

Evaluation of Drying Behavior of Broccoli (*Brassica oleracea* L.) in Hot air and Microwave Drying Systems

By

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LIST OF SYMBOLS AND ABBREVIATIONS

$\pm$	-	plus or minus	<i>i.e.</i>	-	that is
<	-	less than	kHz	-	kilohertz
>	-	greater than	KMS	-	potassium metabisulphite
ϵ'	-	dielectric constant	L*	-	Whiteness color value, dimensionless
ϵ''	-	dielectric loss factor	m	-	meter
λ	-	wavelength	mm	-	millimeter
%	-	percent	mL	-	milliliter
$^{\circ}\text{C}$	-	degree Celsius	MV	-	microwave
μg	-	micro gram	MAE	-	Microwave assisted extraction
μm	-	micro meter	MC	-	moisture content
Abs	-	absorbance	MHz	-	megahertz
ANOVA	-	Analysis of variance	min	-	minute
a*	-	Redness color value, dimensionless	P_r	-	the proportion of reflected energy
b*	-	Yellowness color value, dimensionless	PLE	-	pressurized liquid extraction
BC	-	before Christ	SFE	-	supercritical fluid extraction
BP	-	homogenate peroxidase isozyme	SSE	-	sum of squared errors of prediction
CCD	-	Central composite design	SRD	-	Surface response design
cm	-	centimeter	tanδ	-	loss tangent or dissipation factor
d_p	-	the penetration depth	HTST	-	high temperature short time
DNA	-	deoxyribonucleic acid	TR-1	-	thioredoxin reductase
E	-	electric field	UHT	-	ultra-high temperature
<i>etc.</i>	-	<i>et cetera</i>	USDA	-	the United States Department of Agriculture
<i>et al.</i>	-	and others	R²	-	R-square (square of correlation coefficients)
FAO	-	Food and Agricultural Organization	RC	-	rehydration capacity
FCC	-	Federal Communications Commission	RF	-	radio-frequency
FDA	-	Food and Drug Administration	RMSE	-	root mean square error
GSL	-	glucosinolates	v/v	-	volume/volume

ABSTRACT

A common and well-accepted green vegetable, broccoli (*Brassica oleracea* L.) plays a significant role in both domestic and international markets. While rich in nutritional compounds, it is difficult to preserve. When dealing with broccoli spoilage issues in Quebec and elsewhere, drying presents a method to extend the shelf life of broccoli. A brief review of drying is followed by a more specific discussion and experimental investigation of broccoli's drying behavior under both hot air and microwave-assisted drying. The results of this investigation served to formulate practical recommendations for the vegetable processing industry.

The drying kinetics under different conditions were determined. Overall drying time was significantly reduced under microwave-assisted (vs. hot air) drying. Under hot air drying temperature had the greatest influence on drying rate, whereas under microwave-assisted drying microwave power had the greatest influence on drying rate. Under microwave drying a thicker layer of small broccoli particles was helpful in achieving rapid dehydration of broccoli. The semi-empirical Midilli-Kucuk equation accurately described broccoli drying kinetics under both hot air and microwave-assisted drying. Dielectric properties of broccoli at different temperatures and under different frequencies were also studied using the open ended coaxial probe technique (Network-Analyzer with a high temperature probe).

While microwave-assisted drying provided a more uniform color appearance of the dried broccoli particles, these were darker and slightly yellower than those produced by hot air drying. A marginally better rehydration capacity was observed after microwave-assisted (vs. hot air) drying. To obtain a higher total phenolic content (TPC), total flavonoid content (TFC), and free radical scavenging ability (measured AEAC) in the final product, a suitable experimental design (Surface Response Design) was used to measure these quality parameters under a range of drying conditions. This data served to develop models to predict TPC, TFC, and free radical scavenging ability under both hot air drying and microwave drying, and determine the optimal drying conditions. Compared to hot air drying, microwave-assisted generated a product with more TPC, less TFC, and similar levels of free radical scavenging ability. Further, several pretreatments were studied to establish how they affected after-drying quality of broccoli.

RÉSUMÉ

Un légume des plus courants, tenu en haute estime par le consommateur, le brocoli (*Brassica oleracea* L.) joue un rôle important dans les marchés intérieurs et internationaux. Quoique riche en éléments nutritifs, il est difficile à conserver. Face au problème de gaspillage du brocoli au Québec et à l'extérieur, le séchage présente une méthode intéressante pour prolonger la durée de conservation du brocoli. Un bref aperçu du séchage en général, puis plus spécifiquement celui du brocoli, est suivi d'une étude expérimentale sur le comportement du brocoli lors d'un séchage par air chaud ou d'un séchage assistée par micro-ondes. Les résultats de cette étude ont permis de formuler des recommandations pratiques pour l'industrie de la transformation des légumes.

La cinétique de séchage du brocoli fut déterminée sous différentes conditions. Lors d'un séchage assisté par micro-ondes, le temps de séchage global fut réduit par rapport à celui obtenu lors de séchage par air chaud. Lors du séchage par air chaud la température de l'air fut la variable influençant le plus fortement le taux de séchage, tandis que pour le séchage assisté par micro-ondes, ce fut la puissance des ondes. Lors du séchage assisté par micro-ondes une couche plus épaisse de brocoli permit une déshydratation rapide du brocoli. L'équation du modèle semi-empirique Midilli-Kucuk décrivit bien la cinétique de séchage du brocoli par air chaud ainsi que celui du procédé assisté par micro-ondes. Grâce à un analyseur de réseau, les propriétés diélectriques du brocoli à différentes températures et fréquences de micro-ondes furent évaluées.

Quoique le séchage assisté par micro-ondes produisit des morceaux de brocoli sec d'une couleur plus uniforme, ceux-ci étaient plus foncés et plus jaunes que ceux produits par un séchage à l'air chaud. Les morceaux de brocoli secs obtenus par séchage assisté par micro-ondes eurent une capacité de réhydratation à peine meilleure que ceux produits par un séchage à l'air chaud. Afin que le produit final ait des teneurs totales en composés phénoliques et flavonoïdes (TTP et TTF, respectivement) élevées, ainsi qu'une capacité à piéger les radicaux libres (évaluée par AEAC) supérieure à la norme, une méthodologie expérimentale appropriée fut mise en place pour mesurer ces paramètres de qualité sous une gamme de conditions de séchage. Ces données servirent à produire des modèles permettant de prédire le TTP, TTF et la capacité à piéger les radicaux libres pour chacun des systèmes de séchage, et ainsi de déterminer les conditions de transformation optimales. Comparé au séchage à l'air chaud, le séchage assisté par micro-ondes généra un produit avec une teneur plus élevée en TTP, plus basse en TTF, et semblable quant à la capacité à piéger

les radicaux libres. De plus, plusieurs traitements préalables furent étudiés quant à leur habilité à modifier la qualité après-séchage du brocoli.

Chapter I

General Introduction

1.1 Importance of broccoli

Broccoli (*Brassica Oleracea L.*) is a common and welcomed green vegetable in the *Brassicaceae* family, which is edible for its stem and head. Fresh broccoli can be eaten raw, boiled, steamed or cooked. This plant consists of a swelled head which is clustered of green buds, and thick fleshy stalk. It is drawing increasingly wide attention owing to its health-promoting properties.

Broccoli was originally cultivated in the ancient Italy and then it was transported to England from Northern Mediterranean region in the mid-18th century. Currently it is grown and consumed worldwide. The top ten countries which produce broccoli are China, India, Italy, Mexico, France, Poland, United States, Pakistan, Germany, and Egypt in 2012 (FAO,2012). The cultivation of broccoli is important in both developing and developed countries to fulfill economic and health aspects in their domestic and international markets.

Different kinds of nutrients are abundant in broccoli. Broccoli contains a high level of vitamins, especially vitamin C, minerals, bioactive compounds, including flavonoids, carotenoids, phenolics, and dietary fiber. According to statistics from the United States Department of Agriculture (USDA, <http://www.nal.usda.gov/>), fiber content of broccoli is not merely almost highest among green vegetables, but broccoli also contains a high level of vitamin C which is 75% more than an equal weight of oranges. One medium stalk (148 g) of broccoli can provide 200% of the daily recommended intake of vitamin C, 16% of recommended intake of dietary fiber, and 10% of recommended intake of vitamin A in the form of beta-carotene. What deserves to notice is that the nutrient content may vary based on different cultivation condition, storage period and cook method. In recent years, broccoli is becoming a superstar vegetable notable for its bioactive and anti-cancer properties. Various *in vitro* and *in vivo* assays have confirmed the effects of flavonoid compounds in broccoli to present the potential of high antioxidant activity (Rice-Evans et al., 1995), anti-mutagenic activity (Huang &

Ferraro, 1992) and even being utilized as vasodilators (Cheng et al., 1993) or platelet disaggregators (Gryglewski et al., 1987). In conclusion, broccoli contains rich nutrients and shows superior health-promoting properties; and it belongs undoubtedly to healthy food category.

1.2 Microwave drying

Broccoli is one kind of perishable vegetable which is difficult to preserve as fresh for a long time because of its high level of moisture content. Drying, or dehydration, is a significant step in no matter preservation or any other following processing steps of broccoli. The moisture level of food materials is reduced by drying process in order to extend their shelf life. Therefore numerous drying methods have been invented and applied in food industry such as hot air drying, solar drying, freeze drying, fluidized bed drying, osmotic drying, far infrared drying, vacuum drying, *etc.*

Microwaves are electromagnetic waves which range between 0.3 *GHz* and 300 *GHz*. The most popular frequencies used are 915 *MHz* in industrial food processing applications and 2450 *MHz* in domestic food processing applications. It is different from hot air heating of which heat is transferred from the surface to the interior of the material; instead microwave generates heat inside food material caused by the molecule rotation under applied microwave field. The electromagnetic energy is converted into heat by molecular rotation then the moisture content of material is vaporized. Microwave drying is used interchangeably with microwave assisted convective drying in this thesis. There exists extensive body of research in the area of microwave drying techniques, focusing on diverse fruits and vegetables including: parsley (Soysal, 2004), carrot (Sutar & Prasad, 2007), apple (Wang et al., 2007), eggplant (Ertekin & Yaldiz, 2004), spinach (Karaaslan & Tuncer, 2008), banana (Maskan, 2000), grapes (Tulasidas et al., 1995), *etc.* However, data is still currently scarce on microwave drying of broccoli. The application of introducing microwaves into drying techniques could offer an alternative and noteworthy contribution to the vegetable processing industry with evident advantages.

1.3 Problem statements and possible solutions

1.3.1 Food loss and waste

The issue of food loss and waste has become one of the most severe concerns throughout the world. About 30 to 40% of food in both developing and developed worlds is roughly lost to waste, whereas the reasons are not quite similar. North America and Oceania stand the highest with 1520 *kcal* per person per day lost or wasted from farm to fork among all regions (Lipinski et al., 2013). In some developing countries, food losses arise chiefly from the absence of proper food-chain infrastructure and the lack of knowledge about postharvest and storage technologies on the farm; while in the developed world, food, especially fruits and vegetables, is discarded during retail, food service and home stages which have grown dramatically in recent years (Godfray et al., 2010). This food loss and waste issue not only brings the inefficient use of natural resources but may also cause pollution and hygiene problems.

Towards the goal of controlling food loss problem, different strategies are required. Public investments in transport and storage infrastructure would reduce the opportunities for spoilage of raw food materials. An intact and effective information net between farmers, distributors and consumers needs to be established for a better communication and cooperation. Governments have the responsibility to promote a sustainable life style and attitude towards food by advocacy, education or possible legislation. Optimization of the existing machine and process, innovation of new food storage and processing system and study of postharvest storage technologies are also mandatory.

1.3.2 Broccoli waste

Broccoli is not only a kind of fresh vegetable that is apt to spoil under improper preservation, which may cause waste issue. In North America, the large scale production and Industrial processing of broccoli leads to huge amounts of byproducts, such as leaves, stems, and florets which do not meet the required quality properties for fresh markets. Not with standing a small amount of broccoli waste is treated as forage, the rest is normally discarded as solid waste which may cause a pollution problem upon degradation of broccoli waste. We can

assume to exploit this highly available broccoli processing waste as a potential source for developing value-added products. For example, a method was proposed to derive and purify homogenate peroxidase isozyme (BP) from broccoli stems discarded from industrial processing wastes (Duarte-Vázquez et al., 2007). Therefore, broccoli waste can also be a possible source of fiber, biomass, bioactive compounds, etc. To develop byproducts from the broccoli waste, dehydration or drying is a vital step needed for preservations without losing quality.

1.3.3 Microwave drying technique

However, conventional drying methods on broccoli have the problems of long processing time and low energy efficiency in addition to loss of quality of food products such as undesirable color, flavor, and reduced nutrient contents. Microwave drying is therefore an effective way to reduce drying time and improve the product quality resulting from a different drying principle compared to the conventional drying method. A feasible drying method and successful microwave drying system relies on the basic experimental information. The primary knowledge of drying behavior of broccoli under hot air and microwave drying is important in order to verify the possibility of microwave drying and evaluate the attributes of these two drying methods.

1.4 Objective of this study

Dehydration is a vital process in different steps of food manufacturing. It is expected to prolong the shelf-life of broccoli, to counter the problem of insufficiency of fresh vegetable during long distance voyage, to reuse broccoli waste and develop value-added byproducts in vegetable industry and to be used as ingredients in convenience food in order to fulfil the emerging demand of dried vegetable products at the market place.

The main objective of this study is to assess drying behavior, dielectric properties and nutritional status of broccoli under two different drying methods. A brief review of drying is followed by a more specific discussion and experimental investigation of broccoli's drying behavior under both hot air and microwave-assisted drying. The experimental design is based

on a microwave assisted hot air drying system, where microwave power can be adjusted to maintain the core temperature of samples as per the level of parameter established in the design. Drying behavior, including moisture ratio curve, drying rate curve, modeling of drying curve and after-drying property evaluation, including color, rehydration capacity, are to be obtained. Dielectric properties of broccoli under different temperatures and frequencies are to be determined to understand drying behavior of broccoli in an applied microwave field. To analyze the effect of drying temperature, broccoli bed thickness condition on bioactive compounds of broccoli under both hot air drying and microwave drying, surface response design (SRD) is to be established to get the maximum amount of total phenolic content (TPC), total flavonoid content (TFC) and free radical scavenging ability (represented as AEAC) of products. Mathematical models are to be established from the experimental data or predicting drying behavior and nutrient contents under different temperatures and thicknesses under hot air drying and microwave drying. Several pretreatments are to be studied before dehydration process in order to seek a better quality product. At the end it would be necessary to arrive at best treatment condition. The results of this study are to serve to formulate practical recommendations for the vegetable processing industry.

Chapter II

Literature Review

2.1 Broccoli general introduction

Broccoli (*Brassica Oleracea* L.) is a typical brassica vegetable in the *Brassicaceae* family which includes broccoli, cauliflower, cabbage, etc. These vegetables attract people's attention in recent days owing to its health-promoting properties. The name, broccoli, originated from Italy, referring to 'the flowering crest of a cabbage' in Italian. Morphologically, sprouted broccoli resembles cauliflower. This plant forms a swelled head, consisting of green buds, and thick fleshy flower stalks. Normally, the terminal head looks green in color, rather loose and the flower stalks are relatively larger than cauliflower. Both spouts with bud clusters and stalk can be consumed as food.

Wide coverage of original works on agriculture, together with poetry and literary quotations documented the vivid presence of broccoli in the ancient Roman culture, which testified the cultivation of broccoli in the Northern Mediterranean since around 6th century BC (Maggioni et al., 2010). Broccoli was brought to England from Antwerp in the mid-18th century by Peter Scheemakers. This type of vegetable was introduced into the United States by Italian immigrants and didn't become popular until the 1920s.

2.2 Importance of broccoli

2.2.1 Economic benefits of broccoli

Broccoli and cauliflower production is one of the important fresh vegetable sources in the world. China and India are the two largest export country according to Food and Agricultural Organization (FAO) statistics. Canada is reported to have 1265 farms, 4155 hectares land to produce broccoli according to 2011 Census of Agriculture in the category of vegetables (excluding greenhouse vegetables) in Statistics Canada. The top ten cauliflowers and broccoli producers (including Canada) are shown below (Table 2.1):

Table 2.1 Top ten cauliflowers and broccoli producers in 2012

No.	COUNTRY	PRODUCTION (TONNES)	%SHARE
1	China	9,500,000	44.67
2	India	7,000,000	32.92
3	Italy	414,142	1.95
4	Mexico	397,408	1.87
5	France	344,414	1.62
6	Poland	306,776	1.44
7	United States	303,450	1.43
8	Pakistan	224,000	1.05
9	Germany	176,692	0.83
10	Egypt	171,088	0.8
35	Canada	30,599	0.14
	world total	18,837,970	

Source: International Production of Cauliflowers and Broccoli, Food & Agricultural Organization (FAO), 2012

As broccoli can be consumed both as fresh and processed food, it is regarded as a dual use vegetable. Typically, broccoli is processed as dried or frozen for retail sale, or canned for instant soup. Broccoli is generally grown for processing under contract between growers and processors, although processors often purchase raw broccoli when fresh market prices are low. By the booming number of health-conscious consumers, who prefer salad, side dish, entrée component, or a nutritious dietary supplement, broccoli offers great advantage and hence enhances its share of the market. Taking the American broccoli market as example, fresh and processed broccoli consumption in US has followed an apparent increasing trend over the last two decades (Figure 2.1). The leading export market for U.S. broccoli is Canada, which accounts for 53 percent of the value of U.S. broccoli exports (Boriss & Brunke, 2005).

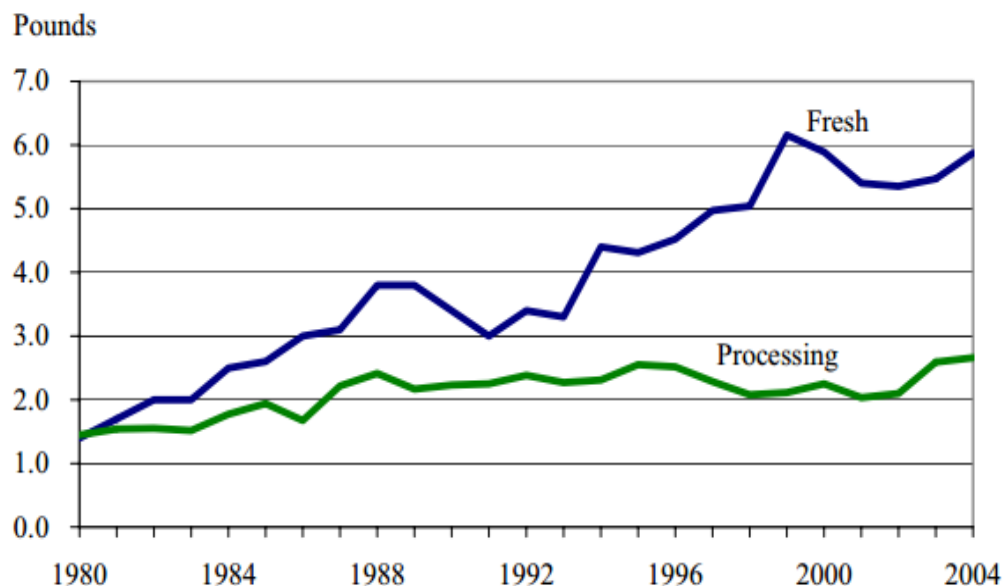


Figure 2.1 U.S. Per Capita Consumption of broccoli fresh and used for processing

Source: USDA Economic Research Service Vegetable and Melons Yearbook (Boriss & Brunke, 2005)

Broccoli industry is playing a more important role in not only in North American market but also in the worldwide trade. The increase in broccoli consumption in international market is good news to growers, processors and consumers. This trend can provide growers and processors increasing opportunities with considerable incomes and profits in both developed and developing countries and can help promote a healthier diet style to consumers.

2.2.2 Health benefits of broccoli

Broccoli is accepted as a nutrient-abundant vegetable not merely because it contains rich vitamins, minerals, and dietary fiber content but also inasmuch as the presence of bio-active compounds, like phenolics, glucosinolates, and sulforaphane, *etc.*, which have been confirmed by researchers to be beneficial to human health (Herr & Büchler, 2010; Mahn & Reyes, 2012; Plumb et al., 1997).

2.2.2.1 Basic Chemical composition

Broccoli contains diverse basic nutrients, such as protein, lipid, carbohydrates, vitamins and minerals. The basic nutritional value of broccoli is shown in Table 2.2:

Table 2.2 The nutritional value of broccoli per 100 g

NUTRIENT	UNIT	VALUE
WATER	g	89.3
ENERGY	kcal	34.0
PROTEIN	g	2.82
CARBOHYDRATE, BY DIFFERENCE	g	6.64
FIBER, TOTAL DIETARY	g	2.60
SUGARS, TOTAL	g	1.70
MINERALS		
CALCIUM, CA	mg	47.0
IRON, FE	mg	0.730
MAGNESIUM, MG	mg	21.0
PHOSPHORUS, P	mg	66.0
POTASSIUM, K	mg	316
SODIUM, NA	mg	33.0
ZINC, ZN	mg	0.410
VITAMINS		
VITAMIN C, TOTAL ASCORBIC ACID	mg	89.2
THIAMIN	mg	0.0710
RIBOFLAVIN	mg	0.117
NIACIN	mg	0.639
VITAMIN B-6	mg	0.175
FOLATE, DFE	µg	63.0
VITAMIN A, RAE	µg	31.0
VITAMIN E (ALPHA-TOCOPHEROL)	mg	0.780
VITAMIN K (PHYLLOQUINONE)	µg	101.6
LIPIDS	g	0.370
FATTY ACIDS, TOTAL SATURATED	g	0.0390
FATTY ACIDS, TOTAL MONOUNSATURATED	g	0.0110
FATTY ACIDS, TOTAL POLYUNSATURATED	g	0.0380

Source: USDA (United States Department of Agriculture) National Nutrient Database for Standard Reference, 2015

Broccoli, consumed raw or as value-added products, is considered to be associated with well-being life style at the current time. According to USDA's nutrition information, broccoli belongs not only to one of the highest-fiber-content green vegetables, but it also contains a high level of vitamin C which is 75% more than an equal weight of orange. One medium stalk (148 g) of broccoli can provide 200% of the daily recommended intake of vitamin C, 16% of recommended intake of dietary fiber, and 10% of recommended intake of vitamin A in the form of beta-carotene. Moreover, other nutrients, such as folate, potassium, calcium (6% of daily need), and iron (4% of daily need), are found in broccoli as well (Lucier, 1999).

2.2.2.2 Bioactive nutrients in broccoli

Broccoli shows excellent health-promoting properties because of its high content of antioxidant and anticarcinogenic compounds. Among the bioactive compounds that have beneficial effects on human health system, polyphenols, glucosinolates, sulforaphane and some special minerals such as selenium has drawn attention from many researchers.

Phenolics, which can be classified as phenolic acids, flavonoids, stilbenes and lignans based on their structures, are secondary metabolites participating in the defense against pathogens and ultraviolet in plant tissues. A scholar (Vinson et al., 1998) measured the amount and percentage of conjugated and free phenols in 23 vegetables. Among them broccoli ranked 8th in terms of phenol antioxidant index, which represented quantity and quality of present antioxidants. Furthermore, the existence of two flavonol glycosides (quercetin 3-O-sophoroside and kaempferol 3-O-sophoroside) and four hydroxycinnamic acid esters ((1,2'-disinapoyl-2-feruloyl gentiobiose, 1-sinapoyl-2-feruloyl gentiobiose, 1,2,2'-trisinapoyl gentiobiose and 1,2-disinapoyl gentiobiose) in broccoli florets were proven and the relationship between their antioxidant properties and chemical structure was testified (Plumb et al., 1997; Price et al., 1998). Structures of these compounds, characterized as aromatic rings substituted with several hydroxyl groups, are shown in Figure 2.2. Polyphenols exhibit free radical scavenging and metal chelating activities to protect cells from oxidative damage so that they are considered as potent antioxidants. Intake of phenol compounds can lead to the reduction of risk to develop degenerative diseases activated by oxidative stress (D Archivio et al., 2007). Some polyphenols,

specifically flavonoids, suppress the enzymes which are responsible for the metabolism of neurotransmitters and certain human hormones. Consequently, intake of flavonoids may prevent the development of neurodegenerative, cardiovascular diseases, and some hormone related cancers (Zhu, 2002).

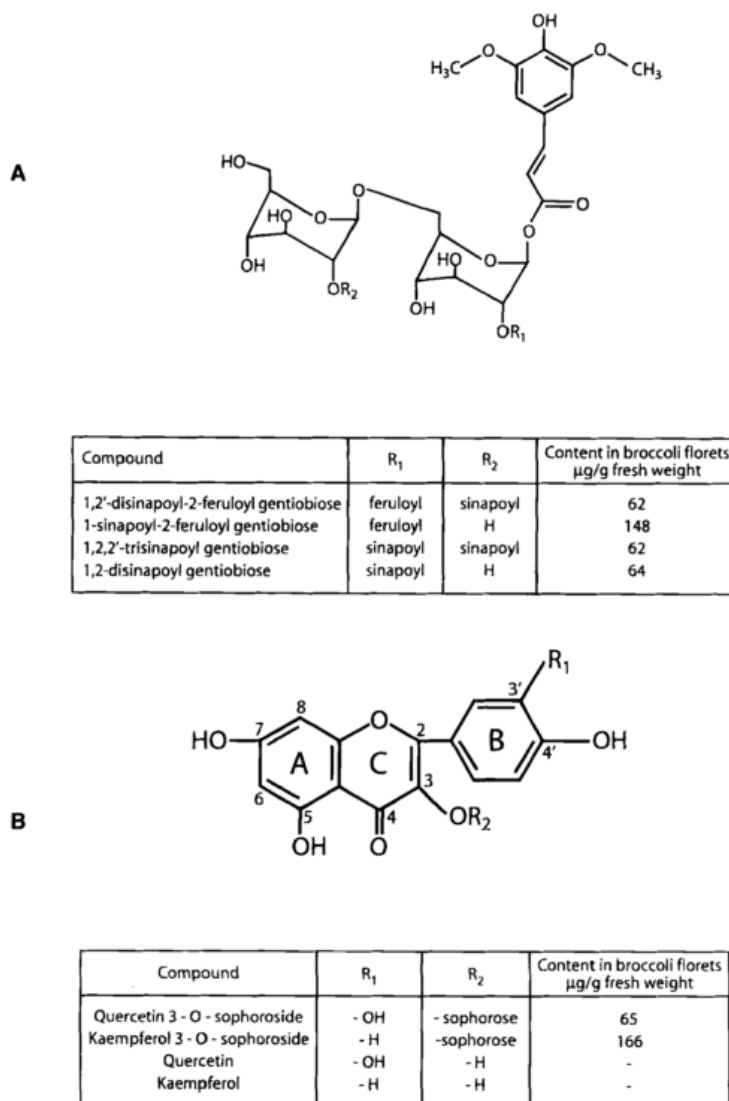


Figure 2.2. (A) Structure of the four hydroxycinnamic acid esters isolated from broccoli. (B) Structure of the two flavonol glycosides isolated from broccoli and their respective aglycones (Plumb et al., 1997).

Glucosinolates (GSL) are a group of secondary metabolites found in cruciferous vegetables such as cabbage, broccoli, cauliflower and watercress. Glucosinolates contribute to the pungent odor and taste when pungent plants are chewed, cut or otherwise damaged. These natural chemicals were considered not only as defense against pests and diseases, but also to contribute to the health beneficial properties in cruciferous vegetables. The basic structure of GSL is illustrated in Figure 2.3. It consists of a β -D-thioglucose group, a sulphonated oxime moiety and a side chain derived from methionine, an aromatic or a branched amino acid (Moreno et al., 2006). Processed by the enzyme myrosinase, GSL can be converted into isothiocyanates as breakdown products. Among these isothiocyanates found in broccoli, sulforaphane is the major type, coming from the hydrolysis of glucoraphanin by myrosinase. Several *in vitro* and *in vivo* studies demonstrated the cancer protective effect of GSL and isothiocyanates, specifically sulforaphane (Fenwick et al., 1982; Johnson, 2002). GSL has the ability to suppress cancer cell division thus enhancing apoptosis which controlled cell death of pre-cancerous cells containing damaged DNA (Conaway et al., 2002). Sulforaphane presents excellent anticarcinogenic properties by modifying detoxification routes, which results in increases in the excretion of carcinogens and the activation of procarcinogens (Zhang & Talalay, 1998). Besides, isothiocyanates together with selenium can up-regulate the expression and activity of thioredoxin reductase (TR-1) in humans (Campbell et al., 2007). In spite of the high amount of bioactive compounds in broccoli, about four fifth of these compounds will be lost during boiling, which needs to be taken into consideration when calculating the dietary intake (Price et al., 1998). Also it suggests that suitable processing methods are essential for the consumption of broccoli.

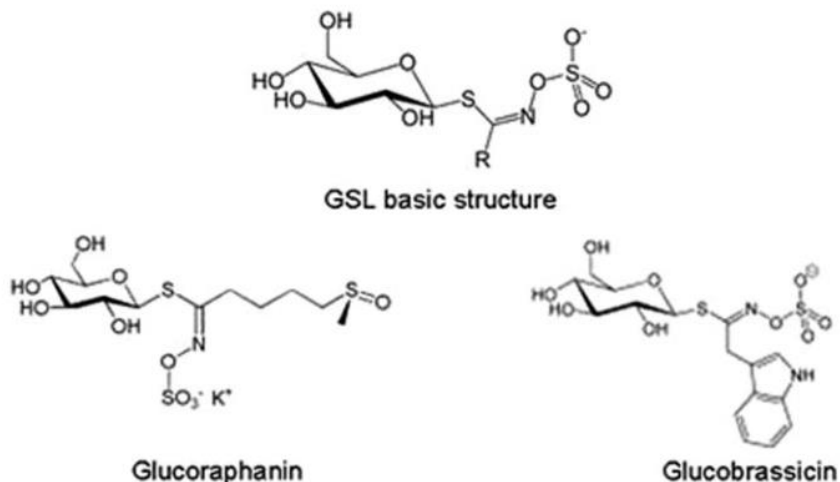


Figure 2.3. General structure of glucosinolates (GSL) and structure of the main GSL found in broccoli (Moreno et al., 2006).

Some special minerals, as selenium, derived from broccoli, also show beneficial bio-active properties. Selenium is capable of accumulation in broccoli, just as other members in the *Brassicaceae* family. Acting as the cellular antioxidant, selenium in broccoli has been linked to reduction in the incidence of certain types of cancer and to the improvement of the overall health status as well (Mahn & Reyes, 2012). A deficient metabolic status of Se brings about a higher risk of developing different kinds of cardiovascular diseases and cancers (Witte et al., 2001).

2.2.3 Effect of processing on bioactive compounds of broccoli

Broccoli can be consumed as fresh vegetable but more likely as processed food. Processing is expected to influence the content, activity and bioavailability of bioactive compounds (Nicoli et al., 1999). Various processing methods, like freezing, blanching, cooking, drying, microwave processing, may lead to desirable or undesirable changes in foods.

Different blanching pretreatments, which are generally in the form of hydrothermal process but in a shorter processing time, were applied to broccoli stems before drying, and it is

found that firmness and chlorophyll content was impaired (Sanjuan et al., 2000). Recently, it was reported that hydrothermal treatment of broccoli florets negatively affected its antioxidant properties (Gawlik-Dziki, 2008); on the other hand, *Roy et al.*(2009) reported that steam processed broccoli showed a relatively higher antioxidant capability because of the significantly increase in extractability of phenols and flavonoids.

Freezing is another common processing method both in pretreatment and preservation, which extends the storage time to keep nutritional and sensorial properties of raw materials. A 58.4% decrease in polyphenols content and a 12.4% decrease in antioxidant activity between fresh and frozen broccoli were observed by *Ninfali and Bacchiocca* (2003). However, no obvious change of glucosinolates content was found in frozen broccoli (Cieřlik et al., 2007).

The effect of dehydration and drying processing on the bioactive compounds of broccoli hasn't been well investigated yet. 50-65°C drying process of intact broccoli maintained the original GSL content and the myrosinase activity; however when broccoli was rehydrated, glucosinolates were hydrolyzed (Rosa, 1997). Another study was carried out to investigate the effect of temperature (50-100°C) and air flow rate (1.20-2.25 m/s) in a pilot tray dryer on the content and activity of bioactive compounds in broccoli. Temperature was found to have a negative effect on the total polyphenol content while air rate was considered to show a positive effect on the antioxidant activity of dehydrated broccoli. The main conclusion of the authors was that the highest antioxidant activity of broccoli was kept under high-temperature, and short-time dehydration processes (Mrkic et al., 2006). Until now, studies have still insufficiently been done to address the effect of operating conditions in microwave, fluidized-bed and freeze drying process on bioactive compounds of broccoli as noted in the literature. Additional researches on this subject are required in order to establish a modified processing condition by which broccoli is developed better as functional food.

2.3 Basic introduction of drying process

Food drying, or dehydration, is one of the essential methods in the domain of food preservation throughout human history. Today the dehydration section becomes a large unit operation widely used in food industry worldwide. The term dehydration describes a process whereby water in foodstuff gets removed to a relatively low level, as a result of the application of heat or other mechanism. The main reason to dry food is to extend its shelf life compared to fresh material. By reducing the moisture, or inhibiting water activity, dehydration restrains the development and growth of spoilage and pathogenic microorganisms, and reduces the activity of enzymes and the rate of other undesirable chemical reaction which deteriorate the quality of food. Moreover, weight and volume of the food product also minimized so that it saves the cost of packaging, handling, storage and transportation.

Various methods of drying have been developed for different purposes, and each of them has its own characteristics. Drying methods include convective air (cabinet, tunnel, fluidized bed, thin layer), solar, microwave, far infrared, spray, drum, vacuum, freeze, foam mat, osmotic and other novel dehydration methods. The most common and conventional way of broccoli drying is the hot air dehydration method with the benefit of low cost, easy operation and convenience. Nevertheless, conventional methods may have disadvantages which cannot be neglected, especially while considering the long operation time and high cost of energy compared to other new-born dehydration techniques. The long dehydration time deteriorates properties of products, particularly those ones which are sensitive to high temperature.

2.3.1 Drying characteristics

In order to understand drying characteristics of material, a thin-layer model system is needed to be established. It is assumed that there is a thin slab material which consists of an inert solid wetted with pure water to be placed in a current of heated air during drying. Attributes including temperature, humidity, and velocity of the ambient air are considered constant. It is also hypothesized that all the heat is transferred to the solid from the air by convection and that drying takes place from the interfacing face only. The moisture content

plotted against time is ideally presented in Figure 2.4, from which it can be seen that several stages or periods exist in drying curve.

The first period is called equilibration or settling down period. This stage is the beginning of drying process and usually very short compared to the total drying time. The second period is normally known as the constant rate period. The surface of solid is saturated with water throughout this period. Water from within the solid moves towards the surface which was kept in a saturated state during the evaporation of the water around surface. In this period, the drying rate is supposed to remain constant, and so as the temperature of material is therefore at a constant value corresponding to the wet bulb temperature of the air. After this period, as drying proceeds at some point, the movement of water to the surface is not enough to maintain the surface in a saturated condition. The break of equilibrium at the surface leads to a decline of the drying rate. This third part of drying is called falling rate period. The temperature at the surface of the solid rises and approaches to the dry bulb temperature of the air from the critical point, and drying is near completion. What deserves to be noticed is that some heat damage to the product is likely to occur in this period.

Besides the conventional theory, some scholars also claimed to have identified two or more falling rate periods where points of inflexion in the curve may occur. Drying generally takes place under the falling period in applications. During this period, drying rate is governed by internal factors which influence the movement of moisture within the solid rather than external factors, such as the velocity of the air, of which influence are reduced compared to the constant rate period.

The best known model to predict drying curve in falling rate period is called *Fick's* second law of diffusion which is based on the assumption that a particular mechanism of moisture movement within the solid prevails. A well-known solution to this law is represented by Eq.2.1

$$\frac{W-W_e}{W_c-W_e} = \frac{8}{\pi^2} \left[\exp \left[-Dt \left(\frac{\pi}{2l} \right)^2 \right] \right] \quad \dots \text{(Eq.2.1)}$$

Where W (wet basis) is the average moisture content at time t , W_e (wet basis) is the equilibrium moisture content, W_c (wet basis) is the moisture content at the start of the falling rate period, D is the liquid diffusivity, and l is the thickness of the slab

Other factors may affect the fitness of models in practical drying applications compared to simplified drying models. For example, shrinkage alters the dimensions of foodstuff. The presence of cell walls of plant products can affect the moisture content within the solids. Additionally, the density and porosity of the food material may change during drying. Along with moisture change, some thermal properties of the food material, such as specific heat and thermal conductivity, may also change. A phenomenon known as case hardening may occur when soluble substances, such as sugars and salts, accumulate at the drying surface when the water evaporates at the surface. Considering these factors, the diffusion theory mentioned above had only limited success in modeling falling rate drying (Brennan & Grandison, 2012).

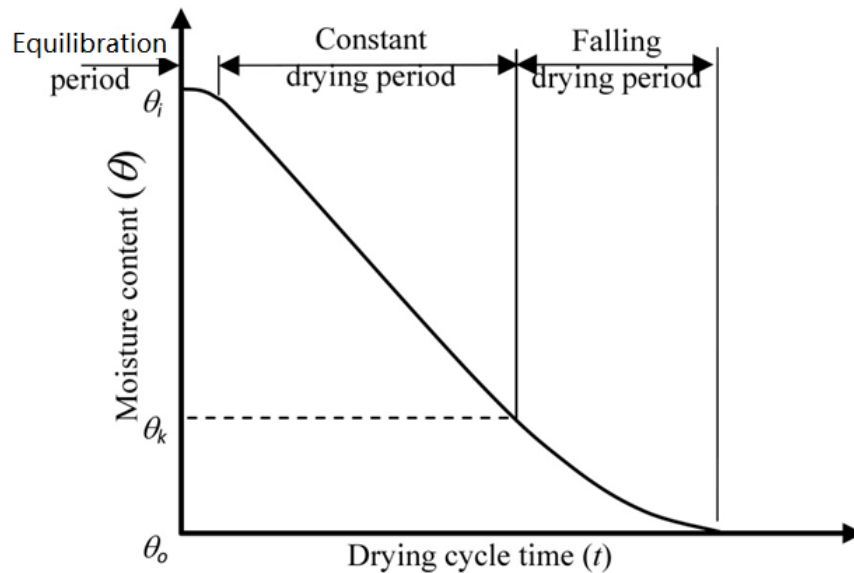


Figure 2.4. Typical moisture drying curve, showing moisture content vs. Time in the dryer and the various stages in the drying process: equilibration period, constant drying period and falling drying period

2.4 Microwave drying

2.4.1 Microwave (MW) definition and introduction

Microwaves are electromagnetic waves made up of two oscillating perpendicular fields: electrical field and magnetic field. Their frequencies are located between 300 *MHz* and 300 *GHz*. Correspondingly, microwave wavelengths ranges from 1 mm to 1 m, section of the electromagnetic spectrum as shown in Figure 2.5. In North America, only three microwave (915, 2450, 5800 *MHz*) and three radio frequencies (13.56, 27.12, 40.68 *MHz*) are permitted by the Federal Communications Commission (FCC) for dielectric heating applications (Venkatesh & Raghavan, 2004). The most popular frequencies used are 915 *MHz* and 2450 *MHz*. 915 *MHz* is widely used in industrial food processing applications whereas 2450 *MHz* is generally used for domestic applications (Ryynänen, 2002). Generally speaking, the terms microwave and dielectrics can be used interchangeably in this thesis.

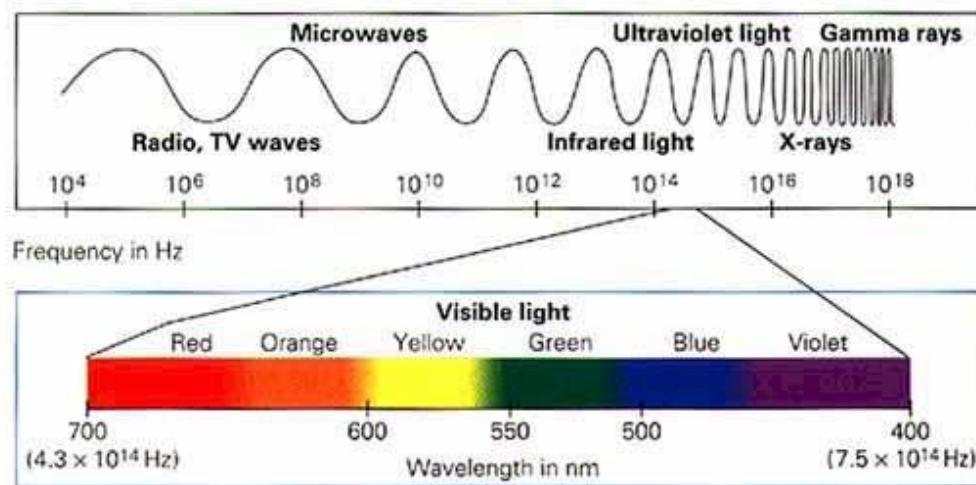


Figure 2.5. The Electromagnetic Spectrum

(Source: ishareimage.com)

All bodies above absolute zero temperature emit electromagnetic waves, which are characterized by frequency and wavelength. An illustration of plane monochromatic electromagnetic wave is shown in Figure 2.6. An electric field (E , V/m) and a magnetic field (H ,

A/m) act perpendicular to each other. They travel at a velocity (C_0) of about 3.0×10^8 m/s analogous to light.

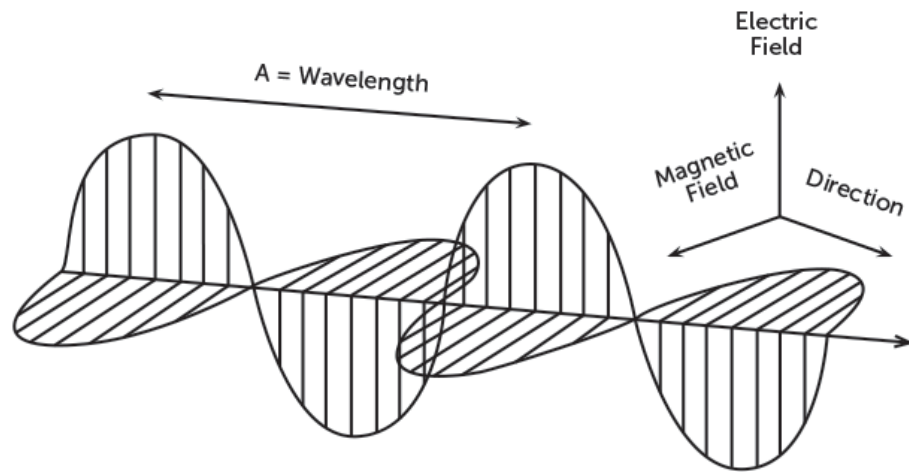


Figure 2.6. Diagrammatic Illustration of a Plane Electromagnetic Wave

2.4.2 Heating principle of MW

Microwaves can be treated as information carriers or as energy vectors. This second application is based on the different characteristics of materials. Accordingly, materials are divided into three kinds: transparent, reflecting and absorbing. Absorbing materials including moist food are able to convert microwave energy into heat.

Two main energy conversion mechanisms are dipolar rotation and ionic polarization (or conduction). Water, the major component in fresh agri-food, is a typical dipolar molecule. In an oscillating field like microwave field, dipole molecules try to align themselves with the changing field, which results in the generation of internal molecular frictional heat. Other nonpolar molecules behave the same way but less in magnitude in terms of heat generation as dipolar if they are asymmetrically charged. The heat generated depends primarily on three variables: the intensity of applied field, its frequency, and the dielectric loss factor of the medium. MW heating is also affected by the state of the constituents, whether they are bound or free, *e.g.*, bound ions have much lower microwave absorptivity. For dipole rotational heating, the

conductivity (σ_0) and the heating rate could respectively be expressed by the following equations (Hui, 2008; Owusu-Ansah, 1991)

$$\sigma_0 = 2\pi f \varepsilon \tan \delta \quad \dots \text{(Eq.2.2)}$$

Where f = frequency of the field; $\tan \delta$ = loss tangent.

The heating rate for dipolar rotation is

$$\frac{P_v}{V_v} = kE^2 f \varepsilon \tan \delta \quad \text{Or} \quad \frac{P_v}{V_v} = kE^2 f \varepsilon'' \quad \dots \text{(Eq.2.3)}$$

Where

P_v = power; V_v = volume of material; k = constant dependent upon the units of measurement used; E = electric field strength, in volts per unit distance; f = frequency; ε = relative dielectric constant; $\tan \delta$ = loss tangent or dissipation factor; ε'' = loss factor

In ionic conduction, ionized compounds randomly collide with non-ionized groups within an electric field. The kinetic energy of these ions are transmitted as heat by collisions. The heating rate due to ionic conduction can be expressed as (Hui, 2008; Owusu-Ansah, 1991)

$$\frac{P_\mu}{V_\mu} = E^2 q n \mu \quad \dots \text{(Eq.2.4)}$$

Where

E = electric field; P_μ = power; V_μ = volume of material; q = the electric charge on each of the ions; n = the number of charges; μ = level of mobility of the ions.

The conductivity (σ_1) may be expressed as:

$$\sigma_1 = q n \mu \quad \dots \text{(Eq.2.5)}$$

The total conductivity is the sum of the individual conductivities of each ions if materials contain different types of ions in a specific volume.

2.4.2.1 Microwave generation

The magnetron is the core part of a microwave oven. It consists of a vacuum chamber which contains a filament spiraled by tungsten to emit electrons when heated up, and a copper anode which is in a circular form with resonant cavities (normally eight). A magnet is placed around the anode to provide a magnetic field. After cathode giving off negatively charged electrons, this magnetic field forces them to move following an orbit rather than a straight line under an electrical pressure of 4000 - 6000 volts. As the electrons approach the anode, they pass by the resonator cavities, and this leads to an oscillation at a specific high frequency (2450 or 915 *MHz*). Microwaves are formed in this way and then distributed into the oven cavity through a waveguide.

2.4.3 Advantages and challenges

Microwave has been successfully studied and applied in food industry, including heating, drying, sterilizing and so on. This form of heating over conventional methods offers the following advantages: (i) Microwave penetrates directly inside the food materials, thereby heat generation occurs internally throughout the whole body of the food material, which is known as volumetric heating, leading to a rapid, energy-saving and uniform performance; (ii) Nutrients such as bioactive compounds, vitamin content, as well as flavor and sensory characteristics, and color of food are well preserved owing to the fast heat transfer; (iii) Since the conveying piping, which is designed for microwave, used in food industry is transparent and remains relatively cooler than the products, fouling depositions decline to minimum level which is common in conventional heating process; (iv) Heating is silent and highly efficient, in which 80% or even higher efficiency can be achieved; (v) Low cost in system maintenance; and (vi) Can be combined with other technologies (Ahmed & Ramaswamy, 2004).

One of the troubles in microwave drying practice is the nonuniformity. Two forms of nonuniformity occur in microwave processing. The first is the fundamental 'Standing wave' effect which shows a repeated pattern of field intensity variation. The field intensity change from maximum to zero periodically. The second type of nonuniformity is associated with

penetration depth problem. Within the high-dielectric-loss material, the microwave fields attenuate eventually, which becomes particularly troublesome in large scale manufacturing process. It is to be noticed that both types of nonuniformity mentioned above are frequency dependent and improve as frequency is lowered. From the prospective of nutrients loss, microwave processing resulted in the highest loss of flavonoids, sinapic acid derivatives and caffeoyl-quinic acid derivatives compared with three other domestic cooking method, such as high-pressure boiling, low-pressure boiling, and steaming (Vallejo et al., 2003). The cost of microwave processing unit is another issue which needs to be considered, especially in small scale food industry. The microwave equipment is required to be designed uniquely and precisely to meet the demands of food processors. For safety concern, additional technical training, maintenance and safeguards are mandatory in the case of radiation leakage.

2.4.4 Factors affecting microwave heating

Several physical, thermal and electrical factors determine the absorption of microwave energy and heating behavior of food material in MW processing. These factors are briefly discussed below.

2.4.4.1 Frequency

As mentioned above, 915 and 2450 *MHz* are the only main two frequencies allocated for microwave heating. Correspondingly, the respective wavelengths of these frequencies are 0.328 and 0.122 m. Microwave heating is affected by wavelength which determines the region where most interactions between the energy and materials occur. It is also significant to select proper microwave equipment components such as waveguide, magnetron and heating cavity based on different frequencies.

2.4.4.2 Dielectric properties

The release of heat is observed only if materials have dielectric losses or conducting losses in a microwave field. The absorbed energy depends on the factor of dissipation δ for which $\tan\delta = \epsilon''/\epsilon'$, with ϵ' and ϵ'' , the real and complex part of dielectric permittivity ($\epsilon = \epsilon' - j\epsilon''$). ϵ' is the dielectric constant, which expresses the capacity of a material to store energy in an applied electric field; while ϵ'' is dielectric loss factor which expresses the efficiency of transformation

of electromagnetic energy into heat. More details are to be discussed in the Chapter 2.6 Dielectric Properties.

2.4.4.3 Moisture content

The moisture content is a main factor affecting the microwave heating of food materials, including the penetration depth of microwave. Uneven heating rate is often observed in high-moisture food because of low microwave penetration depth; meanwhile low-moisture food will show a more uniform heating rate as the result of a deeper microwave penetration (Mudgett, 1989). Moreover, the phase (liquid or solid ice) of water and available free water content remarkably affects the heating behavior of water. At lower frequency (static region), the dielectric behavior of free water remains constant at constant temperature; however when it comes to higher frequency (optical region), dielectric constant decreases exponentially with frequency. Phase change also leads to a change in the dielectric properties, which needs to be considered in freezing pretreatment or freeze drying.

2.4.4.4 Temperature

The level of sample temperature also plays an important role in microwave heating or drying since dielectric properties of samples may vary with temperature. During heating or drying process, both temperature and moisture content change, and as a consequence of the combined effect, dielectric loss factor, loss tangent, and heating behavior change subsequently as well.

2.4.4.5 Geometry and location

The distribution of heat within the product heated in a microwave oven is remarkably affected by the shape of food. The geometry and location of food have an impact on the depth of microwave penetration, heating rate and uniformity during drying. For instance, in one fluidized bed drying system which is quite similar with microwave drying, drying rates decreased at every drying temperature set when L: D and aspect ratio increased respectively for beans and potato (Senadeera et al., 2003). The closer the size or thickness is compared to the wavelength, the higher will be the center temperature (Ahmed & Ramaswamy, 2004). Furthermore, the more regular the shape of material is, the more uniform is the distribution of

the heat within the product. Mostly, different shapes represent different surface-to-volume ratio and a higher surface-to-volume ratio enhances the heating rate. The microwave heating uniformity of multicomponent foods is also affected by factors of food component placement, geometry of products and packages, among which placement had the most notable effect (Ryynänen & Ohlsson, 1996). However, a full understanding of relationship between factors including the geometry, shape, orientation of materials and microwave heating has not been established yet.

2.5 Applications of MW in food processing

For the past 50 years, various investigations towards applications of MW in food industry have been accomplished. Microwave application in food processing becomes attractive for reasons of its volumetric heating trait, rapid increase in temperature, controllable heat deposition, and easy clean-up opportunities. It has been applied successfully in the field of food industry including proofing and frying doughnuts; finish drying of potato chips; precooking of chicken and bacon; drying of various foods; tempering of frozen meat and poultry products; thawing of frozen products; blanching of vegetables; heating and sterilizing of fast food, cooked meals and cereals; and pasteurization and sterilization of numerous foods (Ahmed & Ramaswamy, 2004).

2.5.1 Microwave Pasteurization and Sterilization

Traditionally, pasteurization was designed as a process which selected relatively mild heat treatment to food to kill key pathogens and inactivate enzymes in order to bring consumers a safer product. Later, HTST (high temperature short time) and UHT (ultra-high temperature) processes were as well invented to cover the drawbacks of traditional pasteurization method. For example, pasteurization of milk can be achieved by 30 min heating at 63°C or 15s at 72°C. The temperature and time are determined by what is necessary to remove pathogenic, heat-resistant, disease-causing microorganisms which are possible to be found in food. Microwave energy can be introduced into pasteurization application because of its rapid and clean heating characteristics. An effective continuous flow pasteurizer using microwave energy for citrus juice was set up, avoiding the need for a steam generator (Nikdel et al., 1993). In a study by *M.H.*

Lau, a pilot-scale 915 MHz microwave pasteurization system was established. A uniform heating, reduced processing time by at least one-half compared to water-bath heating, and marked reduction of degradation of asparagus were proved as well (Lau & Tang, 2002). A similar system, but different in frequency (2450 MHz), was set up for pasteurization of apple juice and inactivation of *E.coli* was observed (Cañumir et al., 2002). MW heating also shows great potential for in-shell egg pasteurization by studying dielectric properties of different parts of eggs (Dev et al., 2008).

Sterilization is a comparatively more severe thermal treatment of foods for a long-term shelf stability. Generally, saturated steam at elevated pressures, approaching to 135°C - 140°C, and steam-heated hot water are chosen as heating media for food sterilization. Microwave sterilization has also been studied for potential commercial applications, however, still facing several problems with limited success (Ahmed & Ramaswamy, 2004).

2.5.2 Microwave-assisted extraction (MAE)

Microwave assisted extraction (MAE) is a combination of microwave power and traditional solvent extraction which is a process to separate target components from its solid matrix. It has been applied to the extraction of organic contaminants such as polycyclic aromatic hydrocarbons, polychlorobiphenyls, pesticides, herbicides, phenols, neutral and basic priority pollutants in different matrices such as sediments, soils or atmospheric particles (Letellier & Budzinski, 1999). MAE shows a number of advantages, for instance, a shorter extraction time, less solvent consumption, higher extraction rate and lower cost. This microwave assisted method at atmospheric pressure or in closed cell can be excellent alternatives to Soxhlet extraction (Letellier & Budzinski, 1999). Furthermore, this technique is easy to handle and the apparatuses are cheaper compared to other modern techniques such as SFE (supercritical fluid extraction) and PLE (pressurized liquid extraction).

The reduction of extraction time can mainly be attributed to the difference in heating method. A finite period of time is needed to heat the vessel before the heat is transferred to the solution in conventional heating, while microwaves heat the solution directly. This inherent heating method maintains the temperature gradient to the minimum level and accelerates the

speed of heating. The influence of parameters such as solvent choice, solvent volume, temperature, time and matrix characteristics have been discussed in numerous reviews and papers (Letellier & Budzinski, 1999; Sparr Eskilsson & Björklund, 2000). In spite of the advantages discussed above, drawbacks of MAE includes: extraction solvent must have the ability to absorb microwaves; Clean-up step is needed; waiting time needs to be included for the vessels to cool down.

Applications of MAE in the field of bio-products includes optimizations of MAE techniques, comparison between MAE and traditional extraction method and implementation for different bioactive compounds in different products. The extraction of tea polyphenols and tea caffeine with MAE for 4 min (30 °C and 4%) were higher than other traditional methods (Pan et al., 2003). An efficient MAE process has been developed for fast extraction of flavonoids from *Radix Astragali*. The highest yield of flavonoids was under the optimal extraction condition (microwave power: 1000 W, ethanol concentration: 90%, extraction temperature: 110°C, irradiation time 25 min, and solvent to material ratio 25 mL/g).

2.5.3 Microwave blanching of vegetables

Blanching, a common unit operation widely used in canning, dehydration and freezing industry, exposes products for a short time in boiling water, steam or microwave for the purpose of inactivating oxidative enzymes, by which undesirable changes in color, flavor or texture of food may occur during storage. Steam blanching is a relatively conventional and effective method, however, microwave blanching also come into the sight of researchers. The first microwave blanching, selecting 3000 MHz as working frequency for certain green vegetables, was reported by *Proctor* and *Goldblith*, and it was found to retain maximum amounts of vitamin C (Ahmed & Ramaswamy, 2004). Different blanching methods were compared on spinach, bell peppers and carrots, and it was verified for the possibility of the potential microwave drying application in reducing the loss of valuable nutrients, which may result from leaching losses during conventional processing of steam or water blanching (Ramesh et al., 2002).

2.5.4 Application in microwave assisted heating and drying

For the past 50 years, the use of MW heating has shown great success in various aspects in agriculture field, especially in grain drying and insect control (Huang, 2013). MW heating may be used to preheat the food to a hot air dryer, by which the temperature of the food is quickly raised and the cost of energy is less. It may also be applied in the early stages of the falling rate period of drying, or toward the end of the drying circle, to reduce the drying time. More applications use microwave to help finish drying in the end.

Talking about microwave drying, microwave is seldom used as the sole source of energy for drying wet food materials. Microwave drying, microwave assisted hot air drying, microwave vacuum drying have thus been investigated as potential methods for obtaining high quality of products (Zielinska et al., 2013). Microwave power is normally used in conjunction with heated air, which is termed as microwave assisted hot air drying. In terms of food drying, numerous applications in microwave assisted drying were conducted by researchers. These investigations covered diverse varieties of vegetables and fruits, such as parsley (Soysal, 2004), carrot (Sutar & Prasad, 2007), apple (Wang et al., 2007), eggplant (Ertekin & Yaldiz, 2004), spinach (Karaaslan & Tuncer, 2008), banana (Maskan, 2000), grapes (Tulasidas et al., 1995), etc.

Prahbanjan et al. (1995) evaluated drying characteristics of carrot cubes in a domestic microwave oven and compared it with conventional convective drying method. Substantial decreased time and better quality were observed at the lower power level in this combined microwave assisted hot air drying. A positive relationship was testified between drying rate and microwave power density, air temperature, but negative relationship was also observed at varied air velocity during a grape drying experiment (Tulasidas et al., 1995).

Microwave vacuum drying is another possible way to combine microwave energy with existing drying methods. Microwave-vacuum drying was found to produce a big difference in the total carotene and chlorophyll retention with the conventional method, thus microwave vacuum drying or microwave-vacuum-air drying were better ways for drying high-carotenoid vegetables and also green vegetables (Cui et al., 2004). In banana slices, similar positive results, including better taste, aroma, smell and rehydration characteristics, were obtained (Drouzas &

Schubert, 1996). However, the process is slow and involves high investment and operational costs because of the need to produce and maintain a high level of vacuum.

2.5.5 Other applications

One of the largest industrial applications of microwave energy is tempering of meat for further processing (Decareau, 1985). It is a process during which the temperature of products is raised from storage temperature (usually below -18°C) to a temperature just below freezing point. The reason of tempering is for an easier handling process, such as dicing, slicing or separating after tempering the hard frozen solid block into a softer point. Conventional tempering techniques subject the outer surfaces of the bulk, with either water or air, to warmer temperatures for a long period. This method results in large temperature gradients and takes too long a time, normally several days, which usually leads to loss of protein and becoming an expensive process. On the other hand, microwave can easily penetrate into the whole frozen product and effectively approaches the inner regions within a short time. All the process can be performed in few minutes for a large amount of frozen products (5-10 min for 20-40 kg). In microwave tempering, the lower frequency (915 *MHz* band) has an advantage for tempering of thick products because of its deeper penetration and longer wavelength compared to 2450 *MHz* microwave.

Besides microwave tempering, microwaves are ideal for producing puffed snack foods as ultra-rapid internal heating by microwave causes puffing or foaming when the rate of heat transfer is made greater than the rate of vapor transfer out of the product's interior. In some highly corrosive or viscous solutions, microwave heating can also be used to concentrate heat-sensitive solutions and slurries at relatively low temperatures (Ahmed & Ramaswamy, 2004).

2.6 Dielectric properties

2.6.1 Definition and related quantities

When a material is directed by microwaves, the energy is divided into three parts: reflection, absorption and dissipation. These proportions of energy, which belong to three categories, are defined in terms of the dielectric properties. The fundamental electrical property, described as the complex relative permittivity, is mathematically expressed as:

$$\epsilon^* = \epsilon' - j \epsilon'' \quad \dots \text{(E.q.2.6)}$$

where $j = \sqrt{-1}$. The real part of the complex relative permittivity, ϵ' , known as the dielectric constant, expresses the capability of a material to store energy in response to an applied electric field; and the imaginary part of complex relative permittivity, ϵ'' , known as the dielectric loss factor, describes the ability to dissipate energy in response to an applied electric field, and sometimes can also describe the efficiency of transformation of electromagnetic energy into heat (Wang et al., 2003).

Dielectric properties are important to help understand the behavior of materials subjected to radio-frequency (RF) or microwave (MW) fields for purposes of heating, drying or processing. Most of useful quantities required in the design of microwave thermal process and system, such as proportion of reflected energy, penetration depth and rate of heating, can be described by using these parameters.

The proportion of reflected energy P_r is a function of the dielectric constant ϵ' and the angle of incidence. For an angle of incidence of 90° , it is simply:

$$P_r(90) = \frac{(\sqrt{\epsilon'} - 1)^2}{(\sqrt{\epsilon'} + 1)^2} \quad \dots \text{(Eq.2.7)}$$

For example, at room temperature the value of ϵ' for water is 78, while the reflectivity is greater than 0.64.

The penetration depth d_p is usually defined as the depth into a sample where the microwave power has dropped to $1/e$ or 36.8% of its transmitted value. The penetration depth

can also be defined as the distance at which the microwave power has been attenuated to 50%. It is a function of ϵ' and ϵ'' :

$$d_p = \frac{\lambda_0 \sqrt{\epsilon''}}{2\pi\epsilon''} \quad \dots \text{(Eq.2.8)}$$

where λ_0 is the free space microwave wavelength (for 2450 MHz, $\lambda_0 = 12.2\text{cm}$). The most common foods have $\epsilon'' < 25$, which implies a d_p of 0.6-1.0 cm.

The rate of heating can be expressed by the power equation:

$$P_v = 2\pi f \epsilon_0 \epsilon'' |E|^2 \quad \dots \text{(Eq.2.9)}$$

Where: P_v is the energy developed per unit volume in W/m^3 , f is the frequency in Hz; and $|E|$ is the electric field strength inside the load in V/m.

2.6.2 Factors influencing dielectric properties at a given frequency

Several different factors affect dielectric properties of bio-products. In terms of the hygroscopic characteristics of food materials, the amount of water in the material is normally a dominant factor. At the same time, the dielectric properties also depends on the frequency of the applied electric field; on the temperature, density, composition, and structure of the material.

2.6.2.1 Temperature and moisture content

Water, or moisture factor, plays a vital role in microwave heating. It is a major absorber of microwave energy in food, hence the higher the moisture content, the better is the condition of heating. Now assuming a perfect and pure structure of water molecule, it is a classic example of polar dielectric. Adapted from the work of Hasted (1973), the microwave dielectric properties of liquid water are listed in Table 2.3 for several microwave frequencies at temperatures of 20 and 50 C°.

Table 2.3. Microwave dielectric properties of water at indicated temperatures adapted from (Hasted, 1973)

Frequency, GHz	Dielectric constant (ϵ')		Dielectric loss factor (ϵ'')	
	Temperature		Temperature	
	20C°	50C°	20C°	50C°
0.6	80.3	69.9	2.8	1.3
1.7	79.2	69.7	7.9	3.6
3.0	77.4	68.4	13.0	5.8
4.6	74.0	68.5	18.8	9.4
7.7	67.4	67.2	28.2	14.5
9.1	63.0	65.5	31.5	16.5
12.5	53.6	61.5	35.5	21.4
17.4	42.0	56.3	37.1	27.2
26.8	26.5	44.2	33.9	32.0
36.4	17.6	34.3	28.8	32.6

From this table, it can be concluded that the dielectric constant is very high under room temperature (around 78), therefore free moisture of the material significantly affects the dielectric constant. However, it is rare when only pure free water state exists in fresh agri-products. Hence it is still very difficult to predict the microwave dielectric properties of every specific products because of the interaction of various types of molecules.

The microwave dielectric properties on total 23 kinds of common fresh fruits and vegetables were obtained by the work of *S.O.Nelson* (1994), under the microwave field with frequencies ranging from 200 MHz to 20 GHz. The dielectric properties of these fresh fruits and vegetables at 915 MHz and 2.45 GHz are presented in Table 2.4 with some other descriptive information. The dielectric constant almost decreases steadily with increasing frequency, dropping even more rapidly at frequencies above 5 GHz. Values of loss factor decline when frequency increases above 200 MHz to the minimum in the 1- to 3- GHz region and then increase again when the frequency approaches 20 GHz. This behavior of fruit and vegetable tissues may be affected by ionic conductivity and bound water relaxations at the lower frequencies and by free water relaxation at the higher end of the frequency range.

Table 2.4. Dielectric properties and other characteristic of fresh fruits and vegetables at 23 C° and indicated frequencies at 915 MHz and 2.45 GHz, adapted from (Nelson et al., 1994)

Fruit/Vegetable	MC, % (w.b.)	Tissue density, g cm ⁻³	Dielectric constant (ϵ')		Dielectric loss factor (ϵ'')	
			Frequency		Frequency	
			915 MHz	2.45 GHz	915 MHz	2.45 GHz
Apple	88	0.76	57	54	8	10
Avocado	71	0.99	47	45	16	12
Banana	78	0.94	64	60	19	18
Carrot	87	0.99	59	56	18	15
Cucumber	97	0.85	71	69	11	12
Grape	82	1.1	69	65	15	17
Grapefruit	91	0.83	75	73	14	15
Kiwifruit	87	0.99	70	66	18	17
Lemon	91	0.88	73	71	15	14
Lime	90	0.97	72	70	18	15
Mango	86	0.96	64	61	13	14
Onion	92	0.97	61	64	12	14
Orange	87	0.92	73	69	14	16
Papaya	88	0.96	69	67	10	14
Peach	90	0.92	70	67	12	14
Pear	84	0.94	67	64	11	13
Potato	79	1.03	62	57	22	17
Radish	96	0.76	68	67	20	15
Squash	95	0.7	63	62	15	13
Strawberry	92	0.76	73	71	14	14
Sweet potato	80	0.95	55	52	16	14
Turnip	92	0.89	63	61	13	12

2.6.2.2 Influence of composition

The chemical composition, especially how dipole molecules, like water, and salt or ash content bind together, determines the dielectric properties of materials. For many food, this influence between water and salt content on dielectric properties is large and cannot be neglected, especially at 450 and 900 MHz (Ohlsson et al., 1974). In the case of high carbohydrate content of food or syrup, the dissolved sugar in water is the main MW susceptor (Venkatesh & Raghavan, 2004). In some high carbohydrate food and beverage, such as alcoholic beverage and bakery products, effects of alcohol and dissolved carbohydrates cannot be ignored. Since the effects are related to stabilization of hydrogen bonding patterns through hydroxyl-water interaction (Kudra et al., 1992). However, based on the data of single ingredient, it is still hard to predict the total dielectric property of the mixture.

2.6.2.3 Physical structure

Dielectric properties vary with a number of physical attributes including bulk density, particle size, and homogeneity of target materials.

In granular or particulate materials, the bulk density of the mixture is an important factor which influences the dielectric properties. The relation for the dielectric properties of whole and powdered grains at different bulk densities, moisture content and frequency was developed by *Nelson*(1992). This relation could be as well applied in the control of continuous in-line processing of grains (Venkatesh & Raghavan, 2004). Upon knowing the permittivity of the pulverized sample at its bulk density, which is the air-particle mixture density, and the specific density of the solid material, several equations were developed to represent the dielectric properties in a two-component mixtures (Nelson, 1992):

$$(\varepsilon)^{1/2} = \omega_1(\varepsilon_1)^{1/2} + \omega_2(\varepsilon_2)^{1/2} \quad \dots \text{(Eq.2.10)}$$

Where ε represents the effective permittivity of the mixture, ε_1 is the permittivity of the medium in which particles of permittivity ε_2 are dispersed, and ω_1 and ω_2 are the volume fractions of the respective components, where $\omega_1 + \omega_2 = 1$

And the *Landau and Lifshitz, Looyenga* equation (Nelson, 1992):

$$(\varepsilon)^{1/3} = \omega_1(\varepsilon_1)^{1/3} + \omega_2(\varepsilon_2)^{1/3} \quad \dots \text{(Eq.2.11)}$$

2.6.3 Applications of measurements of dielectric properties

Dielectric properties of various materials were investigated by numerous researches. Once basic data on the relationships between dielectric properties and other factors have been established, a rapid and non-destructive method can therefore be established for quality analysis or monitoring of relevant properties or states. There are some examples listed below.

Measuring the dielectric properties can be used in monitoring frying oil quality, since the dielectric constant was found to be the most significant indicator for quality control in commercial deep fat frying operations (Paul & Mittal, 1996). Compared to the conventional methods of analysis (viscosity, refractive index, iodine value, peroxide value, and the fatty acids) for evaluating the frying quality of a blend of cotton seed and sunflower oils, it is also a possible way to analyze and predict occurring of deterioration by measuring dielectric properties (El-Shami et al., 1992). *Raveendranath* and *Mathew* (Venkatesh & Raghavan, 2004) applied microwave technique into studies and assessed water quality aspects. They related the dielectric behavior of polluted water at microwave frequencies (2.685 GHz) to the evaluation of water quality. In cereal grains, mathematical models for the dielectric constant versus density have been developed (Nelson, 1992); it was also proved to be a promising potential method in estimating certain engineering properties such as mass, density, thickness, and fat content (Trabelsi et al., 1998). In baking processes, microwave and radio-frequency heating has been widely used and microwave permittivity of bread doughs was measured under the frequency ranging from 600 MHz to 2.4 GHz as a function of water-flour composition, proofing time and baking time (Venkatesh & Raghavan, 2004). In dairy products, the representative dielectric properties of milk and its constituents at 2.45 GHz was determined by *Kudra et al.* (1992).

2.7 Mathematic Modeling

On the basis of drying data, various mathematic models have been invented and modified in thin layer drying to predict drying kinetics. Nine of these common models for drying curves includes namely: Newton, Page, Henderson and Pabis, Logarithmic, Wang and Singh, Two Term, Two Term Exponential, Simplified Fick's Diffusion and Midilli-Kucuk Equation Models, as listed in Table 2.5. Generally speaking, the fitness of models can be illustrated by statistical values such as the sum of squared errors of prediction (SSE), root square error (RMSE), Chi-square (χ^2), and coefficient of determination (R^2).

Table 2.5. Mathematical models tested for the moisture ratio values

	Model name	Model equation	References
1	Newton	$MR = \exp(-kt)$	(Lewis, 1921)
2	Page	$MR = \exp(-kt^n)$	(Agrawal & Singh, 1977)
3	Henderson and Pabis	$MR = a \exp(-kt)$	(Henderson & Pabis, 1961)
4	Logarithmic	$MR = a \exp(-kt) + c$	(Yagcioglu et al., 1999)
5	Wang and Singh	$MR = 1 + at + bt^2$	(Wang & Singh, 1978)
6	Two-term	$MR = a \exp(-k_0t) + b \exp(-k_1t)$	(Henderson, 1974)
7	Two-term exponential	$MR = a \exp(-kt) + (1-a)\exp(-kat)$	(Sharaf-Eldeen et al., 1980)
8	Simplified Fick's diffusion equation	$MR = a \exp(-c(t/L^2))$	(Toğrul & Pehlivan, 2003)
9	Midilli-Kucuk equation	$MR = a \exp(-kt^n) + bt$	(Sacilik & Elicin, 2006)

Different pretreatments affected drying constants, but it was found that the drying behavior of treated grapes agreed well with Page's model (Pangavhane et al., 1999). In the field of herbal drying, the semi-empirical Page's equation also gave an excellent fit for all the data points to describe the drying kinetics of parsley leaves (Soysal, 2004). Besides, a researcher confirmed that the Page model was most adequate in predicting moisture transfer for fresh and pre-dried apple pomace in microwave drying (Wang et al., 2007). Two diffusional periods were observed in a drying experiment of carrots. Considering heat, mass transfer and shrinkage, three different models were determined by parametric identification and proved to be useful to predict a good process description (A et al., 1989). A thin layer modeling in eggplant hot air drying showed that the *Midilli et al.* model could be used to explain moisture transfer with drying air temperature between 30 and 70 °C and velocities between 0.5 and 2.0 m/s (Ertekin & Yaldiz, 2004). Similar finding was observed as well when the *Midilli-Kucuk* model gave the best results in microwave and hot air drying of spinach (Karaaslan & Tuncer, 2008).

2.8 Effect of pretreatment in drying

Multiple pretreatments can be applied in solid form products. Generally they are divided into physical and chemical treatments. Physical pretreatments include blanching, freezing, microwave and high pressure. Chemical pretreatments of material include sulfating, immersion in sodium chloride, calcium chloride or sugars, use of surfactants or alkali and impregnation with biopolymers (Lewicki, 2006).

Nieves Sanjuan (2001) studied the relationship between stepwise blanching temperature, rehydration temperature and firmness and chlorophyll content. He pointed out some conditions to get better products but also admitted that it is still difficult to obtain firm samples with a high chlorophyll content without additives. Freezing pretreatment provided the highest drying rates presumably due to the retention of cell wall structures (Eshtiaghi et al., 1994). In an eggplant drying study, *Ertekin* observed that pre-treatment decreased drying time, and increased the brightness of the dried samples, but decreased the rehydration ratio (Ertekin & Yaldiz, 2004).

The chemical treatment of the material before drying include sulfating; immersion in sodium or calcium chlorides, sodium carbonates, sugars and salts; use of surfactants and impregnation with biopolymers (Lewicki, 2006). By the work of *Martinez-Soto* (2001), different types of dryer and pretreatments were tested on mushrooms and it is proved that sodium metabisulphite improved the attractiveness of dry mushrooms while blanching pretreatment reduced this attractiveness. The ΔE value was found to be the highest for sweet potato slices treated at 50 °C with 0.5:1.0% KMS (potassium metabisulphite) and citric acid (Singh et al., 2006).

Chapter III

Material and Methods

This chapter presents the materials and methods used in the evaluation of drying performance of broccoli under both hot air drying and microwave drying, including its drying characteristics (moisture ratio curve, drying rate curve, modeling of drying curve), dielectric properties measurement, color measurement, rehydration capacity measurement, chemical analysis (total phenolic content, total flavonoid content and free radical scavenging ability), and tests of pretreatments.

3.1 Experimental material

Fresh green broccoli used throughout the study was obtained from local markets in Montreal, Quebec. They were all well sealed in plastic food wrap and stored in a refrigerator at 4 °C. All the samples after drying were kept under the same storage condition as well. The moisture content of chopped broccoli on wet basis was $89.6 \pm 0.2\%$. Before drying process, fresh or pretreated broccoli were chopped into small pieces by a food processor (DLC-2009CHBC, Cuisinart, Prep 9 Food processor, Canada). The broccoli particles were selected by sieve (opening of 6.3 mm.) to make sure that the sizes of particles are as even as possible. Different thicknesses of broccoli were placed in the sample container according to the surface response design. The sample container used in this study is shown in Figure 3.1. 50% aqueous methanol used in the study for the exaction of bioactive compounds was prepared from analytical reagent grade chemicals.

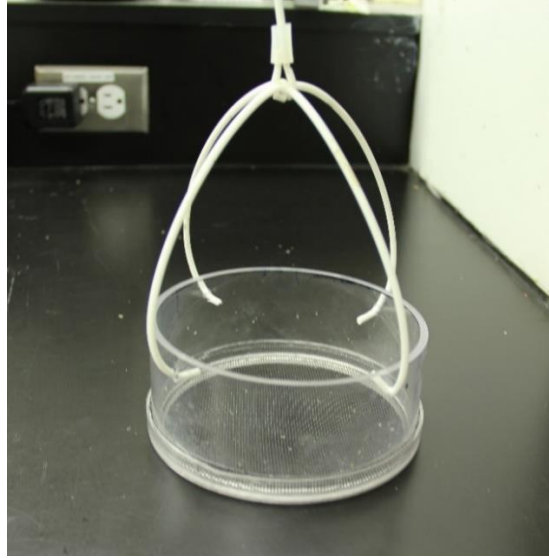


Figure 3.1. Sample container used in the drying unit

3.2 Initial moisture content

The moisture content of the chopped broccoli on a wet basis (w.b.) was measured by drying 10 g samples in a hot air oven for 24 hours at 105 °C (ASAE S352.2 DEC97) and calculated as follows:

$$\text{Moisture content (MC) \%} = \frac{(M_{\text{initial}} - M_{\text{final}})}{M_{\text{initial}}} \times 100 \quad \dots \text{(Eq.3.1)}$$

Where, M_{initial} is the initial mass of samples (g),

M_{final} is the final mass of samples (g)

The samples were measured in triplicates.

3.3 Drying equipment

A laboratory-scale microwave-assisted convective drying unit used for this experiment is shown in Figure 3.2, and the schematic diagram of this unit is also presented in Figure 3.3. It consists of a microwave generator of which power is variable from 0 to 750 kW and operating frequency is 2450 MHz. The microwaves are introduced through a series of rectangular (7.5 × 4.0 cm) wave guides into a metallic cavity, acted as multimode chamber, with the dimension as 40 × 35 × 25 cm. The reflected microwave power is collected in a circulator which connects the

metallic cavity. The control circuits are modified to ensure the microwave power to be controlled by a phase controller, which is designed to continuously and automatically adjust the microwave power output with a range of 0 - 750 W. An extra fan is also installed at the back of the cavity prompting fast moisture removal. The speed of this fan was kept constant during this study.

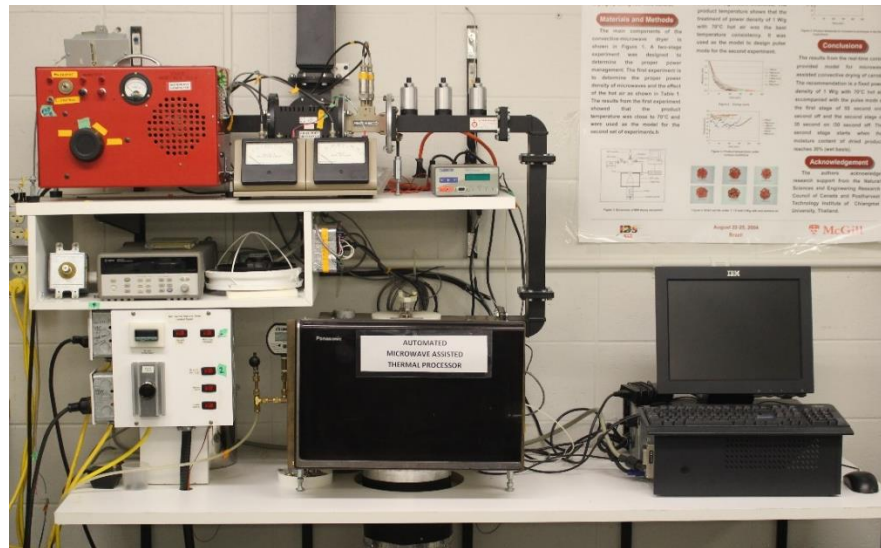


Figure 3.2. Microwave drying unit

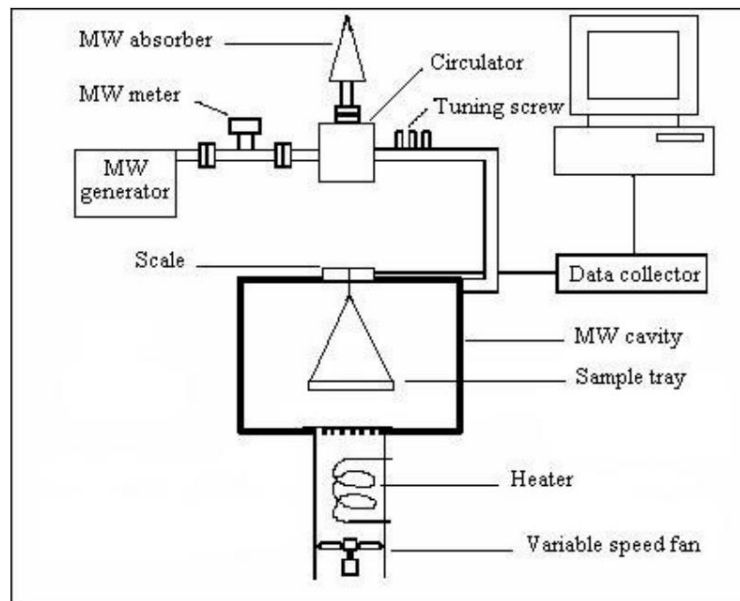


Figure 3.3. Schematic diagram of microwave drying unit, adapted from (Nair, 2010)

Samples were placed in a sample container shown in Figure 3.1. The sample container was equipped with transparent plastic wall to let the microwave power through and a porous net plate in the bottom to hold samples and allow the air flow through. The temperature of broccoli was measured by an optical fiber sensor probe (Nortech EMI-TS series, Quebec City, Canada) which was inserted into the core of a randomly selected broccoli particle. The temperature probe and mass measurement information were collected and connected to an Agilent 34970A data acquisition unit (Agilent, Santa Clara, USA) and then sent to a computer. A LabView program (National Instruments, Austin, USA) was developed to realize microwave power control, sample mass reading, temperature monitoring and control. An air-speed-adjustable hot air supply was attached to the main chamber to heat the samples up and help remove the moisture evaporated from the samples (Nair, 2010).

The sample mass was recorded at a 0.5 min interval by mass change recorded during drying. According to the mass record, moisture ratio and drying rate can be calculated. This drying unit can be used for either hot air drying or microwave drying. In hot air drying, the drying temperature is the set of the temperature of inlet air. In microwave drying, the drying temperature means the temperature limit of materials when power of microwave is adjusted during drying process to maintain the core temperature of samples, while the convective air at the same temperature is supplied simultaneously.

3.3 Dielectric properties measurement

As shown in Figure 3.4, an automated Agilent 8722 ES *s*-parameter Network Analyzer (Agilent, Santa Clara, CA) with an open-ended coaxial 2 mm diameter slim probe (model 85070E) was used in determination of the dielectric properties of the samples. Measurements were controlled by a computer software (Agilent 85070D Dielectric Probe Kit Software Version E01.02, Santa Clara, USA). The calibration was performed in a three point way by using air, a short block, and water, which is described in the manual of Agilent Technologies (2001). The samples were made of peeled broccoli stalk, which shaped as 2 cm height cylinder. The cutting surface of broccoli was required to be plain and smooth in order to interface closely to detective probe. The broccoli samples which were sealed well in plastic bags were heated in

water bath up to 50, 60 and 70 °C, respectively, for 20 min. Samples of room temperature, 50, 60 and 70 °C were measured in triplicates and data was recorded by the dielectric property analysis software. The detective probe was cleaned after every measurement.

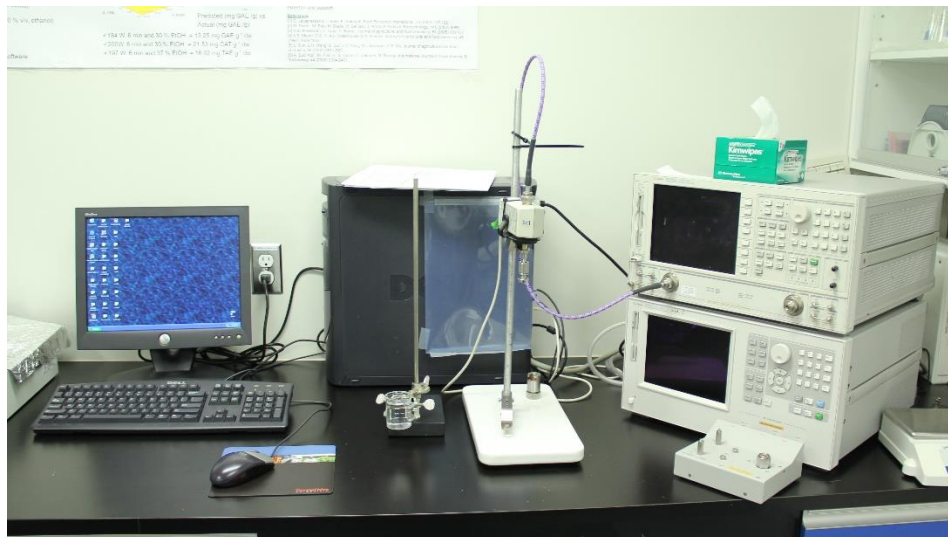


Figure 3.4. Network analyzer for dielectric properties measurement

3.4 Pre-drying treatments

To test the effect of different pretreatments on the quality of broccoli, this experiment was designed. The pretreatments given to broccoli before drying included: (a) blanching in hot water at 80 °C for 3 min; (b) dipping in the solution containing 1, 3, 5 g/L citric acid; (c) held in frozen storage at -10 °C for 24h. Untreated broccoli was also dried as control. Quality measurements consisted of color measurement, rehydration capacity measurement and chemical analysis (determination of TPC, TFC and Free radical scavenging ability represented as AEAC).

3.5 Drying procedure

The drying procedure was as follows:

(1) Hot air convection: Different temperature intensities (50, 60 and 70°C) was investigated in fan-assisted convection at different broccoli bed thicknesses of 10, 20, 30 mm. Samples were

placed in the sample container at the center of the cavity. The change of moisture ratio was calculated at a 10-min interval through the mass change recorded during drying.

(2) Combined hot air convection and microwave: The microwave power density was determined at 1 W/g while temperatures of the convective hot air were set at 50, 60 and 70°C at different broccoli bed thicknesses of 10, 20, 30 mm. According to surface response design, 13 groups of combination were experimented.

Unpretreated broccoli and pretreated broccoli followed the same processing procedure. The pretreated broccoli experiment was carried out by setting the same drying condition rather different pretreatment method.

3.6 Mathematical modeling of the drying curves

The initial moisture ratio (MR) and drying rate during drying experiments were calculated using the following equations:

$$MR = \frac{M - M_e}{M_0 - M_e} \quad \dots \text{(Eq.3.2)}$$

$$\text{Drying rate} = \frac{m_{t+\Delta t} - m_t}{\Delta t} \quad \dots \text{(Eq.3.3)}$$

Where M , M_0 and M_e are the moisture content at any time, initial moisture content, equilibrium moisture content; m_t and $m_{t+\Delta t}$ are the mass at t and mass at $t+\Delta t$ (kg water/kg dry matter), respectively, t is drying time (min). The initial moisture content (w.b.) was calculated by the method mentioned before.

Drying curves were fitted to Midilli-Kucuk equation model:

$$MR = a \exp(-kt^n) + bt \quad \dots \text{(Eq.3.4)}$$

The sum of squared errors of prediction (SSE), root mean square error (RMSE) and coefficient of determination (R^2) were used as the primary criterion to illustrate the result of regression in the drying curves of the dried broccoli (Ertekin & Yaldiz, 2004; Henderson & Pabis, 1961; Soysal, 2004; Wang & Singh, 1978). These statistical values can be calculated as follows:

$$SSE = \sum_{i=1}^N (MR_{i,pre} - MR_{i,exp})^2 \quad \dots \text{(Eq.3.5)}$$

$$RMSE = \sqrt{\frac{\sum_{i=1}^N (MR_{i,pre} - MR_{i,exp})^2}{N}} \quad \dots \text{ (Eq.3.6)}$$

$$R^2 = 1 - \frac{(MR_{i,pre} - MR_{i,exp})^2}{(MR_{i,exp} - MR_{expmean})^2} \quad \dots \text{ (Eq.3.7)}$$

Where $MR_{exp,i}$ is the i th experimental moisture ratio, $MR_{pre,i}$ is the i th predicted moisture ratio, N is the number of observations and $MR_{expmean}$ is the mean value of experimental moisture ratio (Sacilik & Elicin, 2006).

3.7 Color measurement

Color is one of main attributes, along with texture, that characterizes the freshness of most vegetables (Rico et al., 2007). The browning issue of dried broccoli cannot be ignored, thus we need to evaluate the color change during the drying process. A measurement of tri-stimulus color co-ordinates is widely used as a quality indicator for monitoring of color changes during food processing (Koca et al., 2007). The measurement was fulfilled by a chroma meter (CR-300X, Minolta Camera Co. Ltd., Japan) with a 5 mm diameter measuring area was used for surface color measurements (Li et al., 2011). The calibration of the system was performed with the calibration plate (CR-A43). Color parameters on the CIE Lab scale include: L^* (brightness), a^* (redness), and b^* (yellowness). The criterion established by the International Commission on Illumination (CIE) was applied (Hutchings, 2003). In addition chroma and hue angle were calculated from the values for L^* , a^* and b^* value and used to describe the color change during drying. The saturation index or chroma indicates color saturation and is proportional to its intensity. The hue angle is another parameter frequently used to characterize color in food products. An angle of 0° or 360° represents red hue, while angles of 90° , 180° and 270° represent yellow, green and blue hues, respectively. It has been extensively used in the evaluation of color parameters in green vegetables, fruits and meats (Karaaslan & Tuncer, 2008).

$$C = \sqrt{a^2 + b^2} \quad \dots \text{ (Eq.3.8)}$$

$$\alpha = \tan^{-1}(b/a) \quad \dots \text{ (Eq.3.9)}$$

3.8 Rehydration capacity measurement

The rehydration capacity (RC) was used as a quality parameter of the dried broccoli particles, which expressed the ability of dried material to absorb water and regain weight. Rehydration capacity measurement were performed by immersing a weighed amount (0.5 g) of dried samples into water bath filled with distilled water at 95°C for 10 min. Each sample was then taken out and blotted with the paper towels gently in order to eliminate the surface water. These rehydrated samples were reweighed quickly afterwards. The rehydration capacity, which describes the percentage of water gained by the sample, was calculated as the sample weight ratio after and before the rehydration as follows (Maskan, 2001):

$$\text{Rehydration Capacity (RC)} = \frac{W_r}{W_d} \quad \dots \text{(Eq.3.10)}$$

Where, W_r is the weight of rehydrated sample,

W_d is the weight of dried sample after hot air drying or microwave drying.

All samples were measured in triplicates.

3.9 Extraction method

The extraction efficiencies of different solvents (dichloromethane, ethyl acetate, methanol, and 50% aqueous methanol) were tested by following the method described by Chan et al. (2009). According to the research, 50% aqueous methanol was proved to highest extraction efficiency in order to extract bioactive compounds from broccoli. This extraction method was as follows: 150 mg of sample was extracted for 2 h with 6 mL of 50% methanol at room temperature (22°C) on a shaker set at 200 rpm. The mixture was then centrifuged at 1000 g for 15 min, and the supernatant was decanted into new clean tubes. Extracts of dried broccoli were stored at 4°C in refrigerator for further analysis.

3.10 Total phenolic content determination

Total phenolic content (TPC) of extracts was determined as the method described by Al-Farsi et al.; Chan et al. with slight modification (Al-Farsi et al., 2005; Chan et al., 2009). The

extract (300 μ L) was introduced into test tubes mixed with 1.5 mL of *Folin-Ciocalteu* reagent which was diluted 10-fold with distilled water and 1.5 mL sodium bicarbonate solution (60 g/L). The mixture was required to stand at room temperature (22 °C) for 30 min. The absorbance was afterwards measured at 765 nm using a UV/Visible Spectrophotometer (Ultraspec 2100 pro Biochrom Ltd., Cambridge, England). The mean of three readings was used. Total phenolic content (TPC) was determined according to the position in the standard curve obtained from measuring the absorbance of a known concentration of gallic acid standard (0, 1.0, 2.0, 3.0, 4.0, 5.0 mg/100 mL of 50% methanol). The equation of standard curve was thus established and TPC were expressed as milligrams of gallic acid equivalents (GAE) per 100 g of fresh weight.

3.11 Total flavonoid content determination

The total flavonoid content (TFC) of samples was determined following the method adapted by *Meta et al.* (2005). Briefly, 1 mL of 2% aluminum trichloride (AlCl_3) in methanol was mixed with the same volume of extract solution which was obtained by the above method. After standing under room temperature for 20 min, absorption readings of the mixture at 415 nm were taken using the spectrophotometer. The blank sample consisted of a 1 mL methanol with 1 mL AlCl_3 solution. The total flavonoid content was determined using a standard curve with quercetin (0–50 mg/L) as the standard. The mean of three readings was used. TFC was calculated and expressed as mg of quercetin equivalents (QE) per 100 g of fresh weight.

3.12 Free radical scavenging activity

The free radical scavenging activity was determined by the method of *Meda et al.* and *Miliauskas et al.* with slight modification and DPPH (2, 2-diphenyl-1-picrylhydrazyl) was selected as free radical (Meda et al., 2005; Miliauskas et al., 2004). The solution of DPPH in methanol (5.9 mg/100 mL methanol) was prepared daily, before UV measurement. 0.75 mL of each sample was mixed with 1.5 mL of DPPH in methanol. The mixtures were left for 15 min at room temperature and the absorbance of samples was then measured at 517 nm in the spectrophotometer. In blank sample, extraction sample was substituted with methanol. Ascorbic acid (0 - 40 mg/L) were used as positive controls. The radical scavenging activity was calculated as follows:

$$\% \text{ Inhibition} = [(Abs_{\text{blank}} - Abs_{\text{sample}}) / Abs_{\text{blank}}] \times 100 \quad \dots \text{ (Eq.3.11)}$$

Where, Abs_{blank} is the absorption of blank

Abs_{sample} is the absorption of sample.

The antioxidant content was determined using standard curves for ascorbic acid (0-10 μl). The means of three values were obtained, then the free radical scavenging ability was calculated and expressed as mg of ascorbic acid equivalent antioxidant content (AEAC) per 100g of fresh weight.

3.13 Experimental design

The experimented data was subjected to statistical analysis by using response surface methodology (RSM) with central composite design (CCD) which aimed to minimize total number of experimental runs and to determine the significant factors affecting the drying of broccoli (Lozano-Acevedo et al., 2011). The experiment was constructed using a central composite face centered (CCF) design with two factors at three levels. These factors were set at varying temperature (50 to 70°C) and varying bed thickness of samples (10, 20, 30 mm). The experiment was carried out in both hot air drying and microwave drying. The experimental levels of these two factors are as follows in Table 3.1:

Table 3.1. Experimental design for two factors at three level

Factor levels	Factors	
	Bed Thickness (mm)	Temperature (°C)
1	10	50
2	20	60
3	30	70

3.14 Statistical analysis

Statistical analysis of investigations in this thesis was performed by JMP software (SAS Institute Inc., Cary, NC, version 10). To estimate the parameters of the semi-empirical modeling of moisture content versus time, non-linear regression analysis of drying kinetics was accomplished by JMP. Meanwhile multivariate regression analysis was performed later to verify the effect of combination of the drying processing setting on the nutrient aspect of dried broccoli. The data about chemical contents was analyzed by analysis of variance (ANOVA) and the adequacy of the model was determined by evaluating the coefficient of determination (R^2). Statistical significance of the model and its variables was determined at 5% probability level ($p < 0.05$). Three dimensional response surface plots were also used to obtain the optimal drying condition: drying temperature and bed thickness.

Chapter IV Results and Discussion

This chapter describes results of the evaluation on drying performance of broccoli including its drying characteristics, drying curve model, color measurement, rehydration capacity measurement, chemical analysis (determination of TPC, TFC and free radical scavenging ability), dielectric properties measurement and tests of pretreatments.

4.1 Drying characteristics and model of broccoli in hot air drying and microwave drying

Moisture ratio was plotted as a function of time under hot air drying and microwave drying of broccoli samples for varying drying temperatures and bed thicknesses in Figure 4.1, 4.2 and 4.3. Generally speaking, the required drying time to achieve a certain moisture ratio decreased as the drying temperature of products increased. When the bed thickness of vegetable particles increased, the required drying time to reach a certain moisture ratio increased instead. According to Figure 4.1, 4.2 and 4.3, the drying time was shortened under microwave drying and the time is reduced more obvious when drying material bed thickened. The drying time of broccoli under microwave drying at 30 mm bed was around 150 min for all temperatures, but it varied with temperature set when it comes to hot air drying. 320 min, 350 min and 410 min drying time were required for temperatures of 50 °C, 60 °C and 70 °C (Figure 4.3). The drying time was reduced respectively by 38.9%, 30.7%, 23.1% for 50 °C, 60 °C and 70 °C at 10 mm group; 53.6%, 59.2%, 47.6% for 50 °C, 60 °C and 70 °C at 20 mm group; 65.8%, 51.2%, 43.9% for 50 °C, 60 °C and 70 °C at 30 mm group. A decrease in drying time with the introduction of microwave was also observed for pumpkin (Alibas, 2007), for spinach (Karaaslan & Tuncer, 2008), and for parsley (Soysal, 2004). This shortened drying time would normally influence both the energy consumption and potential cost. From the energy cost point of view, 50 °C, 30 mm and 60 °C, 20 mm saved the most energy thereby the most potential cost.

The drying rate is defined as the quantity of water removed from products in unit time and it is presented in Figure 4.4 for broccoli particles of 20 mm during hot air drying at 50, 60, 70°C. It is clear that the drying rate decreases with increasing time. As can be seen in the figure, it

shows that air temperature is the most important factor affecting the drying rate both in hot air and microwave drying. From Figure 4.5, it can be seen that no major differences were observed between different bed thicknesses in hot air drying. However, in microwave drying, the drying rates of products were much higher than that in hot air drying. In microwave drying, the drying rate increased as broccoli bed thickness increased. Similar results were also reported in the paper of *Karaaslan et al.* (Karaaslan & Tuncer, 2008).

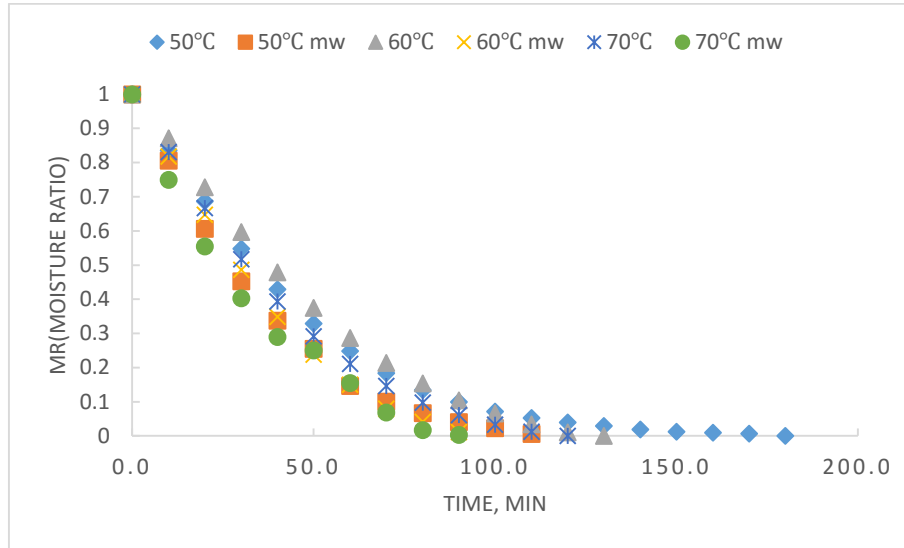


Figure 4.1. Comparison of MR during drying process in 10 mm thick broccoli bed between hot air and microwave assisted drying

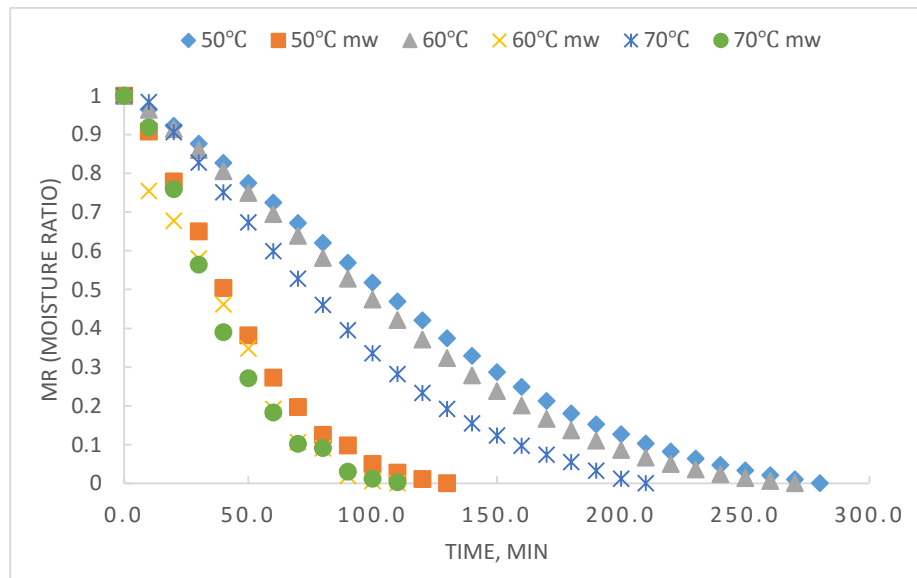


Figure 4.2. Comparison of MR during drying process in 20 mm thick broccoli bed between hot air and microwave assisted drying

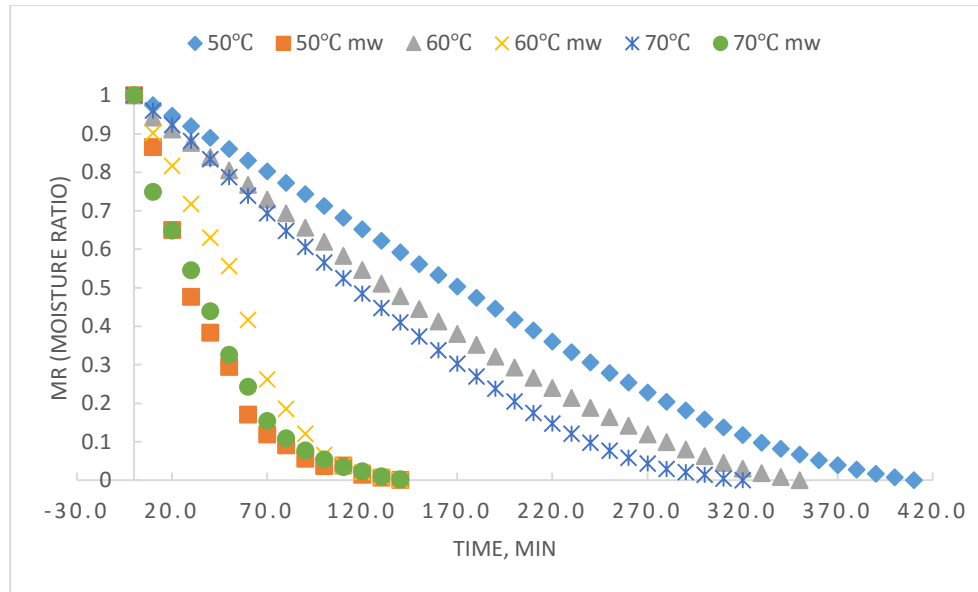


Figure 4.3. Comparison of MR during drying process in 30 mm thick broccoli bed between hot air and microwave assisted drying

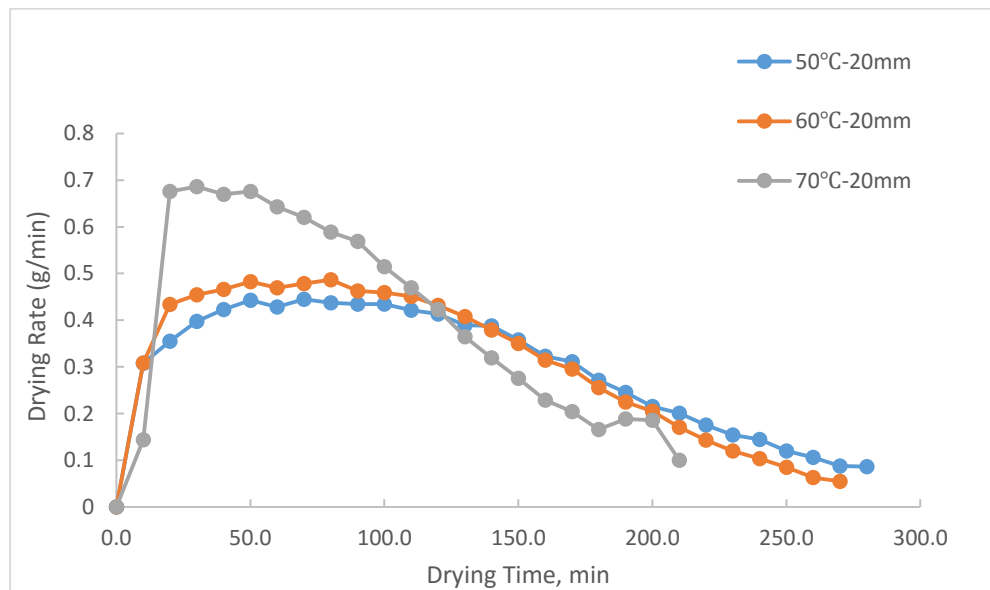


Figure 4.4. Variation of drying rate as a function of drying time for different drying temperatures in hot air drying

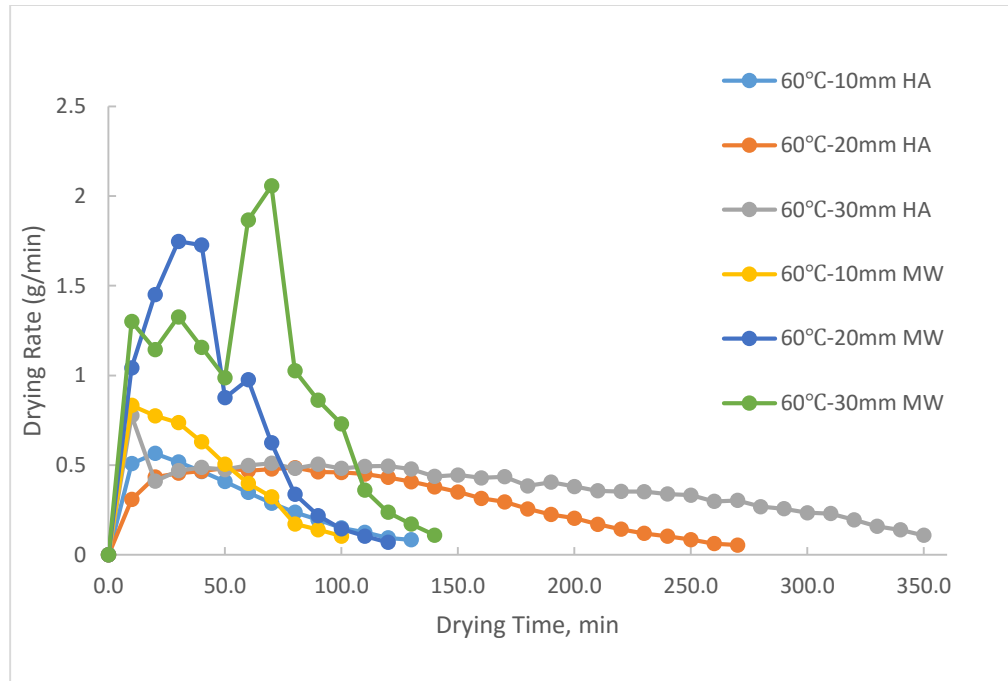


Figure 4.5. Variation of drying rates as a function of drying time for different bed thickness under hot air drying and microwave drying

The drying data were used to describe microwave drying kinetics of broccoli particles. The parameters a , k , n , and b of semi-empirical Midilli-Kucuk's equation for a given drying condition were estimated using non-linear regression technique, as shown in Table 4.1, and the fitness is illustrated in Figure 4.6 and Figure 4.7. The sum of squared errors of prediction (SSE), root mean square error (RMSE) and coefficient of determination (R^2) were used as the primary criterion to evaluate the result of regression in the drying curves of the dried broccoli. The quality of fitness was determined by the lower SSE and RMSE values and the higher R^2 values. Through analysis, it is demonstrated that this model gave an excellent fit for all the experimental data points with values for the coefficient of determination greater than 0.997, SSE values lower than 0.002 and RMSE values lower than 0.02 in most groups. The hot air drying even showed a better fit than microwave drying to this model based on the value of R^2 , because all R^2 s of hot air drying were larger than 0.9996 while several R^2 s of microwave drying were lower than 0.997. These results were in good agreement with the drying rate data which follow the same trends. It can be concluded that the semi-empirical Midilli-Kucuk's equation is

an outstanding model to predict drying curve for both hot air drying and microwave drying of broccoli.

Table 4.1. Non-linear regression analysis results of semi-empirical Midilli-Kucuk's equation for hot air drying and microwave drying of broccoli particles under different drying temperatures and bed thicknesses

Drying method	Non-linear analysis parameters						
	a	k	n	b	SEE	RMSE	R ²
Hot air drying							
50°C-10mm HA	0.99420	0.01000	1.20300	-0.00002	0.00025	0.00409	0.999907
50°C-20mm HA	0.98583	0.00065	1.48647	-0.00023	0.00083	0.00575	0.999864
50°C-30mm HA	0.98225	0.00041	1.40546	-0.00039	0.00224	0.00767	0.999731
60°C-10mm HA	0.99744	0.00736	1.23676	-0.00043	0.00014	0.00367	0.999954
60°C-20mm HA	0.98461	0.00072	1.49681	-0.00020	0.00122	0.00713	0.999795
60°C-30mm HA	0.97768	0.00117	1.25940	-0.00047	0.00138	0.00657	0.999796
70°C-10mm HA	0.99775	0.01100	1.19546	-0.00032	0.00007	0.00281	0.999973
70°C-20mm HA	1.00929	0.00144	1.42862	-0.00023	0.00042	0.00485	0.999911
70°C-30mm HA	0.98652	0.00099	1.35110	-0.00034	0.00241	0.00911	0.999640
MW drying							
50°C-10mm mw	0.99887	0.01427	1.17381	-0.00020	0.00095	0.01027	0.999636
50°C-20mm mw	0.99460	0.00248	1.51927	-0.00014	0.00046	0.00678	0.999857
50°C-30mm mw	1.00586	0.00940	1.26553	-0.00002	0.00283	0.01603	0.999065
60°C-10mm mw	0.99381	0.00915	1.27447	-0.00050	0.00064	0.00960	0.999732
60°C-20mm mw	0.96562	0.00895	1.19600	-0.00105	0.01651	0.04543	0.993422
60°C-30mm mw	0.95538	0.00043	1.86202	-0.00019	0.00936	0.02917	0.997395
70°C-10mm mw	1.00006	0.02931	0.98051	-0.00090	0.00340	0.02204	0.998453
70°C-20mm mw	1.00702	0.00245	1.60419	-0.00001	0.00152	0.01377	0.999480
70°C-30mm mw	0.97348	0.01388	1.11705	-0.00026	0.00856	0.02672	0.997073
SEE: sum of squared errors of prediction; RMSE: root mean square error; R ² : coefficient of determination; a, k, n, b: parameters of Midilli-Kucuk's equation							

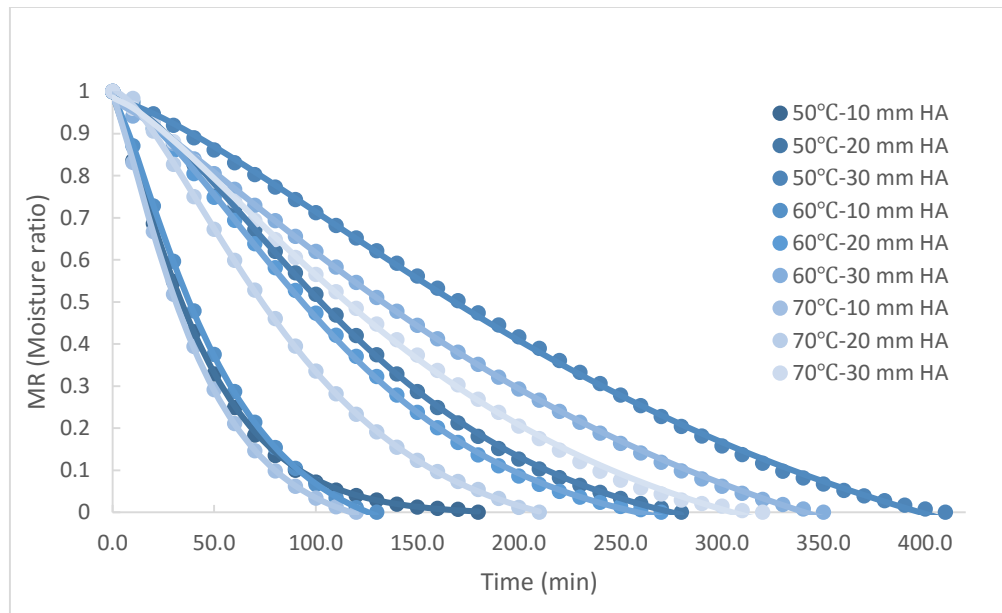


Figure 4.6. Moisture ratio versus time, comparing experimental curve with predicted one through semi-empirical Midilli-Kucuk's equation for broccoli under hot air drying

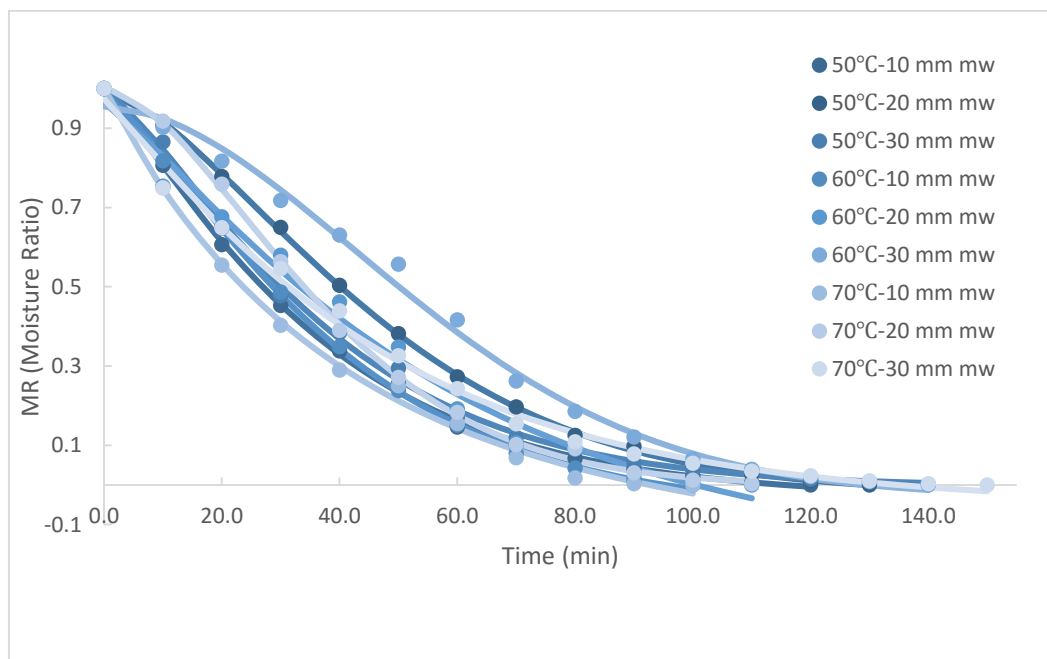


Figure 4.7. Moisture ratio versus time, comparing experimental curve with predicted one through semi-empirical Midilli-Kucuk's equation for broccoli under microwave drying

4.2 Dielectric properties

Microwave energy can be successfully introduced into broccoli drying, thus the design and optimization of the equipment, technique and process requires knowledge of the dielectric properties of the broccoli materials being treated. The dielectric properties of broccoli are measured principally to predict heating rates describing the behavior of materials when subjected to microwave electric fields in dielectric heating applications. The objective of this part in the study was to measure the dielectric properties of broccoli at different temperatures and microwave frequencies.

The dielectric properties of broccoli under different frequencies at 50°C, for example, are presented in Figure 4.8. According to the chart, the dielectric constant ϵ' , decreased slowly as frequencies increased. The dielectric loss factor ϵ'' decreased dramatically from 0 MHz to around 420 MHz, then it increased slightly again as frequencies approached 20 GHz. The relationship between dielectric properties and electric field frequency established from this study corresponds well with the research of Nelson (Nelson, 1996).

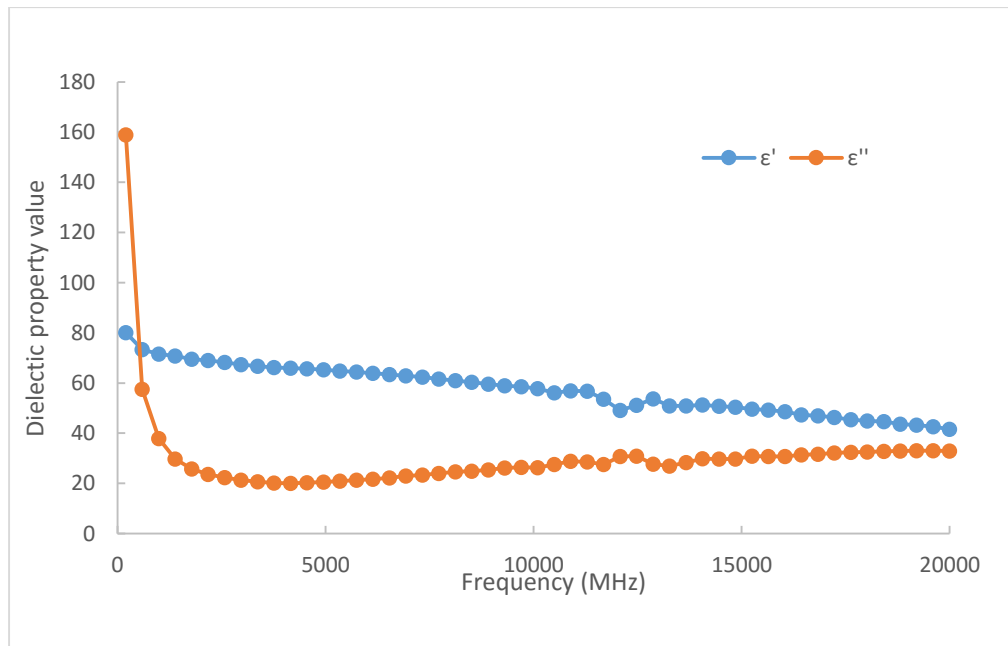


Figure 4.8. Dielectric properties of broccoli under different frequencies at 50°C

The dielectric property values of broccoli under different temperatures (room temperature, 50°C, 60°C, 70°C) and 3 common electric field frequencies (915, 2450, 5800 MHz) are shown in Table 4.2. At each temperature group, it can be seen that generally both dielectric constant ϵ' and dielectric loss factor ϵ'' decreased when frequencies increased. In 915 MHz group, dielectric loss factor ϵ'' of heated broccoli was obviously greater than broccoli sample under room temperature. In both 915 MHz and 2450 MHz groups, dielectric constant ϵ' slightly decreased when heating temperature increased, and the highest dielectric loss factor value appeared at 60°C. In 5800 MHz group, both dielectric constant ϵ' and dielectric loss factor ϵ'' decreased as heating temperature increased, thus the highest value of ϵ' and ϵ'' was located at 50°C.

Table 4.2. Dielectric properties of broccoli under different temperatures

Temperature T (°C)	Frequency f (MHz)	Dielectric properties			
		Dielectric constant ϵ'		Dielectric loss factor ϵ''	
25	915	68.09	±4.53	31.68	±1.14
	2450	64.71	±4.21	20.20	±0.78
	5800	59.00	±3.76	22.87	±1.31
50	915	68.49	±4.12	42.51	±1.12
	2450	65.19	±4.12	22.49	±0.18
	5800	61.00	±3.99	20.83	±0.58
60	915	66.96	±4.57	44.17	±3.38
	2450	64.15	±3.90	22.88	±1.55
	5800	59.85	±4.15	20.36	±1.07
70	915	66.72	±3.36	42.74	±4.60
	2450	64.14	±3.07	21.46	±1.74
	5800	60.60	±2.41	19.50	±0.68

Based on the results in Table 4.2 of dielectric constant ϵ' and dielectric loss factor ϵ'' of broccoli at different frequencies and temperatures, it elucidates how temperature and frequency influence dielectric properties of broccoli in our study. Six factors including: temperature, frequency, moisture content, composition, physical structure, density of target material, can explain changes in dielectric properties of food material (Venkatesh & Raghavan, 2004). Temperature and frequency are two dominating factors which influence the heating behavior in an applied electric field as the change of dielectric properties of food material. Thus in microwave drying application, temperature and frequency can be designed and determined from the angle of dielectric properties. On the other hand, dielectric loss factor determines the heating ability of material, so it should be considered in priority than dielectric constant in microwave drying study. In our study, 2450 MHz was selected for all experiments, so 60 °C, as the highest dielectric loss factor was shown at this temperature; hence it was recommended for the microwave drying practice and further studies.

4.3 Color measurement

Table 4.3 presents the results of the color measurements of fresh and dried broccoli particles under both hot air drying and microwave drying. Measured and calculated color parameters included brightness L^* , redness a^* , yellowness b^* , chroma c and hue angle α° . Figure 4.12 shows the appearance of dried broccoli samples after hot air drying and microwave drying.

Table 4.3. Effect of different drying methods on the color of broccoli bed

Drying method	Color parameters									
	⁺ L		⁻ a		⁺ b		C		α°	
Fresh	56.45	±1.89	13.93	±0.65	24.25	±1.47	27.97	±1.60	60.12	±0.46
After blanching	51.16	±2.75	17.28	±0.74	29.32	±1.83	34.04	±1.91	59.47	±0.81
Hot air drying										
50°C-10mm HA	54.3	±1.86	13.94	±0.80	28.05	±1.23	31.33	±1.41	63.57	±0.76
50°C-20mm HA	48.9	±1.08	11.22	±0.80	27.15	±0.71	29.39	±0.41	67.53	±1.92
50°C-30mm HA	53.36	±3.41	4.82	±0.97	25.89	±2.35	26.36	±2.29	79.39	±2.42
60°C-10mm HA	45.73	±2.28	10.98	±0.21	28.3	±1.28	30.35	±1.20	68.77	±0.94
60°C-20mm HA	48.12	±2.71	8.25	±0.60	26.29	±0.46	27.56	±0.45	72.57	±1.25
60°C-30mm HA	50.93	±3.81	8.76	±1.56	27.8	±1.42	29.19	±1.18	72.46	±3.40
70°C-10mm HA	44.42	±3.62	10.02	±0.53	27.7	±2.19	29.46	±2.17	70.05	±1.24
70°C-20mm HA	48.54	±5.69	9.29	±0.53	26.48	±2.21	28.06	±2.23	70.62	±0.89
70°C-30mm HA	46.46	±2.44	13.41	±1.10	26.98	±1.28	30.14	±1.61	63.6	±0.99
MW drying										
50°C-10mm MW	49.02	±3.51	9.17	±0.22	25.32	±1.58	26.93	±1.55	70.05	±0.80
50°C-20mm MW	48.13	±3.19	8.6	±1.34	27.42	±1.93	28.78	±1.74	72.51	±3.08
50°C-30mm MW	45.4	±3.30	10.01	±1.54	28.41	±2.33	30.13	±2.65	70.67	±1.74
60°C-10mm MW	53.64	±3.31	8.64	±2.29	27.44	±4.03	28.86	±3.88	72.27	±4.83
60°C-20mm MW	49.24	±4.39	11	±0.59	30.51	±2.46	32.46	±2.19	70.07	±2.24
60°C-30mm MW	44.6	±1.61	8.54	±1.30	28.38	±0.79	29.66	±1.05	73.31	±2.15
70°C-10mm MW	45.34	±4.46	11.54	±0.97	27.71	±2.47	30.04	±2.30	67.3	±2.50
70°C-20mm MW	48.26	±1.31	10.19	±0.77	26.44	±1.26	28.34	±1.14	68.89	±1.90
70°C-30mm MW	46.46	±5.82	8.54	±1.56	28.53	±0.87	29.8	±1.21	73.41	±2.53
L, brightness of a color; a, greenness of a color when negative; b, yellowness of a color when positive; C, Chroma of a color; hue angle of a color in °.										

The brightness L* value of fresh broccoli was around ⁺56.5, while for hot air and microwave-convective dried samples, it ranged from ⁺44.4 to ⁺54.3 (Table 4.3). The change in L* value was greatest for the 70°C - 10 mm sample in hot air drying and the 60°C - 30 mm sample in microwave drying. As presented in Figure 4.9, the mean of L value in hot air drying was higher than that in microwave drying. It can be illustrated that microwave drying changed the brightness of broccoli more effectively and evenly than hot air drying. However, from comparisons for all pairs using Tukey-Kramer HSD, the L* values of Fresh products were significantly different from hot air and microwave drying groups however no obvious

differences were obtained by analysis between dried products. Meanwhile drying temperature is another significant factor which affected L^* value of broccoli with a p-Value of 0.0445 between comparison of 50°C and 70°C temperatures from Student's Analysis. The L^* value of broccoli decreased which means 'darker' products as the drying temperature increased. No similar results were found in bed thickness which was the main factor to influence L^* value of broccoli products. The introduction of microwave and the rise of drying temperature shortened the drying time but also maintained a relatively higher and more constant core temperature of broccoli particles than hot air drying. This may be the reason of the difference between the color values. Similar conclusions are obtained that the best color values are achieved during microwave and hot air combined drying method in a pumpkin drying study (Alibas, 2007).

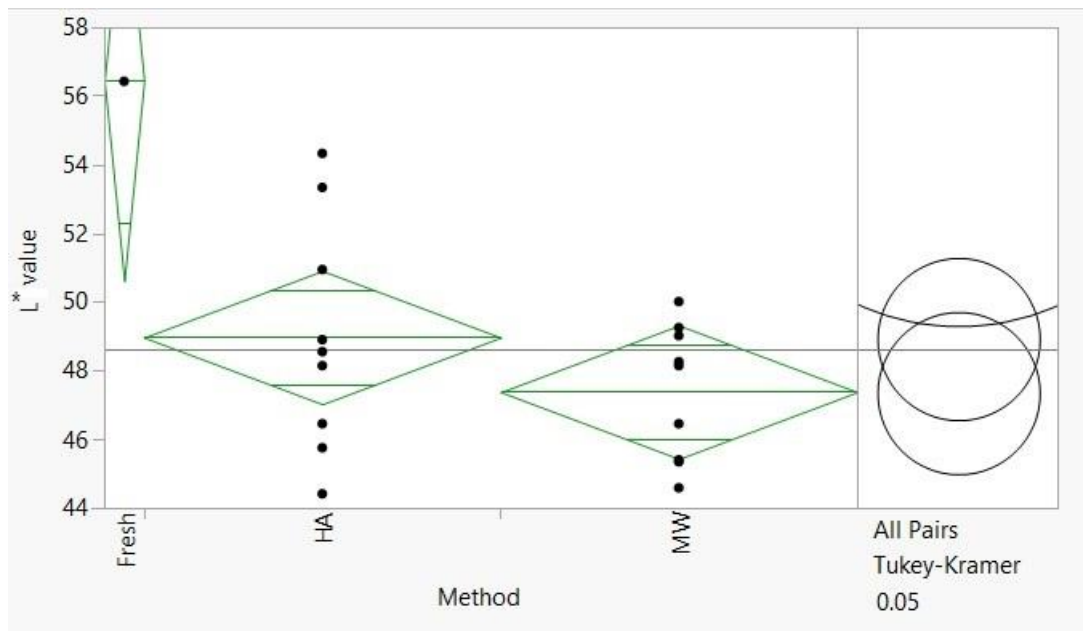


Figure 4.9. One-way and All Pairs Tukey-Kramer Analysis of L^* value by drying method

A negative a^* value of broccoli means greenness of the dried samples. The greenness represented by a^* value of fresh broccoli was around -13.93 , while for hot air and microwave-convective dried samples, it ranged from -4.82 to -13.94 . The largest change in a^* value was spotted at 50°C - 30 mm in hot air drying. The mean a^* value in hot air drying was slightly greater than that in microwave drying which could be seen in Figure 4.10, but in microwave drying the a^* value pattern of broccoli products showed more together for various treatments compared to the results of hot air drying. No significant difference was found between fresh,

hot air drying, and microwave drying group as per Tukey-Kramer HSD comparison. Neither drying temperature nor bed thickness affected a^* value of broccoli significantly as per statistical analysis.

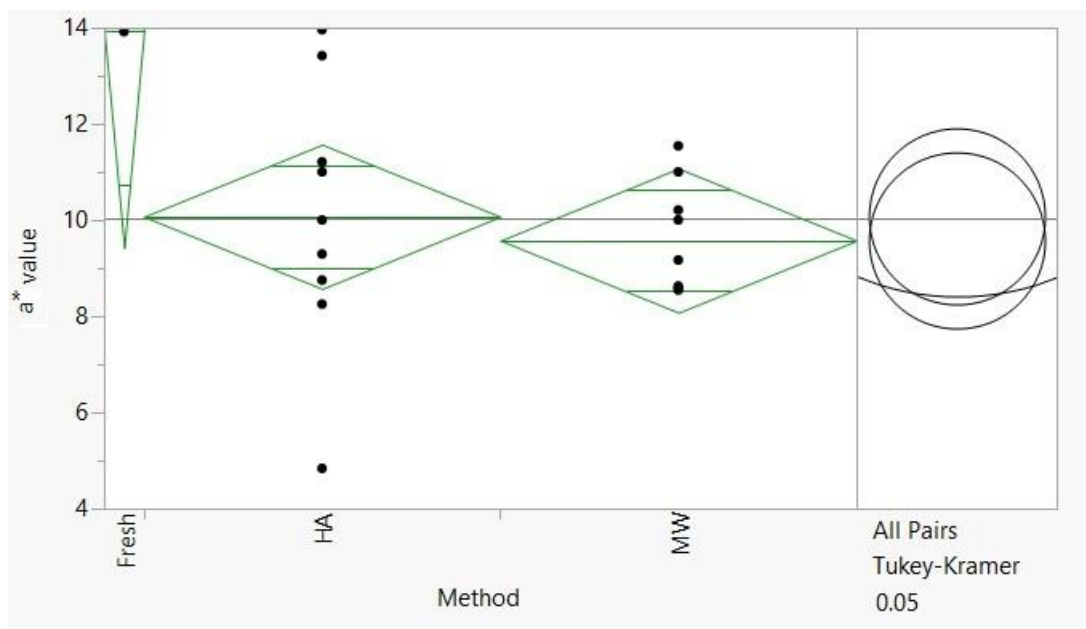


Figure 4.10. One-way and All Pairs Tukey-Kramer Analysis of a^* value by drying method

A positive b^* value of broccoli means yellowness of the products. The yellowness represented by b^* value of fresh broccoli was about +24.25, while for hot air drying and microwave drying, it ranged from +25.32 to +32.51. The largest change in b^* value was spotted at 60°C - 20 mm in microwave drying. As can be seen from Figure 4.11, under both hot air drying and microwave drying, the mean b^* value was above the value found in fresh broccoli, and the meanwhile was higher in microwave drying compared with hot air drying. It means that microwave drying mainly influenced the yellowness of broccoli products to make it look 'more yellow' from exterior appearance. Significant difference was found between fresh and microwave dried broccoli while no significance was found in hot air drying group as per Tukey-Kramer HSD comparison. Neither drying temperature nor bed thickness affected b^* value of broccoli significantly according to the analysis. Furthermore, chroma c and hue angle α , of all

the drying conditions, differed from the values of the fresh broccoli which reflected how microwave and hot air drying affected the color of broccoli.

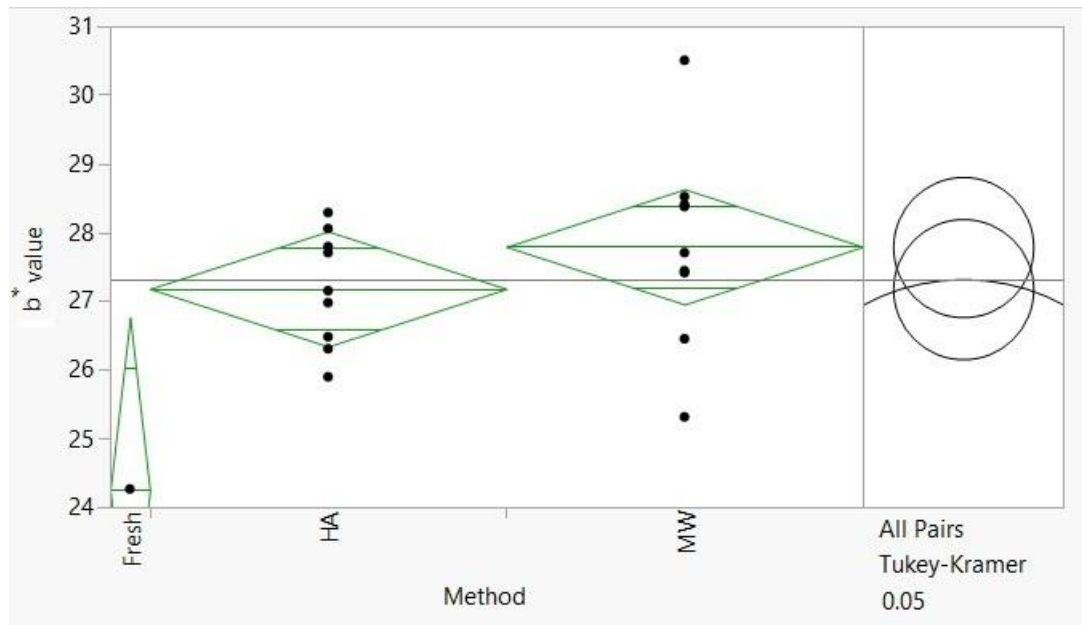


Figure 4.11. One-way and All Pairs Tukey-Kramer Analysis of b^* value by drying method

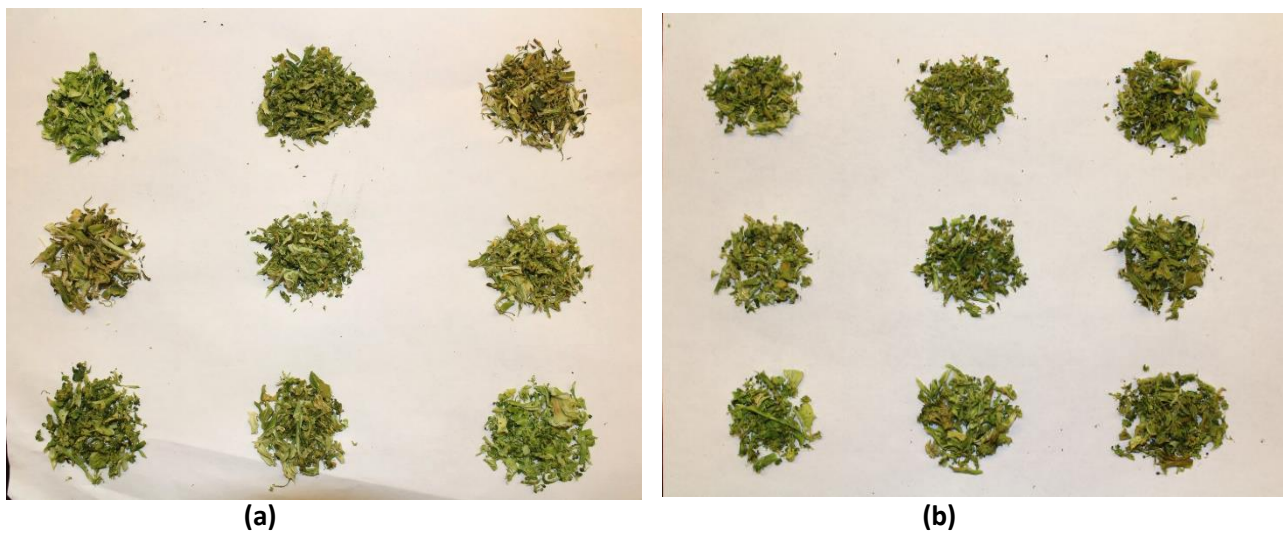


Figure 4.12. Appearance of dried broccoli samples in (a) hot air drying and (b) microwave drying

4.3 Rehydration measurement

The rehydration capacity of dried broccoli products after hot air drying and microwave drying is shown in Table 4.4. The comparison of rehydration capacity between hot air drying and microwave drying is also presented in Figure 4.13. Rehydration capacity was presented as the ratio of the rehydrated weight and initial weight. Microwave dried broccoli particles exhibited better rehydration capacity than hot air dried samples from a general perspective but this difference was not very significant to observe. This might have resulted from changes in the structure, or texture of the samples during microwave drying with a more rapid and constant temperature rise than hot air drying. Same findings were presented in many people's work (Maskan, 2001). No significant effect of drying temperature or bed thickness on rehydration rate of dried samples in hot air drying and microwave drying was found based on the analysis of our data.

Table 4.4. Effect of different drying methods on the rehydration capacity of broccoli bed

Drying Method	Parameter	
	Rehydration Capacity (ratio)	
Hot air drying		
50°C-10 mm HA	6.63	±0.23
50°C-20 mm HA	6.00	±0.01
50°C-30 mm HA	4.58	±0.18
60°C-10 mm HA	4.75	±0.13
60°C-20 mm HA	6.55	±0.49
60°C-30 mm HA	6.61	±0.20
70°C-10 mm HA	6.49	±0.52
70°C-20 mm HA	5.08	±0.16
70°C-30 mm HA	6.67	±0.31
MW drying		
50°C-10 mm MW	5.35	±0.06
50°C-20 mm MW	5.77	±0.15
50°C-30 mm MW	5.96	±0.27
60°C-10 mm MW	4.90	±0.46
60°C-20 mm MW	7.01	±0.42
60°C-30 mm MW	6.67	±0.16
70°C-10 mm MW	6.62	±0.13
70°C-20 mm MW	6.38	±0.18
70°C-30 mm MW	6.92	±0.21

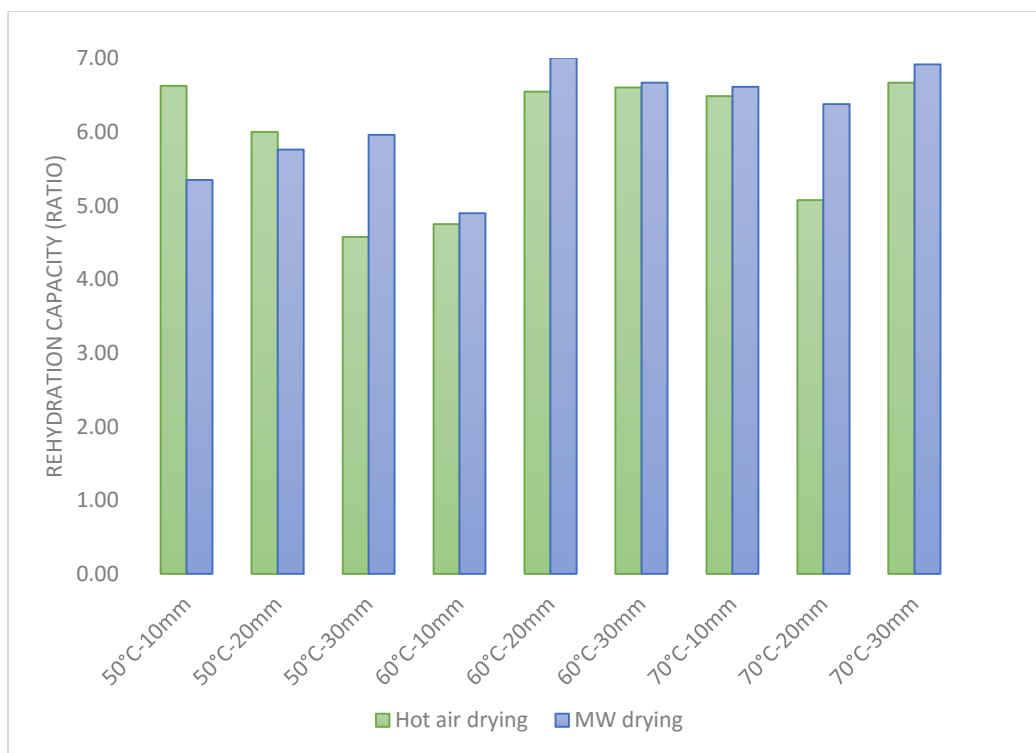


Fig.4.13. The rehydration capacity of broccoli under hot air drying and microwave drying

4.4 Influence of hot air drying and microwave drying on bioactive compounds of broccoli

4.4.1 Effects of hot-air drying on total phenolic content, total flavonoid content and free radical scavenging ability

A two-factorial, three-level experimental design was applied in this study. The investigation was carried under hot air drying, and studied factors and their levels were: the drying temperature at 50, 60, and 70 °C; the broccoli bed thickness at 10, 20, and 30 mm. The different combinations of the independent variable and their corresponding response in terms of TPC (Total phenolic content), TFC (Total flavonoids content) and AEAC (ascorbic acid equivalent antioxidant content) were obtained and are shown in Table 4.5. TPC was expressed as milligrams of gallic acid equivalents (GAE) per 100 g of fresh weight, and TFC was presented as mg of quercetin equivalents (QE) per 100 g of fresh broccoli. The unit of AEAC was mg per 100 g of fresh broccoli as well.

Table 4.5. Face-centered central composite design (CCD) with observed response for total phenolic content (TPC), total flavonoid content (TFC), and ascorbic acid equivalent antioxidant content (AEAC) from hot air drying of broccoli

Design points	Drying Temperature(°C)	Bed Thickness(mm)	TPC (GAE mg/100g)		TFC (QE mg/100g)		AEAC (mg/100g)	
R1	50	10	2284.25	±25.70	128.63	±16.28	252.76	±23.68
R2	50	20	1607.16	±44.94	92.00	±23.87	201.16	±7.59
R3	50	30	1543.11	±51.96	117.07	±22.80	163.46	±24.07
R4	60	10	2320.85	±20.45	129.87	±17.12	209.19	±26.45
R5	60	20	2307.12	±39.39	85.77	±3.55	236.38	±4.90
R6	60	30	2233.92	±42.52	174.16	±23.81	219.70	±11.83
R7	70	10	2480.97	±29.31	131.12	±6.96	255.85	±27.64
R8	70	20	2009.75	±55.83	67.28	±9.48	276.55	±4.18
R9	70	30	1968.58	±40.82	110.31	±7.08	257.70	±22.78
R10	60	20	2032.63	±52.67	88.44	±14.38	222.48	±29.71
R11	60	20	2316.27	±94.52	79.90	±19.02	225.82	±7.76
R12	60	20	2206.47	±31.39	95.02	±4.37	207.96	±11.14
R13	60	20	2192.75	±74.86	82.93	±8.47	241.02	±6.68

4.4.1.1 Determination of Total phenolic content (TPC)

Response surface regression models were fitted to the experimental data. The ANOVA of the effect of hot air drying on total phenolic content is shown in Table 4.6 and actual-predicted plot is shown in Figure 4.14. The linear model obtained for total phenolic content was

significant with an R^2 value of 0.8091 and a p value of 0.0185. This suggests that the model was good and could be used to predict the total phenolic content from hot-air dried broccoli. The ANOVA result indicated that the linear effect of drying temperature had the most significance on total phenolic content of broccoli under hot air drying with a p value less than 0.05. The prediction equation is presented in Eq.4.1.

$$TPC_{HA} = -8180.86 + 376.11 \times DT - 120.73 \times BT + 0.57 \times DT \times BT - 3.08 \times DT^2 + 1.60 \times BT^2$$

... (Eq.4.1)

Where: TPC_{HA} is the total phenolic content of the sample after hot air drying.

DT is the drying temperature, °C

BT is the bed thickness of broccoli pieces, mm

Table 4.6. ANOVA for total phenolic content of broccoli after hot air drying

Source	SS	DF	MS	P Value
Model	756688.32	5	151338	0.0185
Error	178493.84	7	25499	
Term	Estimate	Std Error	t Ratio	P Value
Intercept	-8180.86	3461.41	-2.36	0.050
Drying temperature (50, 60, 70°C)	376.11	116.58	3.23	0.0145 ^a
Bed Thickness (10, 20, 30mm)	-120.73	61.76	-1.95	0.0915
DT × BT ^b	0.57	0.80	0.72	0.4970
DT × DT	-3.08	0.96	-3.21	0.0148 ^a
BT × BT	1.60	0.96	1.67	0.1394
R²		0.8091		

^aSignificant

^bDrying temperature × Bed Thickness

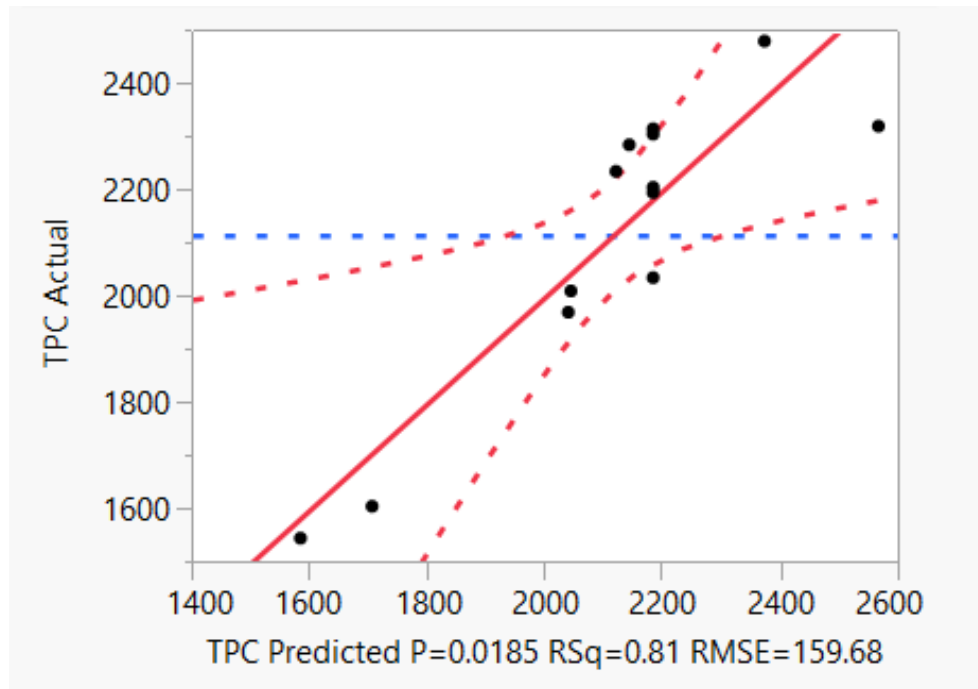


Figure 4.14. Actual-Predicted plot for total phenolic content of broccoli after hot air drying

The response surface plot of the effect of hot air drying on total phenolic content of broccoli is presented in Figure 4.15. According to the ANOVA result, drying temperature showed a relatively more significant effect on TPC compared to bed thickness. As drying temperature raised, more TPC of broccoli was preserved compared to a low drying temperature, 50°C, which may be caused by the much longer time needed in low temperature drying to raise the temperature of broccoli particle bed up to the equilibrium temperature between air flow and broccoli particle. The highest TPC was obtained at 70°C for a bed thickness of 10 mm, while the lowest TPC was obtained at 50°C and 30 mm. As expected, TPC normally showed a negative relationship with drying time. The shortest drying time (120 min) occurred at 70°C, 10 mm and the longest drying time (420 min) occurred at 50°C, 30 mm. At the air temperature of 60°C, no significant difference was found between different bed thicknesses but the average content was higher than the other two temperature groups. Considering a shorter drying time, hot air drying of broccoli at 50°C, 10 mm thickness could be an excellent processing condition for industrial application for the purpose of a better TPC retention.

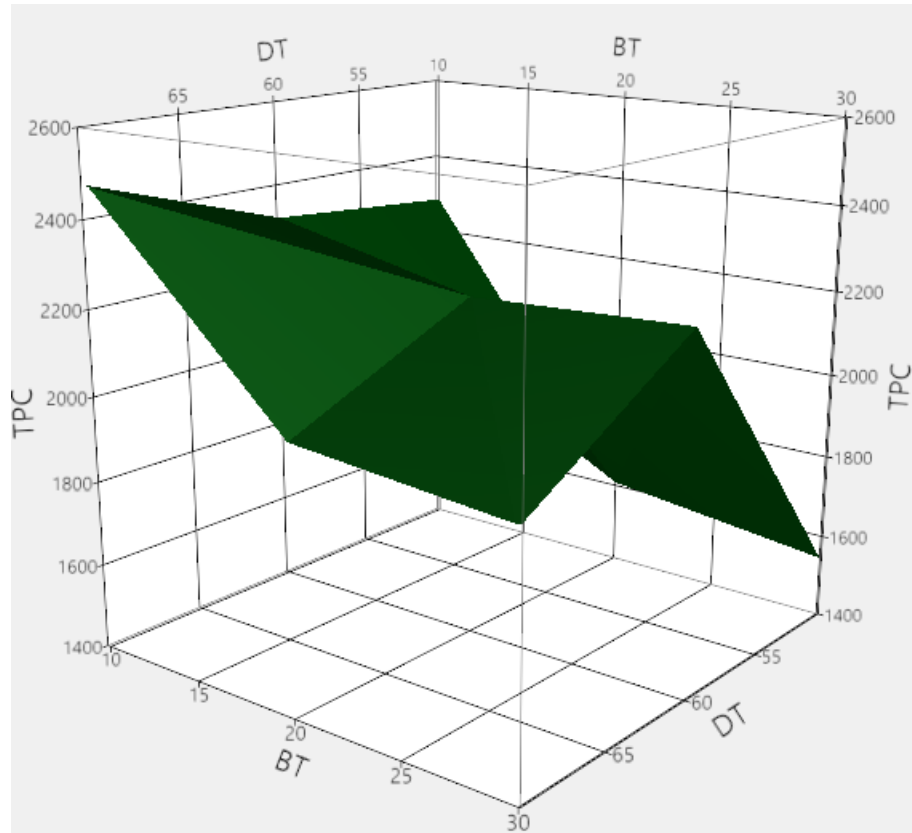


Figure 4.15. Response surface analysis of the effect of hot air drying on total phenolic content of broccoli

4.4.1.2 Determination of Total flavonoid content (TFC)

Response surface regression models were fitted to the experimental data. The ANOVA result of the effect of hot air drying on total flavonoid content is shown in Table 4.7 and actual-predicted plot is shown in Figure 4.16. The linear model obtained for total flavonoid content was significant with an R^2 value of 0.8144 and p value of 0.017. The results indicated that the model was good and could be used to predict the total flavonoid content from hot air dried broccoli. The ANOVA result also showed that the linear effect of bed thickness had the most significance on the total flavonoid content with a p value less than 0.05. The prediction equation is presented in Eq.4.2.

$$TFC_{HA} = -347.5 + 21.70 \times DT - 20.12 \times BT - 0.02 \times DT \times BT - 0.18 \times DT^2 + 0.54 \times BT^2 \quad \dots \text{(Eq.4.2)}$$

Where: TFC_{HA} is the total flavonoid content of broccoli after hot air drying.

DT is the drying temperature, °C

BT is the bed thickness of broccoli pieces, mm

Table 4.7. ANOVA for total flavonoid content of broccoli after hot air drying

Source	SS	DF	MS	P Value
Model	8343.2	5	1668.6	0.017
Error	1901.8	7	271.7	
Term	Estimate	Std Error	t Ratio	P Value
Intercept	-347.50	357.3	-0.97	0.363
Drying temperature (50, 60, 70°C)	21.70	12.0	1.80	0.11
Bed Thickness (10, 20, 30mm)	-20.12	6.37	-3.16	0.016 ^a
DT× BT^b	-0.02	0.08	-0.28	0.78
DT× DT	-0.18	0.10	-1.82	0.11
BT× BT	0.54	0.09	5.47	0.0009
R²		0.8144		

^aSignificant

^bDrying temperature × Bed Thickness

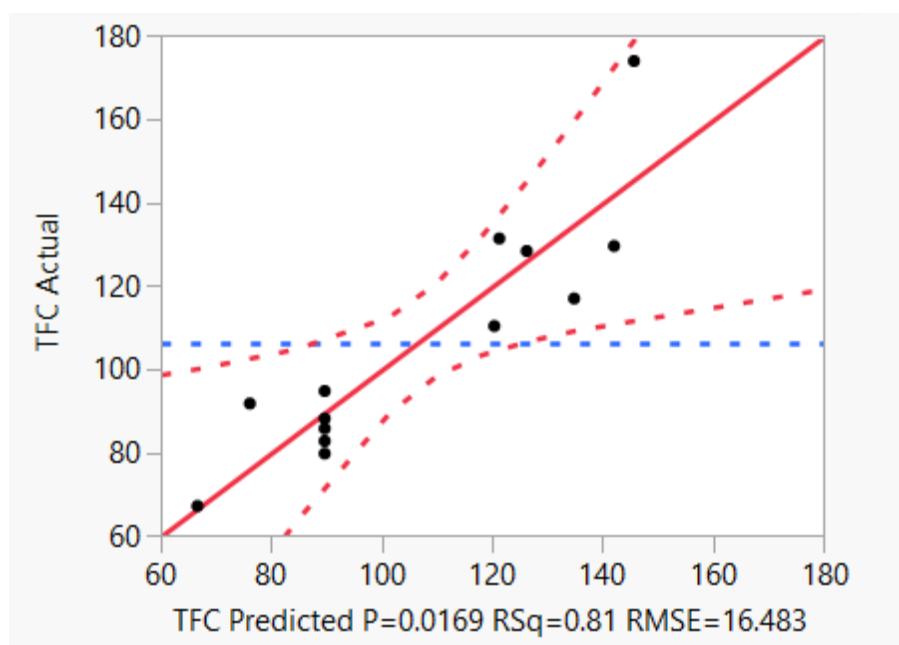


Figure 4.16. Actual-Predicted plot for total flavonoid content of broccoli after hot air drying

The response surface plot of the effect of hot air drying on total flavonoid content of broccoli is presented in Figure 4.17. From the ANOVA result, the bed thickness rather than drying temperature showed a relatively more significant effect on TFC. This situation may be resulted from the relatively low amount of TFC (70 to 180 vs. 1500 to 2500 of TPC) which minimized the effect of drying time. There were no significant differences between different drying temperature groups. Furthermore, 10 mm and 30 mm thick broccoli bed retained more TFC than 20 mm. The highest TFC occurred at 60°C, 30 mm. This condition could be a good option for industrial TFC consideration.

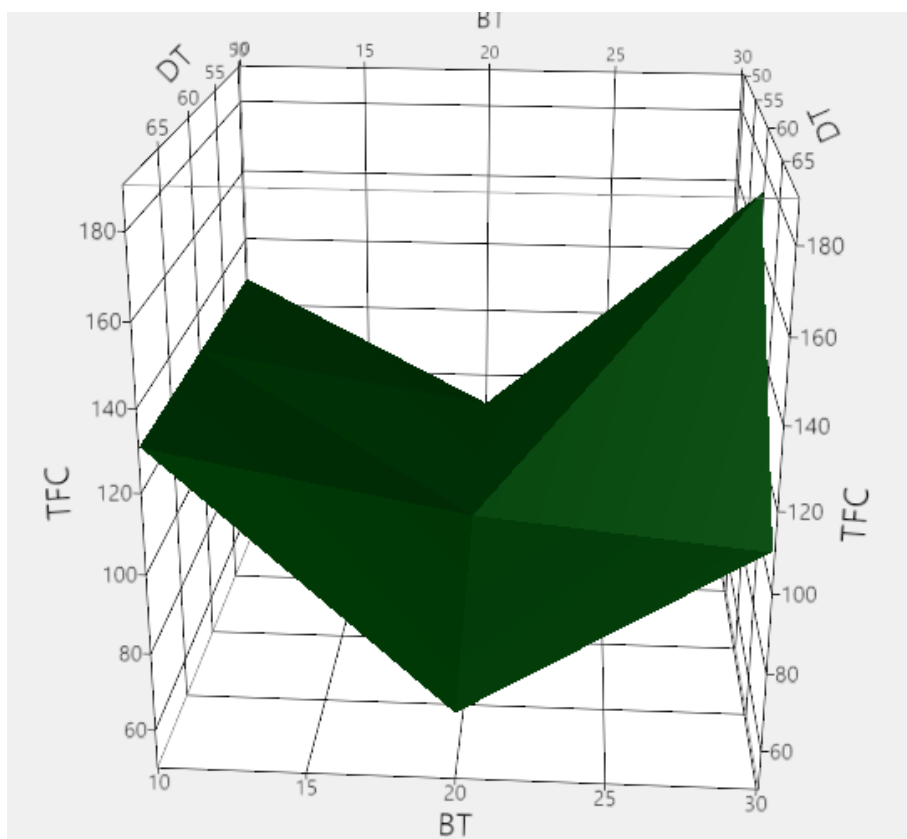


Figure 4.17. Response surface analysis of the effect of hot air drying on total flavonoid content of broccoli

4.4.1.3 Determination of Free Radical Scavenging Ability

Free Radical scavenging ability was presented by ascorbic acid equivalent antioxidant content (AEAC). Response surface regression models of AEAC were fitted to the experimental data. The ANOVA result of the effect of hot air drying on AEAC is shown in Table 4.8 and actual-predicted plot is shown in Figure 4.18. The linear model obtained for AEAC was significant with an R^2 value at 0.8199 and p value of 0.0153. The model fitted AEAC well and was useful to predict the ascorbic acid equivalent antioxidant content (AEAC) from hot air dried broccoli which represented the free radical scavenging ability of products. ANOVA result indicated that the linear effect of drying time multiplied by bed thickness had the most significance on AEAC with a p value less than 0.05. The prediction equation is presented in Eq.4.3.

$$AEAC_{HA} = -853.06 - 19.63 \times DT - 11.17 \times BT + 0.23 \times DT \times BT + 0.15 \times DT^2 - 0.09 \times BT^2 \dots \text{(Eq.4.3)}$$

Where: $AEAC_{HA}$ is the ascorbic acid equivalent antioxidant content of broccoli after hot air drying.

DT is the drying temperature, °C

BT is the bed thickness of broccoli particles, mm

Table 4.8. ANOVA for ascorbic acid equivalent antioxidant content of broccoli after hot air drying

Source	SS	DF	MS	P Value
Model	8699.33	5	1739.87	0.0153
Error	1910.75	7	272.96	
Term	Estimate	Std Error	t Ratio	P Value
Intercept	853.06	358.13	2.38	0.049 ^a
Drying temperature (50, 60, 70°C)	-19.63	12.06	-1.63	0.14
Bed Thickness (10, 20, 30mm)	-11.17	6.39	-1.75	0.12
DT× BT ^b	0.23	0.08	2.76	0.028 ^a
DT× DT	0.15	0.10	1.50	0.17
BT× BT	-0.09	0.10	-0.95	0.37
R^2		0.81991		

^aSignificant

^bDrying temperature × Bed Thickness

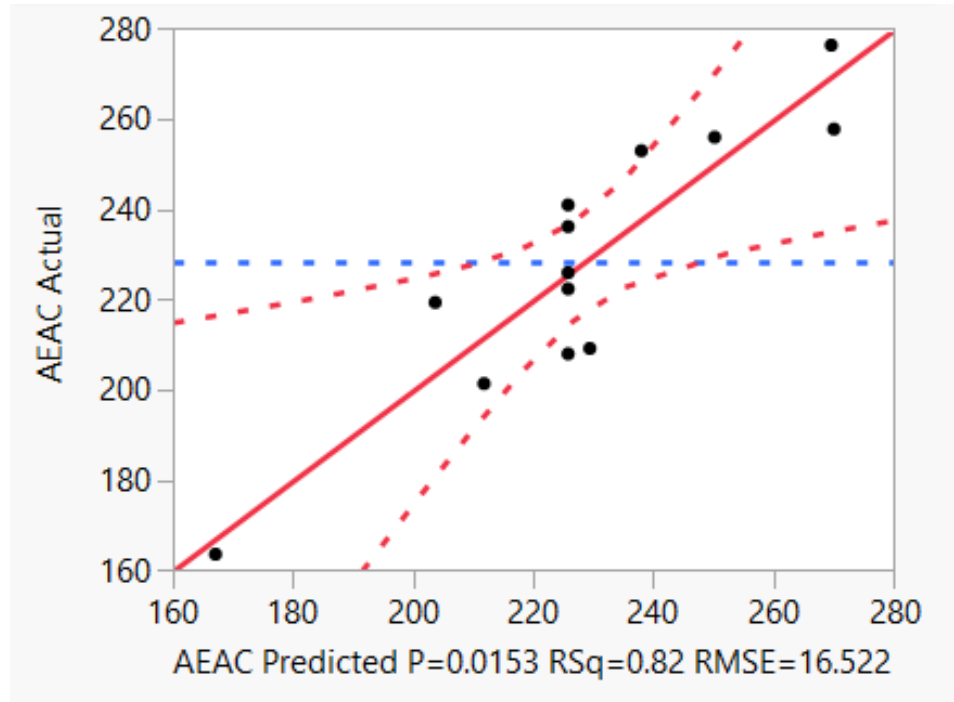


Figure 4.18. Actual-Predicted plot for ascorbic acid equivalent antioxidant content of broccoli after hot air drying

The response surface plot of the effect of hot air drying on ascorbic acid equivalent antioxidant content of broccoli is presented in Figure 4.19. From the ANOVA result, neither drying temperature nor the bed thickness showed a significant effect on AEAC. But from the response surface plot of the effect of hot air drying on ascorbic acid equivalent antioxidant content of broccoli, other than the highest point at 50°C, 10 mm, AEAC increased as temperature of air flow rose. The highest AEAC point might have resulted from a relatively short drying time and lower particle core temperature. But air of temperature at 70°C showed a generally high amount of AEAC. So the condition at 70°C, 20 mm could be recommended in industrial application for hot air drying for purpose of a better free radical scavenging ability of broccoli.

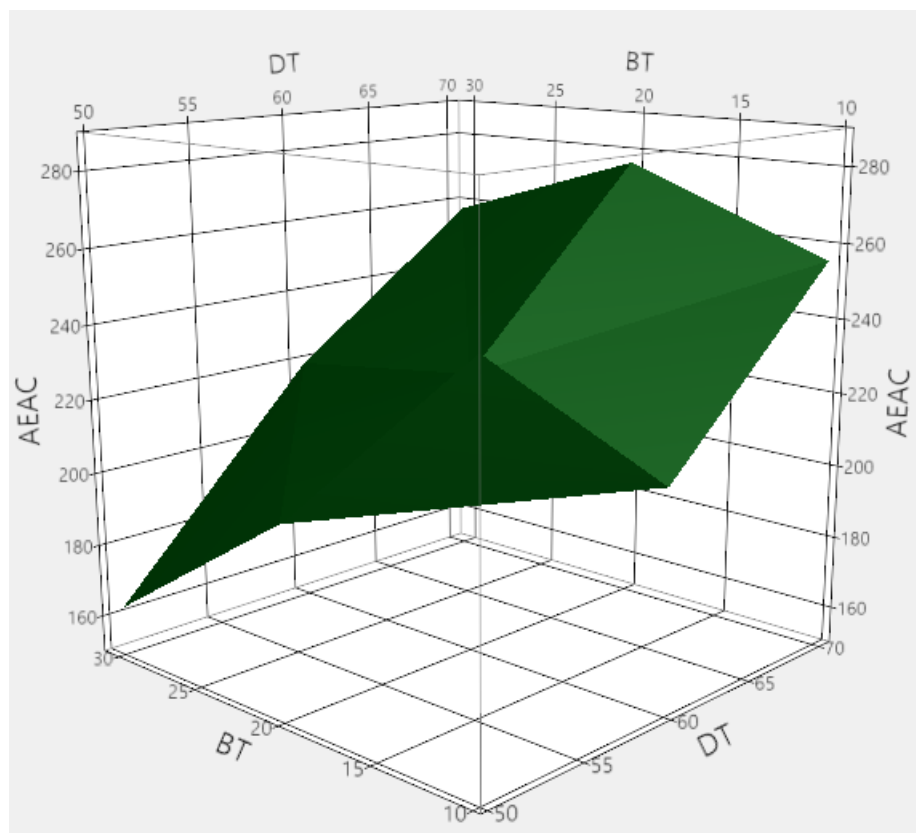


Figure 4.19. Response surface analysis of the effect of hot air drying on ascorbic acid equivalent antioxidant content of broccoli

4.4.2 Effects of microwave drying on total phenolic content, total flavonoid content and free radical scavenging ability

A two-factorial, three-level design was applied in this study. The investigation was carried under microwave-assisted drying, and studied factors and their levels were: the drying temperature set at 50, 60, and 70 °C together with microwave at 1.0 W/g power density; the broccoli bed thickness at 10, 20, and 30 mm. The different combinations of the independent variable and their corresponding response in terms of total phenolic content (TPC), total flavonoids content (TFC) and free radical scavenging ability (presented as AEAC: ascorbic acid equivalent antioxidant content) were obtained and shown in Table 4.9. Total phenolic content was expressed as milligrams of gallic acid equivalents (GAE) per 100 g of fresh weight, and total flavonoid content was presented as mg of quercetin equivalents (QE) per 100 g of fresh broccoli. The unit of AEAC was mg per 100 g of fresh broccoli as well.

Table 4.9. Face-centered central composite design (CCD) with observed response for total phenolic content, total flavonoid content, and ascorbic acid equivalent antioxidant content from microwave drying of broccoli

Design points	Drying Temperature(°C)	Bed Thickness(mm)	TPC (GAE mg/100g)		TFC (QE mg/100g)		AEAC (mg/100g)	
R1	50	10	2362.02	±61.79	63.72	±8.44	29.98	±9.51
R2	50	20	2339.15	±87.82	53.76	±4.35	117.25	±26.19
R3	50	30	2069.23	±160.25	46.11	±3.47	217.91	±8.15
R4	60	10	2613.64	±44.12	85.59	±1.54	67.65	±34.23
R5	60	20	2448.94	±161.85	74.74	±7.41	291.41	±3.76
R6	60	30	2348.30	±265.07	111.02	±8.21	298.29	±11.41
R7	70	10	4256.03	±68.31	98.22	±6.47	282.00	±7.23
R8	70	20	3061.98	±192.15	96.09	±4.65	271.86	±25.86
R9	70	30	2055.50	±275.98	93.24	±9.68	291.41	±17.07
R10	60	20	1872.51	±398.10	77.95	±16.23	288.87	±28.58
R11	60	20	1716.96	±62.89	88.08	±22.48	289.24	±18.84
R12	60	20	2009.75	±249.07	89.86	±19.27	247.96	±52.27
R13	60	20	1977.73	±59.82	85.59	±4.04	297.20	±18.19

4.4.2.1 Determination of Total phenolic content (TPC)

Response surface regression models of TPC after microwave drying were fitted to the experimental data. The ANOVA result of the effect of microwave drying on the total phenolic content is shown in Table 4.10 and actual-predicted plot is illustrated in Figure 4.20. The linear model obtained for total phenolic content was significant with an R^2 value of 0.8472 and a p value of 0.009. This suggests that the model was very good and could be used to predict the total phenolic content from microwave-assisted drying of broccoli. According to the ANOVA result, it is also indicated that the linear co-effect of drying time multiplied by bed thickness had the most significant level on total phenolic content with a p value less than 0.05. The prediction equation is presented in Eq.4.4:

$$TPC_{MW} = 12128.33 - 411.45 \times DT + 144.61 \times BT - 4.77 \times DT \times BT + 4.58 \times DT^2 + 2.39 \times BT^2$$

... (Eq.4.4)

Where: TPC_{MW} is the total phenolic content of broccoli after microwave drying.

DT is the drying temperature, °C

BT is the bed thickness of broccoli particles, mm

Table 4.10. ANOVA for total phenolic content of broccoli after microwave drying

Source	SS	DF	MS	P Value
Model	4440906.3	5	888181	0.0090
Error	801140.88	7	114449	
Term	Estimate	Std Error	t Ratio	P Value
Intercept	12128.33	7333.24	1.65	0.14
Drying temperature (50, 60, 70°C)	-411.45	247.00	-1.67	0.14
Bed Thickness (10, 20, 30mm)	144.61	130.85	1.11	0.31
DT× BT^b	-4.77	1.69	-2.82	0.025 ^a
DT× DT	4.58	2.03	2.25	0.06
BT× BT	2.39	2.03	1.17	0.28
R²		0.84717		

^aSignificant

^bDrying temperature × Bed Thickness

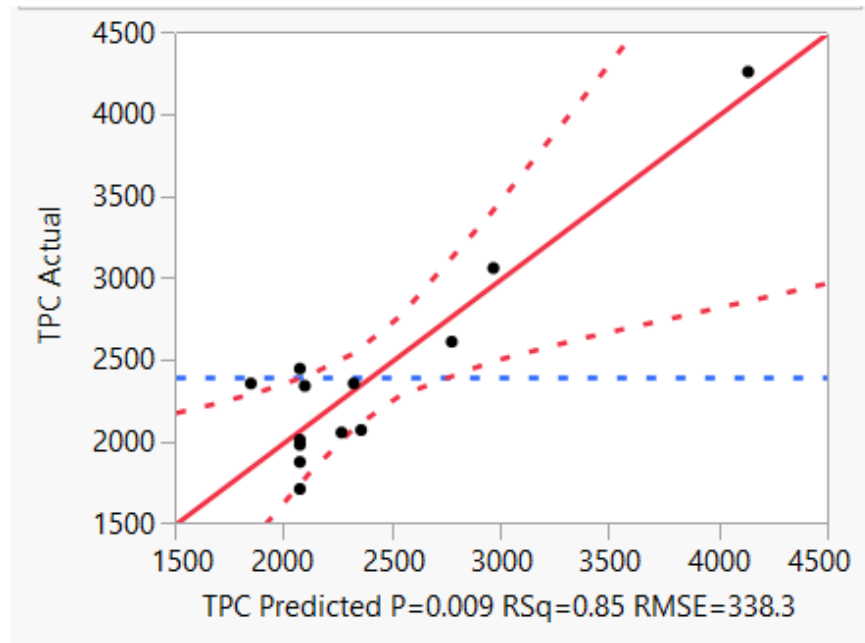


Figure 4.20. Actual-Predicted plot for total phenolic content of broccoli after microwave drying

The response surface plot of the effect of microwave drying on total phenolic content of broccoli is presented in Figure 4.21. It is shown that drying temperature and bed thickness showed a combined effect on TPC, which is different from hot air drying, from the ANOVA result. Microwave drying helped the temperature of broccoli bed increase rapidly to the equilibrium point within 5 min, compared with a normally much longer time up to the same level in hot air drying. The highest TPC point, up to 4256.3 mg GAE/100 g fresh product which is almost twice as that in hot air drying, was obtained at 70°C and 10 mm because of the shorter drying time. Except from the two points of 70°C, 10 mm and 70°C, 20 mm, no obvious differences were observed among other groups. Thus, microwave drying of broccoli at 70°C, 10 mm could be recommended as an excellent processing condition for industrial application for seeking a better TPC retention of broccoli.

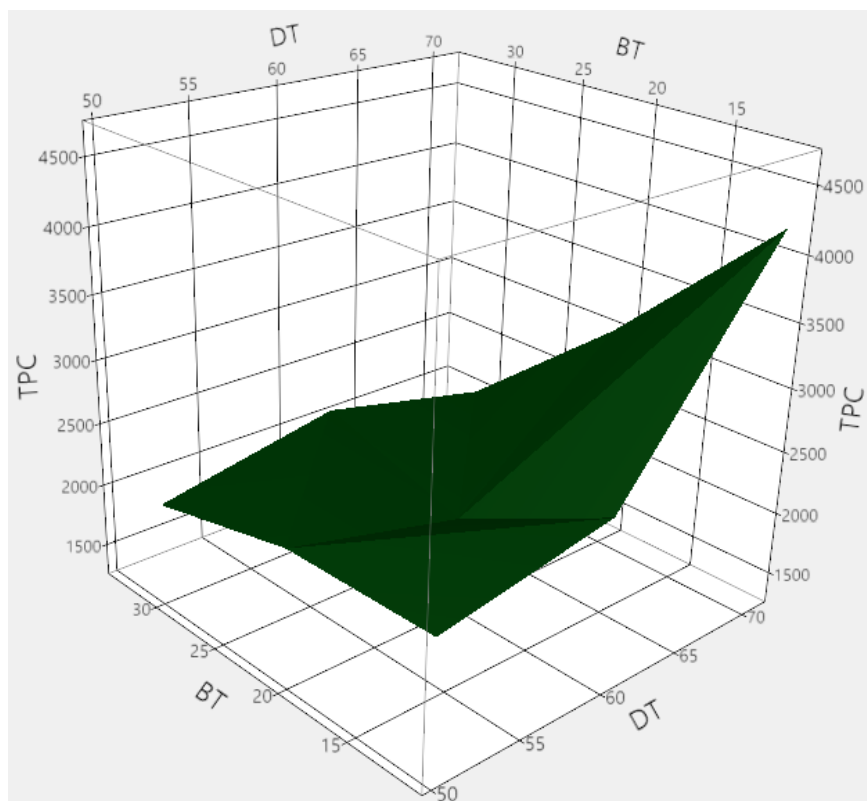


Figure 4.21. Response surface analysis of the effect of microwave drying on total phenolic content of broccoli

4.4.2.2 Determination of Total flavonoid content (TFC)

Response surface regression models of TFC after microwave drying were fitted to the experimental data. The ANOVA result of the effect of microwave drying on total flavonoid content is presented in Table 4.11 and actual-predicted plot is presented in Figure 4.22. The linear model obtained for total flavonoid content was significant with a p value of 0.018 and an R^2 value of 0.8091. This suggested that the model was good to be used to predict the TFC (total flavonoid content) from microwave air dried broccoli. Also the ANOVA result indicated that the linear effect of drying temperature had the most significant effect on total flavonoid content with a p value less than 0.05. The prediction equation is presented in Eq.4.5:

$$TFC_{MW} = -524.15 + 19.91 \times DT - 5.04 \times BT + 0.03 \times DT \times BT - 0.15 \times DT^2 + 0.08 \times BT^2 \quad \dots \text{(Eq.4.5)}$$

Where: TFC_{MW} is the total flavonoid content of broccoli after microwave drying.

DT is the drying temperature, °C

BT is the bed thickness of broccoli particles, mm

Table 4.11. ANOVA for total flavonoid content of broccoli after microwave drying

Source	SS	DF	MS	P Value
Model	3271.5	5	654.3	0.018
Error	771.6	7	110.2	
Term	Estimate	Std Error	t Ratio	P Value
Intercept	-524.15	227.6	-2.30	0.054
Drying temperature (50, 60, 70°C)	19.91	7.6	2.60	0.035 ^a
Bed Thickness (10, 20, 30mm)	-5.04	4.1	-1.24	0.254
DT× BT ^b	0.03	0.05	0.60	0.56
DT× DT	-0.15	0.06	-2.24	0.045 ^a
BT× BT	0.08	0.06	1.26	0.25
R ²		0.8091		

^aSignificant

^bDrying temperature × Bed Thickness

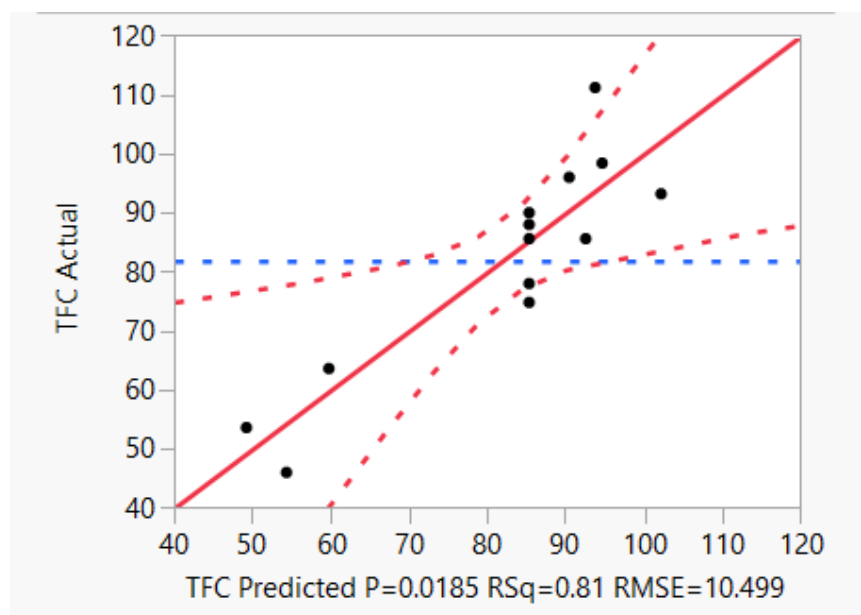


Figure 4.22. Actual-Predicted plot for total flavonoid content of broccoli after microwave drying

The response surface plot of the effect of microwave drying on total flavonoid content of broccoli is presented in Figure 4.23. From ANOVA result and plot, it could be concluded that drying temperature of microwave drying had the main significant effect on total flavonoid content (TFC) other than bed thickness. Besides the highest point at 60°C and 30 mm, TFC increased as drying temperature increased. In conclusion, both 70°C group and 60°C, 30 mm were excellent conditions for industrial TFC consideration in microwave-assisted drying.

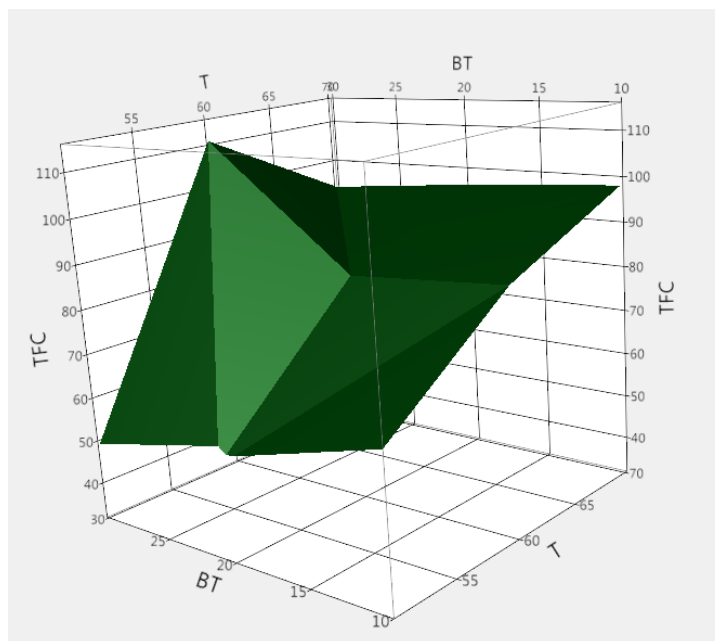


Figure 4.23. Response surface analysis of the effect of microwave drying on total flavonoid content of broccoli

4.4.2.3 Determination of Free Radical Scavenging Ability

Free Radical scavenging ability was presented as ascorbic acid equivalent antioxidant content (AEAC). Response surface regression models of AEAC were fitted to the experimental data. The ANOVA result of the effect of microwave drying on ascorbic acid equivalent antioxidant content, which could reflect the free radical scavenging ability, is shown in Table 4.12 and actual-predicted plot is illustrated in Figure 4.24. The linear model obtained for ascorbic acid equivalent content was significant with a p value of 0.0079 and an R^2 value of

0.8527. These parameters illustrated that the model was very excellent to predict the ascorbic acid equivalent antioxidant content (AEAC) which reflects the free radical scavenging ability from microwave air dried broccoli. Moreover, this model showed that the linear effect of bed thickness had the most significance on total flavonoid content with a p value less than 0.05. The prediction equation is presented in Eq.4.6

$$AEAC_{MW} = -2333.88 + 58.83 \times DT + 52.51 \times BT - 0.44 \times DT \times BT - 0.35 \times DT^2 - 0.46 \times BT^2 \dots \text{(Eq.4.6)}$$

Where: $AEAC_{MW}$ is the ascorbic acid equivalent antioxidant content of broccoli after microwave drying.

DT is the drying temperature, °C

BT is the bed thickness of broccoli particles, mm

Table 4.12. ANOVA for total flavonoid content of broccoli after microwave drying

Source	SS	DF	MS	P Value
Model	91838.88	5	18367.8	0.0079
Error	15857.67	7	2265.4	
Term	Estimate	Std Error	t Ratio	P Value
Intercept	-2333.88	1031.718	-2.26	0.0581 ^a
Drying temperature (50, 60, 70°C)	58.83	34.75	1.69	0.1343
Bed Thickness (10, 20, 30mm)	52.51	18.41	2.85	0.0246 ^a
DT× BT ^b	-0.44	0.24	-1.88	0.1029
DT× DT	-0.35	0.29	-1.22	0.2622
BT× BT	-0.46	0.28	-1.62	0.1484
R ²	0.8527			

^aSignificant

^bDrying temperature × Bed Thickness

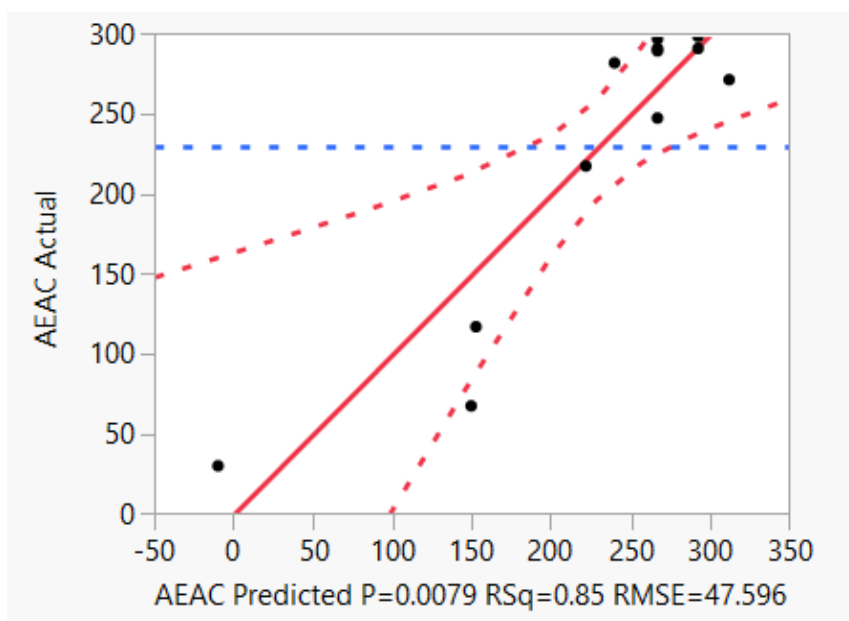


Figure 4.24. Actual-Predicted plot for ascorbic acid equivalent antioxidant content of broccoli after microwave drying

The response surface plot of the effect of microwave drying on ascorbic acid equivalent antioxidant content (AEAC) of broccoli after microwave drying is presented in Figure 4.25. According to the ANOVA result and response surface plot, it can be seen that bed thickness presented the significant effect on AEAC over drying temperature. While no obvious high point was observed in this plot, the trend was found that thicker bed of broccoli showed a better free radical scavenging ability than thin bed. Perhaps this phenomenon resulted from a more even heat distribution in the thick bed of broccoli particles under microwave drying. From the point view of balancing process time and energy cost, condition at 60°C and 30mm could be suggested in industrial application of microwave drying for a better free radical scavenging ability of broccoli.

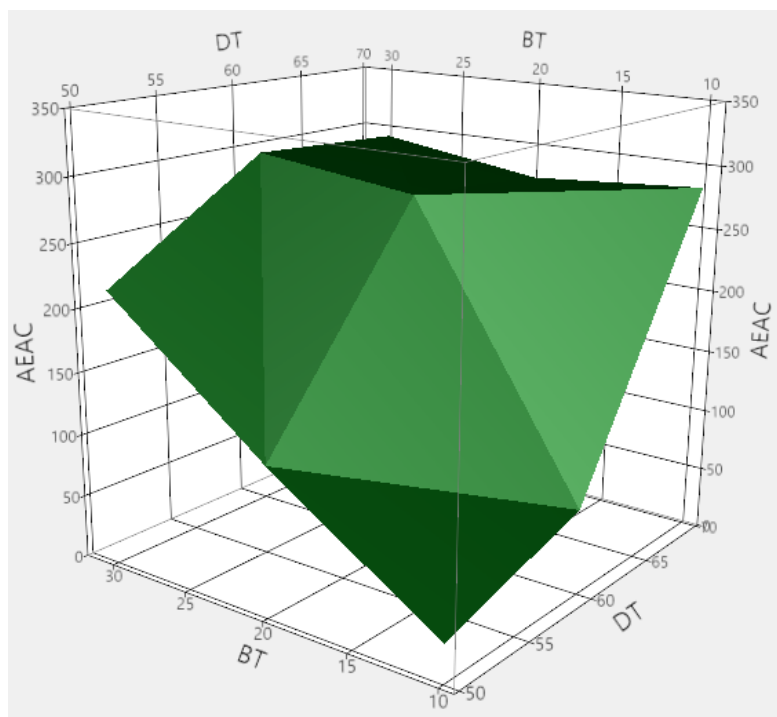


Figure 4.25. Response surface analysis of the effect of microwave drying on ascorbic acid equivalent antioxidant content of broccoli

4.5 Effect of pretreatments on microwave drying of broccoli

The pretreatments given to broccoli before drying were: (a) Blanching in hot water at 80 °C for 3 min; (b) Dipping in the solution containing 1, 3, 5 g/L citric acid; (c) Held in frozen storage at -10 °C for 24h. Untreated broccoli was also dried under the same condition for comparison.

The L^* value, of whiteness, a^* value, of greenness when negative, b^* value of yellowness when positive, of fresh broccoli were respectively 56.45 ± 1.89 , 13.93 ± 0.65 , 24.25 ± 1.47 (Table 4.13). These main color parameters of dried broccoli under microwave drying are listed in the Table 4.10 and graphed in Figure 4.26. The highest L^* value, 59.73 ± 2.83 , which means that the best performance in terms of brightness was spotted in 5 g/L citric acid processing group, while frozen sample seemed relatively darker than other groups. In terms of a^* value, only in the acid processing group a^* value decreased when citric acid concentration increased. No apparent differences were found in other processing groups. In terms of b^* value, only blanched sample showed a slightly higher value than non-treated ones. The effect of different pretreatments on

the color of dried broccoli might be the result from the change in tissue structure (as freezing disorders cell structure), the inactivation of enzymes such as blanching or acid processing (Lewicki, 2006). These pretreatments can help better color retention to some extent.

Table4.13. Effect of different pretreatments on the color of broccoli

Pretreatment method	Color parameters									
	L*		a*		b*		C		α°	
Fresh	56.45	±1.89	13.93	±0.65	24.25	±1.47	27.97	±1.60	60.12	±0.46
No treatment	49.24	±4.39	11	±0.59	30.51	±2.46	32.46	±2.19	70.07	±2.24
blanched	45.78	±0.97	9.11	±2.02	30.78	±1.74	32.15	±1.82	73.54	±3.52
1g/L citric acid	46.66	±5.09	7.43	±1.84	23.62	±1.42	24.83	±1.20	72.51	±4.64
3g/L citric acid	45.19	±4.45	4.61	±0.44	28.21	±2.19	28.59	±2.19	80.7	±0.89
5g/L citric acid	59.73	±2.85	3.48	±1.78	28.58	±1.82	28.83	±1.84	83.06	±3.45
frozen	42.02	±5.31	8.56	±1.45	26.16	±3.33	27.56	±3.38	71.79	±2.68

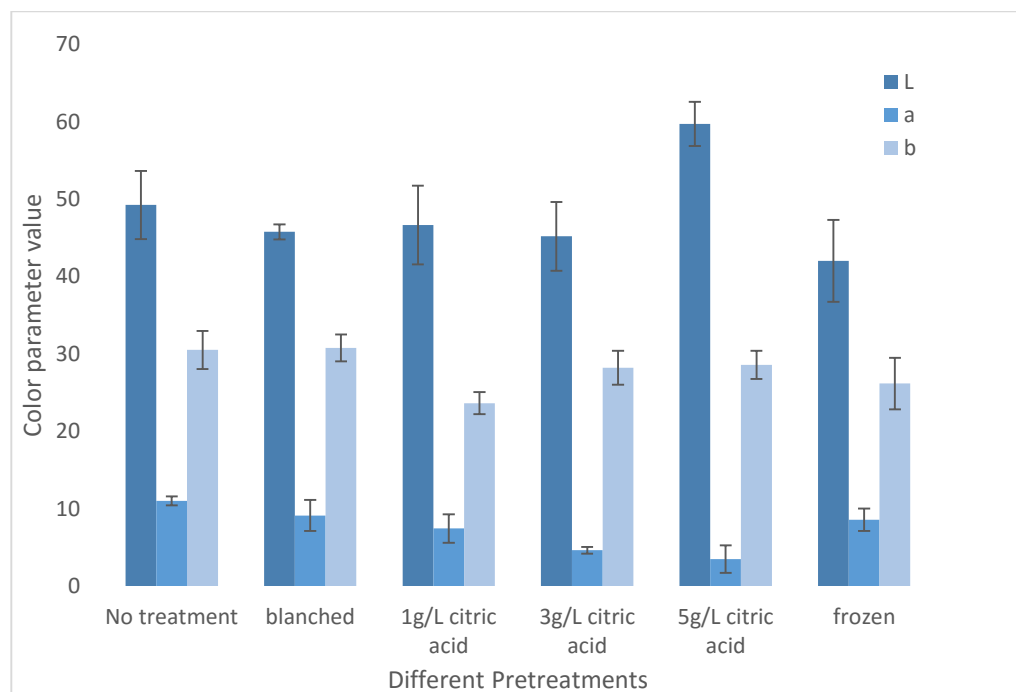


Figure 4.26. Effect of different pretreatments on the main color parameters of broccoli

The rehydration capacities of different pretreated broccoli under microwave drying are shown in Table 4.14 and graphed in Figure 4.27. Other than 5 g/L citric acid group, no obvious differences were observed between pretreated samples and non-treated ones. Additionally, it can be concluded that high-concentration citric acid pretreatment of broccoli would harm its rehydration capacity but other pretreatments were feasible.

Table 4.14. Effect of different pretreatments on the rehydration capacity of broccoli

Drying method	parameter	
	Rehydration Capacity (ratio)	
MW drying (60°C-20mm)		
blanched	6.66	±0.30
1g/L citric acid	6.16	±0.36
3g/L citric acid	6.80	±0.26
5g/L citric acid	4.73	±0.18
frozen	6.49	±0.26

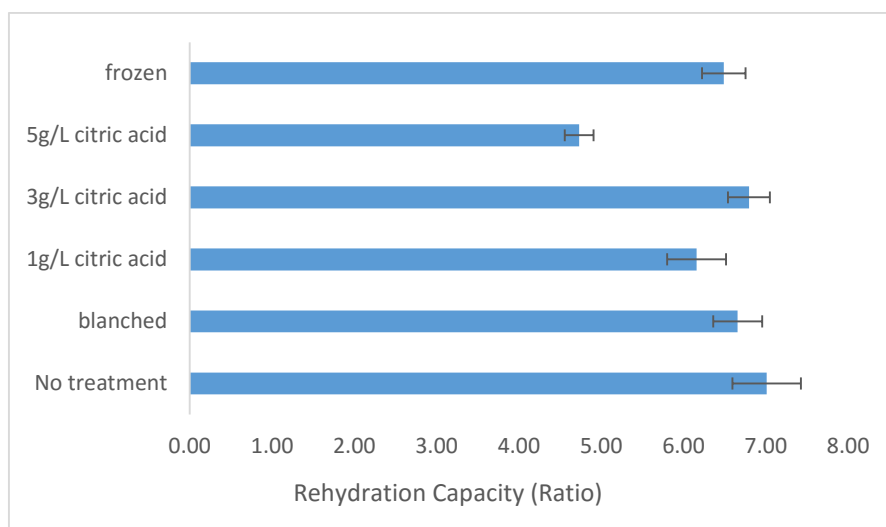


Figure 4.27. Effect of different pretreatments on rehydration capacity of dried broccoli

The total phenolic content (TPC), total flavonoid content (TFC), free radical scavenging ability (presented as AEAC) are presented in Figure 4.28, Figure 4.29 and Figure 4.30. The frozen and 3 g/L citric acid pretreatments generated more TPC than no-treatment control group.

Blanching treatment reduced TPC to some extent. In terms of TFC, only blanching treatment showed a relatively better performance compared to non-treatment group. No obvious differences were observed between different pretreatment when it comes to the free radical scavenging ability, while blanching and 3 g/L citric acid treatment only showed a marginally better ability than others.

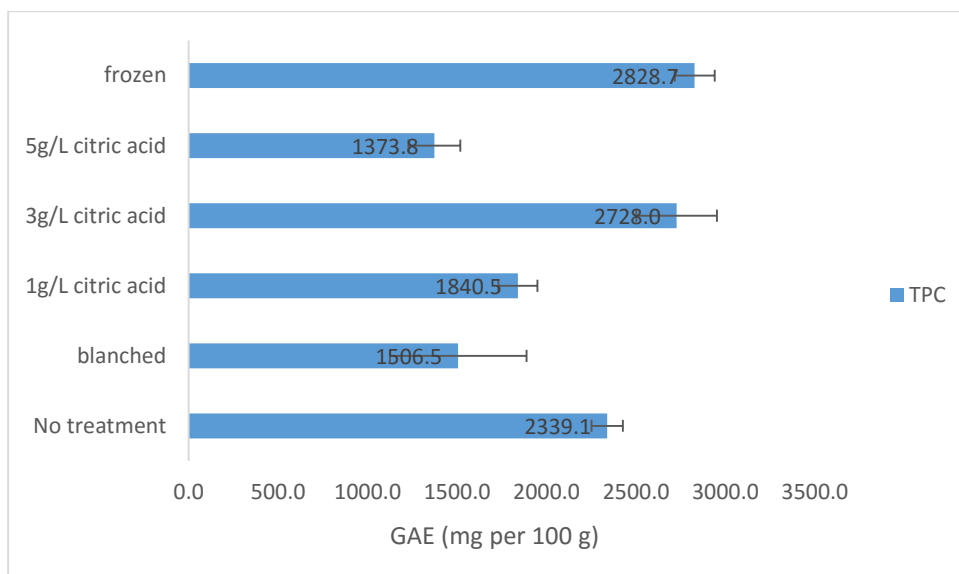


Figure 4.28. Effect of different pretreatments on total phenolic content of dried broccoli

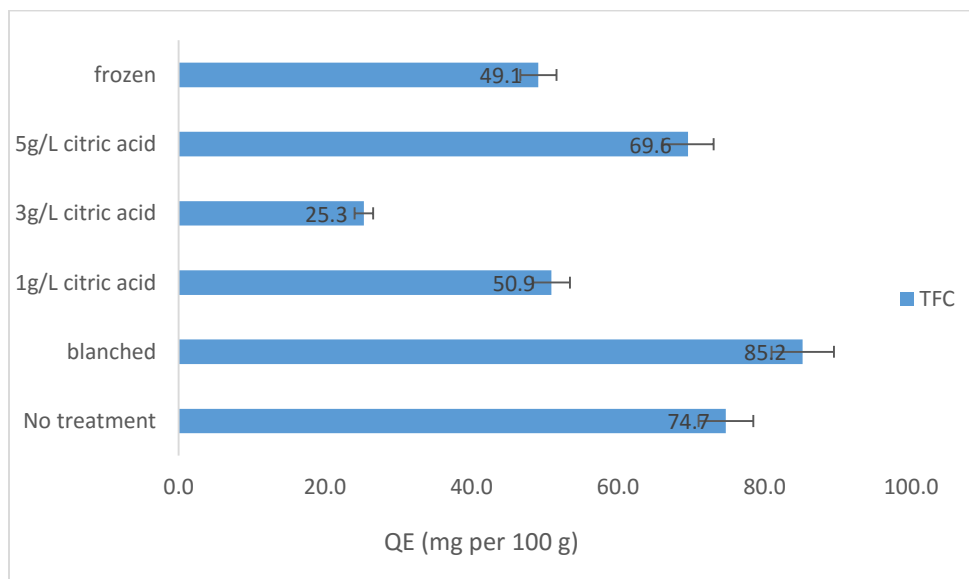


Figure 4.29. Effect of different pretreatments on total flavonoid content of dried broccoli

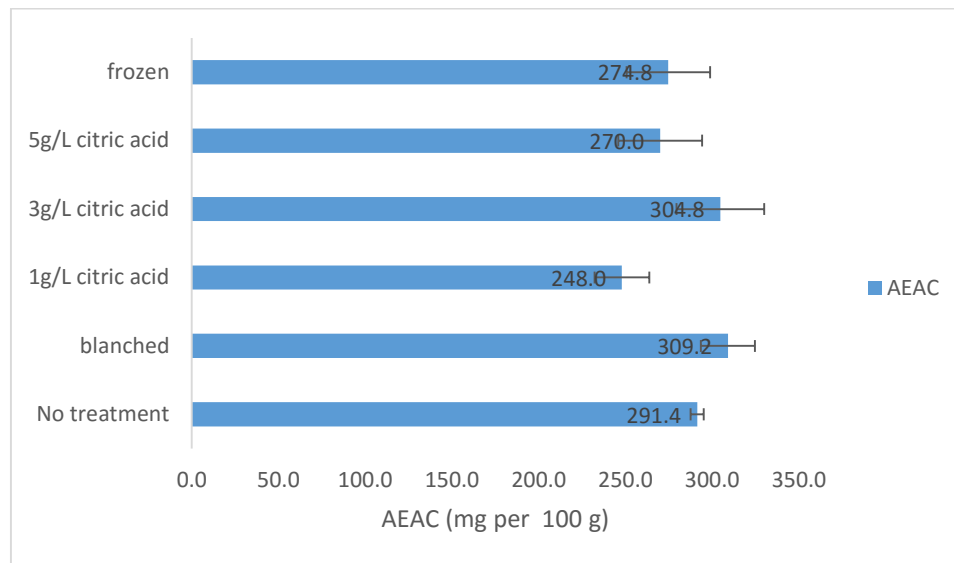


Figure 4.30. Effect of different pretreatments on ascorbic acid equivalent antioxidant content of dried broccoli

Chapter V

Summary and Conclusion

Broccoli (*Brassica oleracea* L.) is a common and well-accepted green vegetable which plays a significant role in both domestic and international markets. It is a rich source of nutritional compounds, such as vitamins, minerals, flavonoids, phenolics, carotenoids and dietary fiber. In recent years, broccoli has even been more attractive to consumers notable for its anti-cancer properties. Different *in vitro* and *in vivo* assays have presented that compounds of flavonols show high antioxidant activity, anti-mutagenic activity and it can even be utilized as vasodilators and platelet disaggregators. Because of the high level of moisture content, broccoli is difficult to preserve as fresh vegetable for a long period. Meanwhile, huge amounts of broccoli wastes after processing are discarded in Northern American markets, which may cause pollution and hygiene problems. Drying is a good option to prolong the shelf-life of broccoli, to counter the problem of insufficiency of fresh vegetable during long distance voyage, to reuse broccoli wastes and develop value-added byproducts in vegetable industry and to be processed as ingredients in convenience food in order to fulfil the emerging demand of dried vegetable products in markets.

Numerous drying techniques have been researched to understand the drying behavior of broccoli and to obtain better quality products. Compared with conventional hot air drying method, microwave assisted drying, which was also sometimes expressed as microwave drying, is an effective way to minimize the negative effect of long operation time. This method is rapid and energy efficient. Notwithstanding certain work has been done to study the microwave drying of broccoli, still little data currently exists on the microwave drying of broccoli which are chopped into particles and gathered in form of broccoli bed consisting of chopped florets and stems. A brief review of drying is followed by a more specific discussion and experimental investigation of broccoli's drying behavior under both hot air and microwave drying. The results of this investigation served to formulate practical recommendations for the vegetable processing industry.

In this study, work of the application of broccoli bed drying under both microwave-assisted drying and hot air drying has been done to obtain the drying dynamics of broccoli, modeling of drying curves, dielectric properties at different temperatures and under different frequencies; to study the effect of different drying conditions on the color performance, rehydration capacity and bioactive compounds, such as total phenolic content (TPC), total flavonoid content (TFC) and free radical scavenging ability (presented as AEAC); and to determine how pretreatments affect the quality of dried broccoli.

Conclusions included:

1. Overall drying time was remarkably reduced, *e.g.* from 320 - 420 min to around 120 min at 30 mm broccoli bed, under microwave drying (vs. hot air drying). And the difference of drying time between microwave drying and hot air drying increased as broccoli bed thickness increased, i.e. drying time was reduced more obviously in a thicker broccoli bed by microwave drying. From the energy cost point of view, the sets: 50 °C, 30 mm and 60 °C, 20 mm reduced correspondingly 65.8%, 59.2% drying time from hot air drying to microwave drying thus saved the most energy and potential cost.
2. The drying rate was raised by the introduction of microwave power. In hot air drying, temperature showed as the most significant factor on drying rate. In microwave drying, the drying rate increased as broccoli bed thickness increased. Under microwave drying a thicker bed of broccoli was helpful in achieving a rapid dehydration of broccoli.
3. The semi-empirical Midilli-Kucuk equation: $MR = a \exp(-kt^n) + bt$ was used to describe the drying kinetics of broccoli under hot air drying and microwave drying which gave an accurate fit for all the data points with high coefficient of determinations (R^2) and low sum of squared errors of prediction (SSE) and root-mean-square-error (RMSE). Hot air drying fitted this model better than microwave drying since most R^2 s of drying curves under hot air drying were greater than 0.9996.
4. Dielectric properties of broccoli at different temperatures and under different frequencies were determined in this study using an open ended coaxial probe technique (Network-Analyzer with a high temperature probe) which provides fundamental data to study the drying behavior of broccoli. Besides, at 60°C broccoli in an applied microwave

field shows the highest dielectric loss factor which stands for the highest heat-electromagnetic energy conversion ratio at this temperature. At 60 °C, 2450 MHz, the dielectric constant ϵ' of broccoli is 64.15 ± 3.90 ; the dielectric loss factor ϵ'' of broccoli is 22.88 ± 1.55 .

5. While microwave drying provided a more uniform appearance of the dried broccoli particles, the products of microwave drying looked darker (the average L^* value decreased from $+48.97$ to $+47.79$) and slightly yellower (the average b^* value increased from $+27.18$ to $+27.80$) than those produced by hot air drying.
6. Better rehydration capacity of dried broccoli was observed in microwave drying but this phenomenon was not obvious (the average rehydration capacity was 6.18 in microwave drying while 5.93 in hot air drying).
7. To obtain a better total phenolic content (TPC), total flavonoid content (TFC), and free radical scavenging ability (measured ascorbic acid equivalent antioxidant content AEAC), a suitable experimental design was used to measure these quality parameters under a range of drying conditions. Models were established to predict the amount of TPC, TFC, and free radical scavenging ability under both hot air drying and microwave drying. In hot air drying, highest TPC of 2480.97 ± 29.31 mg GAE/100 g was obtained at 70°C, 10 mm; highest TFC of 174.16 ± 23.81 mg QE/100 g was obtained at 60°C, 30 mm; highest AEAC of 276.55 ± 4.18 mg/100 g was obtained at 70°C, 20 mm. In microwave drying, highest TPC of 4256.03 ± 68.31 mg GAE/100 g was obtained at 70°C, 10 mm; highest TFC of 111.02 ± 8.21 mg QE/100 g was obtained at 60°C, 30 mm; highest AEAC of 298.29 ± 11.41 mg/100 g was obtained at 60°C, 30 mm. Compared with hot air drying, microwave drying provided a product with more TPC, but less TFC, and similar levels of free radical scavenging ability.
8. Several pretreatments were also studied to understand how they affected the after-drying quality of broccoli products. These pretreatments helped a better color retention to some extent but high-concentrated acid pretreatment would harm the rehydration capacity. Moreover, only blanching treatment showed a relatively better performance compared to non-treatment group in terms of TPC, TFC and AEAC.

Further research to study the effect of different drying method on other kinds of nutrients, of which only several limited kinds has ever been studied, in broccoli is suggested. An improved drying equipment can also be developed to obtain a more precise, prompt and sensitive control on dehydration process. Additional types of pretreatment should be considered to study on whether they would influence the quality of product in a positive way.

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