-water/ kg-dry solid
$Ws_0$	initial dry matter	kg
X	water (moisture) content	kg-water/ kg-dry solid
X <sub>sugar</sub>	equilibrium water content of sugar (single component)	kg-water/ kg-dry solid
$X_{potato}$	equilibrium water content of potato (single component)	kg-water/ kg-dry solid
$X_{ m sugar+potato}$	equilibrium water content of sugar- potato mixture	kg-water/ kg-dry solid
Greek letters		
au'	Normalized time based on the shrinking coordinate system	$m^4s/kg^2$

## LIST OF REFERENCES

- Aktas, T., S. Fujii., Y. Kawano.,S. Yamamoto. 2006. Effect of some osmotic pre-drying treatments on drying kinetics, desorption isotherms and quality of vegetables, 15<sup>th</sup> International Drying Symposium. Budapest. Hungary. pp: 877 – 883.
- Aktas, T., S. Fujii., Y. Kawano., S. Yamamoto. 2007. Effects of pre-treatments of sliced vegetables with trehalose on drying characteristics and quality of dried products. Food and Bioproducts Processing. Trans IChemE. Part C. 85(C3):178 – 183.
- Antonia, G.C. and F.E.X, Murr. 2002. Microscopic analysis of papaya (Carica, papaya L.) osmotically dehydrated. Proceedings of the 13<sup>th</sup> International Drying Simposium, pp:960 967.
- Barret D.M., J.C. Beaulieu., R. Shewfelt. 2010. Color, flavor, texture, and nutritional quality of fresh-cut fruits and vegetables: desirable levels, instrumental and sensory measurement, and the effects of processing. Critical Reviews in Food Science and Nutrition, 50:369–389
- Barta, J., C. Balla., G. Vatai. 2012. Dehydration preservation of fruits, in Handbook of fruits and fruit processing – Second edition, Ed. Sinha, N. K., Sidhu, J.S., Barta, J., Wu, J. S. B., Cano, M. P. Wiley & Sons, Ltd. United Kingdom, pp. 133 – 151.
- Blahovec, J. 2004. Sorption isotherm in materials of biological origin mathematical and physical approach. J. Food Eng. Vol.65. pp: 489 495.
- Ceballos, A. M., G. I. Giraldo., C. E. Orrego. 2012. Effect of freezing rate on quality parameters of freeze dried soursop fruit pulp. Journal of Food Engineering. 111: 360–365.
- Chen X.D., A. S. Mujumdar. 2008. Drying technologies in food processing. Blackwell Publishing Ltd. United Kingdom
- El-Aouar, A.A., P.M. Azoubel., F. E. X. Murr. 2003. Drying kinetics of fresh and osmotically pre-treated papaya (Carica papaya L.). J. Food Eng., 59 : 85–91.
- Eren, I., F. Kaymak-Ertekin. 2007. Optimization of osmotic dehydration of potato using response surface methodology. J. Food Eng. 79: 344–352
- Fujii, S., N.Yoshimoto., S.Yamamoto. 2013. Enzyme Retention during Drying of Amorphous Sugar and Carbohydrate Solutions: Diffusion Model Revisited. Drying Technol., 31, 1-7.
- Fujii, S., N. Yoshimoto, T. Aktas., S. Yamamoto. 2011. Drying of sliced vegetables pretreated with sugar solutions. J. Agricultural Machinery Science. 7: 347-350.
- Garau M.C., S. Simal., A. Femenia., C. Rosello. 2006. Drying of orange skin: drying kinetics modelling and functional properties. Journal of Food Engineering 75: 288 295.
- Chen, H.H., C. E. Hernandez., T-C. Huang; A study of the drying effect on lemon slices using a closed-type solar dryer, Solar Energy., 78, 97-103(2005).
- Hashimoto, A., K. Yasui., M. Takahashi., S. Yonekura., T. Hirozumi., T. Mishima., R. Ito., K. Suehara., T. Kameoka. 2006. Remote monitoring of color of agricultural products in the field using digital camera and the field server. Computers in Agriculture and Natural

Resources. Orlando, Florida: American Society of Agricultural and Biological Engineers.pp. 66 – 71.

- Hawa, L. C., S. Fujii., N.Yoshimoto., T. Aktas, S. Yamamoto. 2012. Drying of sliced vegetables and fruits at relatively high humidities for producing high quality products. Proceedings of the 18th International Drying Symposium. Xiamen, China, X.D.Chen ed., paper no. 183
- Gianfrancesco, A., G.Vuataz., X. Mesnier., V. Meunier. 2012. New methods to assess water diffusion in amorphous matrices during storage and drying. Food Chem., 132, 1664-1670.
- Gianfrancesco, A., X. Mesnier., L. Forny., S. Palzer. 2010. Determination of drying kinetics and water diffusion coefficients in amorphous-crystalline matrices. Proceedings of the 17th International Drying Symposium, Magdeburg, E. Tsotsas, T. Metzger, M. Peglow eds., Vol. 3, pp. 1498-1503.
- Gupta, R. K., P. Kumar., A. Sharma., R. T. Patil. 2011. Color Kinetics of Aonla Shreds with Amalgamated Blanching During Drying. International Journal of Food Properties. 14:1232–1240
- Katsiferis, T., N. Zogzas., V.T. Karathanos. 2008. Mechanical properties and structure of unripe oranges during processing of "spoon sweets". Journal of Food Engineering, 89, 149–155.
- Kawata, S., L.C. Hawa., S. Fujii., N.Yoshimoto., T. Aktas., S. Yamamoto. 2012. Drying rates and desorption isotherms of amorphous sugar solutions containing crystalline materials. Proceedings of the 18th International Drying Symposium, Xiamen, China, X.D.Chen ed., P37.
- Khin, M.M., W. Zhou., S. Y. Yeo. 2007. Mass transfer in the osmotic dehydration of coated apple cubes by using maltodextrin as the coating material and their textural properties. Journal of Food Engineering. 81: 514 522.
- Krokida, M. K., V. T. Karathanos., Z. B Maroulis and D.Marinos-Kouris. 2003. Drying kinetics of some vegetables. J. Food Eng., 59, 391-403.
- Ladaniya, M.S. 2008. Citrus Fruit Biology, Technology and Evaluation. Academic Press Elsevier. Oxford. United Kingdom
- Lang, K.W. and M.P. Steinberg.1980. Calculation of moisture content of a formulated food system to any given water activity. Journal of Food Science. Vol.45. pp: 1228 -1230.
- Leeratanarak N., S. Devahastin., N. Chiewchan. 2006. Drying kinetics and quality of potato chips undergoing different drying techniques. Journal of Food Engineering, 77:635 643.
- Levkowitz, H., G. T. Herman. 1993. GLHS: A generalized lightness, hue and saturation color model. CVGIP: Graphical Models and Image Processing. Vol. 55. No.4. pp: 271 285.
- Martinelli, L, A. L. Gabas, J.Telis-Romero. 2007. Thermodynamic and quality properties of lemon juice powder as affected by maltodextrin and arabic gum. Drying Technol., 25, 2035-2045.

- Moreno-Perez L. F., J. H. Gasson-Lara., E. Ortega-Rivas.1996. Effect of low temperaturelong time blanching on quality of dried sweet potato,. Drying Technology, 14, 1839-1857.
- Morton, J. F.1987. Lemon. In: "Fruits of warm climates", Creative Resource Systems, Winterville, 1987, pp. 160-168. /http://www.hort.purdue.edu/newcrop/morton/lemon.html
- Motonaga, Y., H. Kondou., A. Hashimoto., T.A. Kameoka. 2004. Method of making digital fruit color chart for cultivation management and quality control. Journal of Food, Agriculture & Environment, 2 (3&4), 160-166.
- Murakami, P. F., M. R. Turner., A. K. Van den Berg., P. G. Schaberg. 2005. An instructional guide for leaf color analysis using digital imaging software. Gen. Tech. Rep. NE-327. Newtown Square, PA: U.S. Department of Agriculture, Forest Service, Northeastern Research Station. 33 p.
- Phisut, N. 2012. Factors affecting mass transfer during osmotic dehydration of fruits. International Food Research Journal 19 (1): 7 18.
- Pimpaporn, P., S. Devahastin, N. Chiewchan. 2007. Effects of combined pretreatments on drying kinetics and quality of potato chips undergoing low-pressure superheated steam drying.Journal of Food Engineering 81: 318–329
- Rahman, S. 1995. Food properties handbook. CRC press. Boca Raton.
- Rastogi, N.K., K. S. M. S. Raghavaro. 2004. Mass transfer during osmotic dehydration determination of moisture and solute diffusion coefficients from concentration profiles. Trans IChemE. Part C. 82(C1): 44 48.
- Ross, K.D. 1975. Estimation of water activity in intermediate moisture foods. Food Technology. Vol.29. pp: 26 30.
- Saeed, I.E., K. Sopian., Z. Z. Abidin. 2008. Thin-Layer drying of roselle (I): Mathematical Modeling and Drying Experiments, Agricultural Engineering International: the CIGR Ejournal, Manuscript FP 08 015. Vol. X. September.
- Taheri-Garavand, A., S. Rafiee and A. Keyhani. 2011. Effect of temperature, relative humidity and air velocity on drying kinetics and drying rate of basil leaves. EJEAFChe, 10(4).
- Van den Berg, C. 1984. Description of water activity of foods for engineering purposes by means of the G.A.B model of sorption. Engineering and foods. Ed. By B. M. McKenna. Vol. 1. New York: Elsevier. pp. 311 – 321.
- Yam, K. L., S. E. Papadakis. 2004. A simple digital imaging method for measuring and analyzing color of food surfaces. Journal of Food Engineering 61.pp: 137–142
- Yamamoto, S. 2001. A short-cut method for determining concentration dependent diffusivity in liquid foods and polymer solutions from regular regime drying curves. Drying Technol., 19, 1479-1490.
- Yamamoto, S, T. Saeki, T. Inoshita.2002. Drying of gelled sugar solutions-water diffusion behavior. Chem.Eng.J., 86,179-184.

- Yamamoto, S. 2004. Drying of gelled sugar solutions:water diffusion behavior in "Dehydration of Products of Biological Origin". A.S.Mujumdar ed. Science Publisher. Enfield. pp.165-201.
- Yamamoto, S. 2006. Analysis of water diffusion and enzyme inactivation mechanisms during drying of liquid foods. Japan J. Food Eng., 7, 215-224(2006).
- Zheng, J., F. Zhang., J. Song., M. Lin, J. Kan. 2013. Effect of blanching and drying treatments on quality of bamboo shoot slices. International Journal of Food Science and Technology. 49. pp: 531–540

## LIST OF PUBLICATION

## Papers

1. <u>La Choviya Hawa</u>, Suriah Binti Ali, Sachie Fujii, Noriko Yoshimoto, Shuichi Yamamoto, 'Drying Rates and Desorption Isotherms of Lemon Juice', Japan Journal of Food Engineering, Vol. 15, No. 2, pp. 105 – 108 (2014)

## Proceedings

- 1. <u>La Choviya Hawa</u>, Sachie Fujii, Noriko Yoshimoto, Turkan Aktas, Shuichi Yamamoto, 'Drying of sliced vegetables and fruits at relatively high humidities for producing high quality products, Proceedings of the 18th International Drying Symposium 2012, Paper No.183 (CD)
- 2. Suguru Kawata, <u>La Choviya Hawa</u>, Sachie Fujii, Noriko Yoshimoto, Turkan Aktas, Shuichi Yamamoto, 'Drying rates and desorption isotherms of amorphous sugar solutions containing crystalline materials', Proceedings of the 18th International Drying Symposium 2012, Paper No.181 (CD)
- 3. <u>La Choviya Hawa</u>, Suriah Bnti Ali, Sachie Fujii, Noriko Yoshimoto, Shuichi Yamamoto, 'Effect of pre-treatments on color changes during drying of lemon products', Proceedings of the 19th International Drying Symposium

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