Drying of Healthy Foods

From Mechanism to Optimization

Xin Jin

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Xin Jin

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Chapter 1

Mechanistic Driven Modeling and Optimization to Produce Dried Healthy Food Products: State of Art and Challenges

1.1 drying of vegetables

Food, either in natural or in processed form, provides energy and essential nutrients for human life. A diet rich in essential nutrients has a positive effect on the human condition. The essential nutrients for humans are carbohydrates, proteins, fats, vitamins and minerals. Vitamins and anti-oxidants in fresh food strengthen the immune system. For example, lycopene contributes to the reduction of prostate, lung and breast cancers, and also a broad range of epithelial cancers (Shi et al., 2000, Goula et al., 2006, Chang et al., 2007, Dewanto et al., 2002). Glucosinolates have significant anticarcinogenic properties in the context of colorectal cancer (Verkerk et al., 2004, Verkerk et al., 2009, Volden et al., 2009, Cieslik et al., 2007).

Fresh cultivated fruits and vegetables contain several essential nutrients, but due to the high moisture content these fresh products have a short shelf life. One of the most applied preservation methods to extend shelf life is drying. At low moisture content the water activity is low and consequently the microbial activity. It allows preservation of foods over a prolonged period. This technology can be traced back to ancient times when people used sun and wind for natural drying of foods. The experience of thousands of years and modern research resulted in various drying methods and drying equipment. Among the available methods convective drying with heated air is one of the most applied methods to preserve vegetable and fruit products. The heat load of this method causes, however, quality changes (color, flavor, texture and nutritional components) in food during drying.

In recent years the demand of consumers in the industrialized world for convenience and processed food products expanded and at the same time also the expectations on product quality, safety nutritional values and sustainability increased. This drives the need for research on drying technologies that retain quality attributes.

1.2 Broccoli

Brassica vegetables (cabbage, cauliflower, broccoli, Brussels sprouts etc.) are common, not only because of the taste but also because of the nutritional components having a positive effect on healthiness. It has been observed that a diet rich in *Brassica* vegetables can reduce the risk of lung, stomach, colon cancers

(Murillo and Mehta, 2001, Verkerk et al., 2004, Volden et al., 2009). Although the mechanism of the reduction of these cancers is not clear, the anti-oxidants in these products (vitamin C, polyphenols, carotenoids, glucosinolates) play a role in the reduction (Gliszczynska-Swiglo et al., 2011, Middleton and Kandaswami, 1993).

Two groups of enzymes in foods are involved in carcinogenic development; 1) phase I enzymes which, depending on the conditions, can activate or deactivate carcinogens, and 2) phase II enzymes that detoxify carcinogens. Inhibition of phase I enzymes, and induction of phase II enzymes suppresses cancer development. *Brassica* vegetables have a high content of glucosinolates which can be hydrolysed by myrosinase to isothiocyanate, nitrile and thiocyanate (Figure 1) (Verkerk et al., 2001). In *in vivo* studies it was observed that isothiocyanate can inhibit phase I enzymes that activate carcinogens, and induces phase II detoxification of carcinogens (Jones et al., 2006). Glucosinolates and myrosinase are present in vacuoles and myrosin cells, respectively, and due to this separation the product does not hydrolyze spontaneously. The hydrolysis occurs only when the cell walls are broken down, for example by cutting, chewing or by heat treatments.

The moisture content of fresh broccoli ranges between 87-93% (wet basis). Due to the high moisture content the shelf life of broccoli at low temperatures (3-4°C) is limited to 7-10 days after harvest. To increase the shelf life drying can be applied to reduce the water activity. Drying can also be used to produce broccoli ingredients for convenience foods (soup powders, vegetable croutons, frozen food products). An interesting option is to activate bioactivity during drying. However, as bioactive components are heat sensitive, the drying system and the operational conditions should be carefully chosen to retain bioactivity.

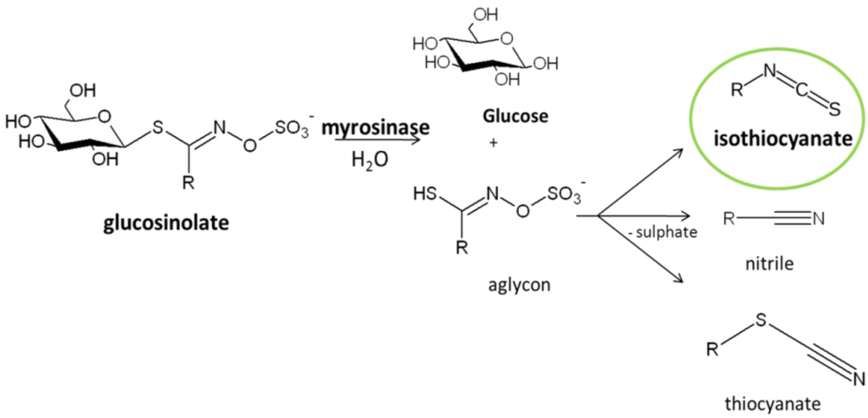

Figure 1 Schematic diagram of hydrolysis of glucosinolates (Verkerk et al., 2001).

1.3 Influence of pre-treatments and drying conditions on quality retention

Besides the activation and retention of bioactive compounds other quality attributes for dried products, like color, porosity, texture, flavor, have to be taken into account. It is therefore important to notice that drying is not the only unit in the chain of vegetable processing. It includes pre-treatment (washing, peeling, blanching etc.), drying and post-treatment (packaging, storage etc.). These treatments affect the quality attributes positively (digestibility, color bioavailability, Krokida et al., 2000) and negatively (breakdown of enzymes and micronutrients, Munyaka et al., 2010, Selman, 1994, Cieslik et al., 2007).

Prior to drying of vegetables, thermal pre-treatments may be needed. The enzymes peroxidase and lipoxygenase in fresh vegetables cause enzymatic reactions that result in color changes (turning products from green into brown) and unpleasant odor (Vamos-Vigyzao, 1995, McEvily et al., 1992). Therefore, before drying, vegetables are blanched to inactivate these enzymes which results in improved color and taste. Furthermore, blanching breaks down the internal cell walls, softens the internal tissue, and influences the elastic properties, which in turn enhance the drying rate and yields uniform shrinkage behavior (Kunzek et al., 1999, Munyaka et al., 2010, Waldron et al., 2003).

For water or steam blanching, the blanching temperatures range between 70-100 °C and the time between 1-10 minutes. Soluble solids partly leach to the blanching medium and compounds necessary for the formation of bioactive products may be inactivated as well. For example, blanching procedures (both steaming and water blanching) reduce the vitamin C content up to 40% of the initial value (Selman 1994, Vallejo et al. 2002). Mild blanching conditions are therefore required to reduce vitamin C degradation. In a recent study Munyaka et al. (2010) showed that high temperature-short time blanching retains vitamin C better than long time low temperature blanching. Water blanching reduces glucosinolates content to 45-58% of the initial content, while with steam blanching 80-82% of the initial value is retained (Vallejo et al. 2002, Volden et al. 2009).

When blanching is a necessary step prior to drying, loss of nutritional components cannot be avoided. The loss of the remaining components should be minimized during drying. A significant advantage of blanching with respect to drying is the softening of the internal tissue which results in an increased drying rate (Lewicki, 1998, Jin et al., 2012) and thus in a shorter drying time, less degradation of components and less energy consumption.

Temperature is a major factor for quality degradation during drying. For convective drying the air temperature in the dryer is often in the range of 40 to 70°C and the product temperature varies between the wet bulb temperature and the air temperature. For products with a long residence time in dryer the degradation of components is significant. Vega-Galvez et al. (2009) reported that for convective drying, vitamin C content falls below 40% of the initial value and that the retention decreases with increasing temperature. Similar results were reported by Goula and Adamopoulos (2006) and Zanoni et al (1998) for the degradation of Vitamin C during drying, and by Oliviero et al. (2012, 2013) for the degradation of glucosinolates and myrosinase during drying of broccoli. Therefore, mild drying conditions and a short residence time in dryer are required to retain these bioactive components.

1.4 Energy demand for drying

In convective drying, moisture vaporizes from the product. The heat required for vaporization makes drying one of the most energy intensive processes. According to a survey by Bahu (1991) in 1988, drying accounted at least 10% of the industrial energy demand in the UK and Europe. As drying is limited by a thermodynamic barrier and because of the market introduction of new dried products (functional foods, fast foods, and pharmaceuticals) the energy demand of drying has increased. Despite governmental programs for energy reduction in industry, drying accounts now for 15-20% of the total industrial energy consumption in developed countries (Kemp, 2012). Furthermore, about 85% of all installed industrial dryers are convective dryers with low energy efficiency (often below 50%) (Kudra, 2012).

The energy efficiency is defined as the ratio of energy for moisture evaporation and the total energy supplied to the dryer. For convective drying, the energy efficiency is based on the inlet air temperature T_{in} (°C), the drier outlet air temperatureT_{out} (°C) and the ambient temperature T_{amb} (°C):

$$\eta = \frac{T_{in} - T_{out}}{T_{in} - T_{amb}} \tag{1}$$

The latent heat for vaporization varies with temperature and ranges between 2501 and 2256 kJ.kg^{-1} over the temperature range of 0 and 100°C. Therefore, to remove 1 kg of moisture from a product in a dryer operating with 50% energy efficiency, over 4500 kJ.kg^{-1} energy is required. In addition, extra energy is required to heat the product to the drying temperature and to compensate for heat losses from the dryer. The state of art in the reduction of energy consumption is heat recovery, adjusting the operation conditions or to reduce heat loss with insulation (Kemp, 2012). Retaining product quality requests for low temperature drying, this according to equation 1 has low energy efficiency. The demands towards product quality and energy efficiency appear to be two conflicting aims!

1.5 Research challenges

In convective driers for vegetables the product temperature varies between the wet bulb temperature and the air temperature which is in the range of 40 to 70°C. Investigations showed that for products that reside at these temperatures the degradation of nutritional components is significant (Vega-Galvez et al., 2009, Goula and Adamopoulos, 2006, Zanoni et al., 1998, Oliviero et al., 2012, 2013). To retain these components during drying, mild drying at low temperatures should be applied. However, the energy efficiency at low temperatures is low. Although quality is regarded as the most important performance indicator, the energy consumption needs increasing attention to reduce the operational costs and to reduce the energy consumption and the emission of greenhouse gasses. Therefore retention of heat sensitive components needs to be combined with energy efficiency which brings two, possibly conflicting, challenges in drying research. The demands of mild and sustainable drying bring the research challenge for drying research.

- **How to dry vegetables with a high retention of nutritional components and high energy efficiency?**

This PhD research project on quality retention in combination with energy saving (this thesis) is part of a larger research project “Energy efficient drying of healthy food products”. The PhD projects in this context were:

1. Influence of drying technology on stability and availability of glucosinolates in broccoli (Teresa Oliviero, thesis writing in progress),
2. Drying of healthy foods: from mechanism to optimization (this thesis), and
3. Energy-efficient low-temperature drying using adsorbents (J.C. Atuonwu, PhD thesis Wageningen University, March 2013)

The goal of this thesis within the overall program is to investigate whether the problem of apparently conflicting demands on quality retention and energy efficiency can be solved by optimization. As the optimal drying strategy is expected not to be solved straightforward, an accurate, mechanistic description of the process and product degradation is required. The mechanistic description of the product degradation is obtained from Project 1. The results from Project 3 can add values to the improvement of energy efficiency.

Mishkin et al. (1984) were the pioneers in using optimization methods to improve the quality of dried food products. Banga et al. (1991, 1994) used various objective functions to optimize quality, energy efficiency or process time for drying. However, these optimization problems considered only one objective at a time. Kaminski et al. (1989), Madamba (1997), Kiranoudis & Markatos (2000) propose to apply multi-objective functions to meet the different requirements in food processing.

Maximizing product quality and energy efficiency are the key performance indicators. Afzal et al. (1999) investigated the influence of temperature and air velocity on quality and energy consumption via experiments. Caceres-Huambo and Menegalli (2009) maximized equipment loading and degradation of ascorbic acid in fruits during drying via numerical modeling. However, the combination of optimizing drying policy for energy efficiency and retention of *multiple* nutritional values is still missing. This will be the focus of this thesis. Therefore, the first research challenge for this thesis will be:

1. **Can the optimization problem for mild, sustainable drying of healthy vegetables be solved by use of mechanistic modeling?**

To solve such an optimization problem, models for moisture transport and sorption isotherm, kinetic models for bioactivity and models for energy efficiency are required. Food is complex soft matter which contains water/moisture, carbohydrates, fat, protein and ash. Drying of food and especially vegetables is effected by the interaction between these components and phase changes in the product matrix. Such physical and chemical changes effect progress of drying and should be reflected in the used model. Most drying models in literature take the coupled mass and heat transport phenomena into account (Mulet et al., 1999, Bon et al., 1997), but not the physical changes in the product matrix and the interaction between the components. The aim of this thesis work was to use a mechanistic driven modeling and optimization approach to produce healthy food. The second research question is:

2. **How to describe the drying rate and moisture sorption isotherm by models based on physical properties related to the product matrix?**

Due to the temperature and moisture gradients in the drying products, the degradation of nutritional components varies throughout particles that are being dried. Models assume ideal transport of moisture in the product matrix. However, validation of this assumption is still lacking. Therefore, the third research question is:

3. **How to validate moisture transport models and how to detect moisture transport phenomena non-destructively, qualitative and quantitatively?**

In this overview of challenges, measurements and modeling of the degradation kinetics of nutritional components is missing. This essential work is part of the parallel thesis work of Mrs. T. Oliviero (Product Design and Quality Management Group, Wageningen University). In this thesis, the kinetic results of her work are used to minimize product quality loss.

To realize the solutions for the above mentioned research questions a mechanistic drying modeling and optimization approach is used. The applied research scheme and required information are introduced in the following sections.

1.6 Simultaneous optimization of product quality and energy efficiency

Two ways of optimization can be considered: static and dynamic optimization. Static optimization searches for the best constant operational conditions or design parameters, and does not use the transient properties of the process. Drying of foods, however, include various stages of moisture transfer, for which dynamic optimization is more suitable. Dynamic optimization results in optimal trajectories for the operational conditions during the passage of food products through a dryer. The optimization uses an objective function, can deal with constraints, and can be applied to real production systems. The optimized trajectories can be continuous functions (Bryson, 1999) or discrete functions (piece wise constant or piecewise linear) (Banga et al., 2005). Discrete functions have the advantage that they can represent succeeding drying stages. For example, Banga et al. (2003) and Chou & Chua (2001) show that for drying of heat sensitive foodstuffs the use of multiple drying chambers, each operating at its optimal level, could lead to better products with significant energy savings.

The dynamic optimization requires knowledge of the drying system formulated as a mathematical model and constraints. A drying model for product particles based on mass and energy balances, physical properties and drying rates, and a quality model for the degradation of nutritional components. All required elements are given in Figure 2.

In this thesis we aim to use mechanistic models using physical and chemical relations and that also consider the spatial distribution of moisture, temperature and nutritional components. The drying model uses thermodynamic properties and takes the mobility of water in the product into account (for example by the glass transition temperature). Measurements of physical properties of broccoli are used in this thesis. In the product quality model myrosinase, glucosinolates and vitamin C in broccoli and the degradation of these components as a function of heat load and moisture levels are considered.

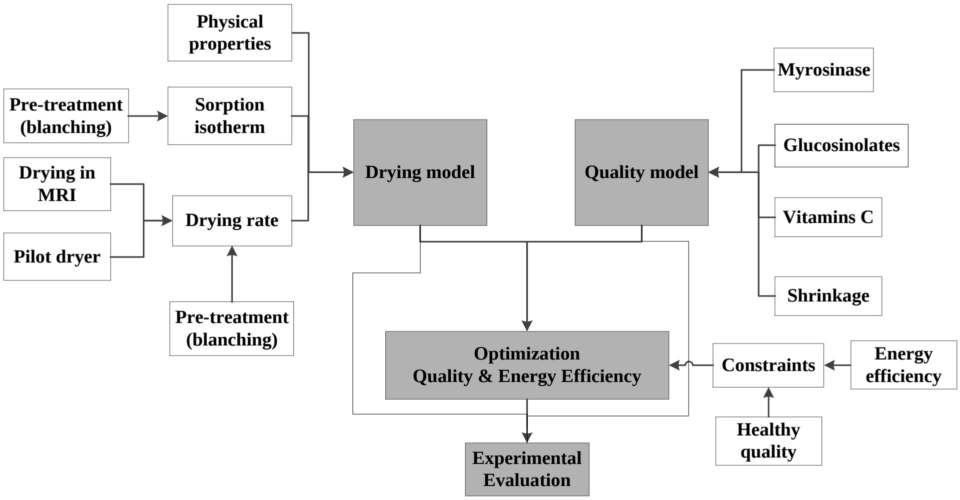

Figure 2 Research scheme according to the objective of this thesis work. The optimization uses a quality and a drying model. The quality model focusses on the retention of myrosinase, glucosinolates and vitamin C. The drying model involves physical properties, sorption isotherm and drying rates.

1.7 Mechanistic driven modeling and optimization

Figure 2 shows the combination of the kinetics on degradation of nutritional components with the drying kinetics. The degradation of nutritional components is a chemical process while drying is a multi-physics process. Models for the drying kinetics and sorption isotherm should therefore be based on the physical properties of the food matrix. As stated before food products as vegetables have a complex matrix due to interaction between the involved components and their effect on the mobility of water. For a good prediction of drying, which is a requirement for optimization; models that reflect the mechanism of moisture transport throughout the product matrix are required.

Optimization techniques have been well developed and have been applied in food process optimization (Hadiyanto et al, 2007). The majority of the process models, however, are still empirical or semi-empirical. Therefore, the emphasis of this thesis is to use mechanistic drying models (Figure 3). The mechanistic models used in this work are based on the Free Volume theories. To our knowledge, this is the first time that these theories are used for moisture transport in a food matrix in combination with quality models for nutritional components and used for the optimization drying trajectories.

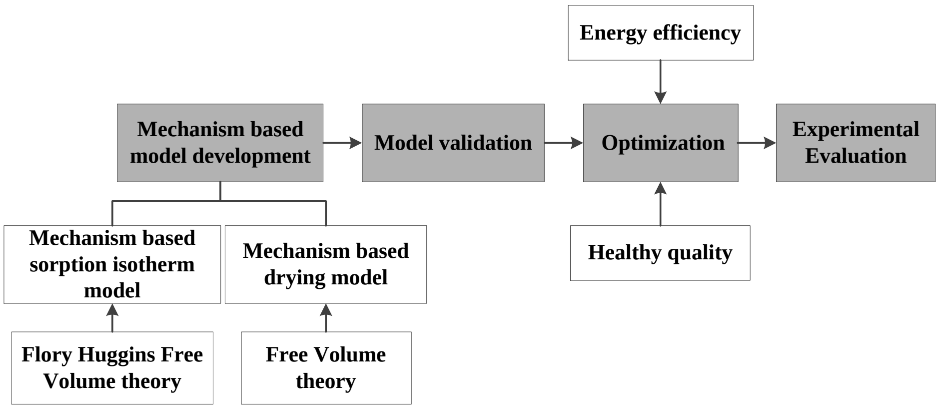

Figure 3 Physics driven modeling and optimization approach

1.7.1 Drying rates based on Free Volume theory

In drying of food products two periods can be distinguished; 1) the constant rate period, and 2) the falling rate period. For vegetable drying the constant rate period is very short; drying of broccoli is diffusion controlled (see for example Mulet et al., 1999). Fick's second law is the basis for modeling the internal moisture transport during diffusion controlled drying. It is commonly accepted that the effective diffusion coefficient in Fick's law is temperature dependent according the Arrhenius equation. This relation, however, has its limitations for food products. During drying the state of the food matrix changes from rubbery to glassy, which influences the mobility of water and hence the diffusion process. Mulet et al. (1999) propose to extend the Arrhenius equation with moisture dependent terms. Slade and Levine (1991) propose as an alternative to link the low moisture diffusion coefficient in the low moisture content range with glass transition temperature. However, their work is not supported by a quantitative model and calculations. In this thesis we use for the falling rate period the Free Volume Theory, which involves moisture mobility and state changes during drying (Vrentas and Duda 1977, Vrentas and Vrentas, 1994, He et al., 2008, van der Sman and Meinders, 2013).

1.7.2 Sorption isotherm model based on Flory Huggins Free Volume theory

The moisture sorption isotherm relationship is also essential for the drying rate. It presents the relationship between moisture content and water activity and provides information on the equilibrium of the sorption of moisture in food at constant temperatures. Besides being important for the boundary conditions during drying, the moisture sorption isotherms also provide information on the storage conditions. State of the art sorption isotherm relations are (semi)-empirical models (GAB, BET etc.) which are based on theory for sorption at hard surfaces. Moisture sorption in food matrices differs from moisture sorption on hard surfaces, and these differences have to be taken into account. In this thesis the Flory-Huggins Free Volume theory (Vrentas & Vrentas, 1991, Ubbink et al., 2007, Zhang and Zografi, 2001, van der Sman, 2013) has been applied to describe the sorption isotherms for fresh and pre-treated foods.

1.8 Non-destructive methods to quantify the moisture distribution

Diffusion results in a moisture gradient with the highest moisture contents in the center and the lowest at the edge of the product particles. Concentration driven transport is a common assumption for drying of foods (Fick's law). One goal of this thesis is to quantitatively validate the internal moisture transport and the spatial distribution of moisture during drying. State of the art methods to measure the internal distribution are destructive methods (e.g. by taking slices from the sample) or non-destructive methods (e.g. γ ray densitometry). The disadvantage of these methods is the limitation on the sample size, limited resolution and the measurement in only one dimensional direction (McCarthy et al., 1991, Ruiz-Cabrera et al., 2005, Chen, 2007). In this thesis MRI (Magnetic Resonance Imaging) is applied as a non-destructive method to monitor and to understand the actual drying behavior.

1.9 Thesis structure

The overall thesis structure is presented in Figure 5. There are three main parts in this thesis: model development, model validation, model based dynamic optimization and validation.

First of all, to meet the objective of this project, a drying model is developed. In **Chapter 2**, the Free Volume Theory is presented as a model for drying. This model is based on physical properties of food, and the mobility of moisture in the product matrix during drying. With this theory, mass and heat transport, shrinkage, and vitamin C degradation during drying are simulated by a spatial model. The sorption isotherm is a key element in the drying model; it defines the relation between moisture content and water activity and gives the boundary conditions for mass transfer. In **Chapter 3,** the Flory-Huggins Free Volume theory is introduced to interpret the sorption isotherm of broccoli. The main advantage of this theory is that it takes into account the mixing properties of water, biopolymers and solutes. Since it is based on product composition and physical properties, it has potential to describe the sorption isotherm relation for large ranges of products, moisture contents, and temperatures.

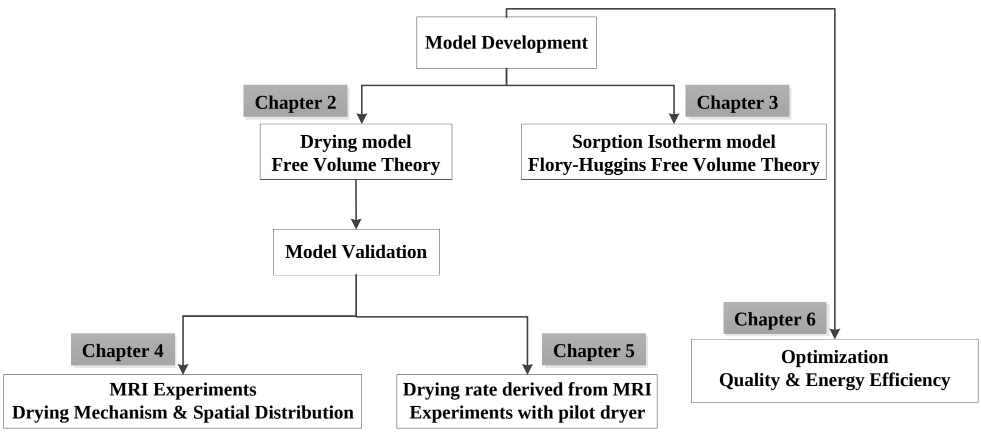

Figure 4 Thesis structure

Chapter 4 and **Chapter 5** concern the validation of the drying model based on the Free Volume theories presented in **Chapter 2 and Chapter 3.** The validation of moisture transport and distribution with a non-destructive technique, Magnetic Resonance Imaging (MRI), to monitor moisture transport during drying is given in **Chapter 4**. The results show the moisture distribution, drying rate, and shrinkage of different pre-treated samples. Anomalous moisture transport is found which is probably due to stress induced diffusion by the elastic impermeable skin.

In **Chapter 5**, drying rates of different pre-treated samples are derived from MRI experimental data. Key parameters of Free Volume Theory based drying model are tuned and the drying behavior of single particles in the MRI unit is compared with the results from a pilot dryer

Chapter 6 concerns the dynamic optimization to find optimal drying trajectories that increase both energy efficiency and product quality. The moisture-temperature state diagram is used to interpret the calculated optimal trajectories. The results presented in the state diagram shows that the optimal drying trajectories circumvent the area with significant product quality degradation rates.

In the end, **Chapter 7** gives the conclusion of this project, and the perspectives for further development.

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Chapter 2

Evaluation of the Free Volume Theory to Predict Moisture Transport and Quality Changes during Broccoli Drying

Abstract

Moisture diffusion in porous broccoli florets and stalks is modeled by using the free volume and Maxwell-Eucken theories. These theories are based on the mobility of water and concern the variation of the effective diffusion coefficient for a wide range of temperature and moisture content during product drying. Mass and heat transport, shrinkage and vitamin C degradation during drying of broccoli are simulated by a spatial model. The effective diffusion coefficient varies strongly with product moisture content and temperature. Vitamin C degradation is high at moisture contents around 2 kg water per kg dry matter. Influences of the size of broccoli on drying rate are evaluated for several types of broccoli florets and stalks.

Keywords: broccoli drying, moisture transport, spatial model, free volume theory, quality changes

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2.1 Introduction

Since low product moisture content allows a safe storage of food products over a long period, drying has gained an important position in the food industry. Water removal is the main function of drying, but at the same time quality changes will take place. For example, changes in shape, texture, color, and deterioration of nutritional components occur during drying. As quality becomes a more and more important aspect of dried products, preservation of such qualities and minimization of deterioration are more essential.

Broccoli is a common vegetable for most families, not only because of the taste but also because of the components with nutritional value and components that contribute to health (e.g. vitamin C and glucosinolates). However, as these components are temperature sensitive, they may deteriorate during drying. From this point of view low and moderate temperatures are requested for drying. Furthermore, the changes in quality depend on the local moisture content and temperature in the product rather than the average moisture content. With dynamic distributed models the quality and moisture content during the drying process can be predicted. These models are also essential to optimize the product quality.

To predict and to optimize the quality it is necessary to know the concentration and temperature profiles in the product as a function of time. In drying there are normally two main drying periods: the constant rate period and the falling rate period. Mulet and Sanjuan [1] showed that drying of broccoli is a diffusion controlled process; capillary transport of water was not detected in their work.

For diffusion controlled drying, Fick's second law is usually applied to describe mass transport. The effective diffusion coefficient which is estimated from drying data represents the overall mass transport of water in the material to be dried. The most common approach to describe the temperature dependency of the effective diffusion coefficient is the Arrhenius equation [1, 2]. Since the Arrhenius equation is an empirical equation, it is limited in its application for complex systems such as foods. At temperatures above the product glass transition temperature, the state of the product matrix changes, and as a result the diffusive behavior changes. Especially at low moisture contents where the mobility of water is low, the diffusion coefficient fits not well to the Arrhenius equation. To deal with this problem, it is proposed to include the influence of the moisture content by adding another factor to the Arrhenius equation[1,3], Levine and Slade[4], Achanta and Srinvas [5] analyzed the reasons of possible low diffusion coefficient in the low moisture content region, by referring to the glass transition. However, a model that includes these aspects is not given.

As an alternative, the effective diffusion coefficient can be predicted from the free volume theory, which is used for diffusion of polymer solutions[6,7]. The main idea of this theory is that the free volume between polymer chains (voids) is the limiting factor for diffusion. Water molecules move between such voids with acquired sufficient energy to overcome forces attracting them to neighboring molecules[8,9]. The free volume theory is based on physical and chemical properties of the product and involves the glass and state transition parameters of the polymeric chains in food. By calculating the diffusion coefficient according the free volume theory, the drying rate can be predicted over a large temperature and moisture content range. A recent example on the moisture migration of trehalose solution drying introduces this theory for drying of bio-products[10].

In this work the free volume theory is applied to broccoli drying. The result is compared with the common diffusion model which uses the Arrhenius equation. Furthermore, the moisture distribution in the product is given for a spatially distributed model and the effect on product quality is determined. As the size of the samples influences the drying time, different types of broccoli florets and stalks are defined and the influence of size on the drying time is evaluated.

2.2 Theory and Modeling

2.2.1 Basic balance equations and boundary conditions

The mass balance equation according to Fick's second law is:

$$\frac{\partial W}{\partial t} = \frac{\partial}{\partial r}\left(D_{eff}\frac{\partial W}{\partial r}\right) \quad (1)$$

with W the moisture content (kg water per kg dry matter), D_{eff} the effective diffusion coefficient ($m^2.s^{-1}$), r the distance from the centre (m) and t the time (s) .

This equation is applied for florets and stalks by using respectively spherical and cylindrical coordinates [2,11]. Figure 1 shows how the natural structure of broccoli is translated into a form for spatial calculations of moisture and temperature.

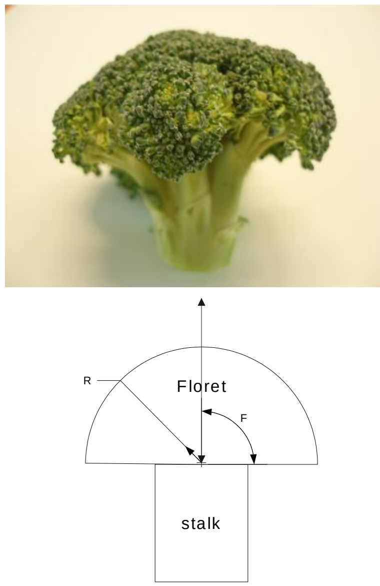

Figure 1 Top: the natural structure of broccoli, Bottom: the applied model structure for broccoli

Heat transport follows Fourier's law:

$$\rho_p C_{pp} \frac{\partial \mathrm{T}}{\partial \mathrm{t}} = \lambda \frac{\partial^2 \mathrm{T}}{\partial \mathrm{r}^2} \tag{2}$$

With T the temperature (K), λ the thermal conductivity ($W.K^{-1}.m^{-1}$), C_{pp} the specific heat of the product ($J.kg^{-1}.K^{-1}$), and ρ_p the product density ($kg.m^{-3}$). Again spherical and cylindrical coordinates are applied for broccoli florets and broccoli stalks respectively.

For the surface where r=R, the boundary condition for equation (1) is given by:

$$k_c\left(C_{surface} - C_{air}\right) = D_{eff}\rho_p \frac{\partial W_{r=R}}{\partial r} \tag{3}$$

with k_c the mass transfer coefficient (m.s^{-1}), $C_{surface}$ the vapor concentration at the product surface (kg.m^{-3}) and C_{air} the vapor concentration in the air (kg.m^{-3}). This equation indicates that the liquid flux to the surface equals to the vapor flux from the surface to the bulk drying air.

Similarly, the boundary conditions for the heat balance equation (2) at the surface with r=R is:

$$h(T_{air} - T_{surface}) = \Delta H_{evap} D_{eff} \rho_p \frac{\partial W_{r=R}}{\partial r} - \lambda \frac{\partial T_{r=R}}{\partial r} \qquad (4)$$

with h as the heat transfer coefficient (W.m^{-2}.K^{-1}), ΔH_{evap} the latent heat for evaporation (J.kg^{-1}). The term $\Delta H_{evp} D_{eff} \rho_p \frac{\partial W_{r=R}}{\partial r}$ represents the amount of energy required to evaporate the liquid flux at the product surface.

For the center of the product (r=0), there is no mass and heat transfer over that surface of the drying product. Thus:

$$\frac{\partial W_{r=0}}{\partial r} = 0 \text{ and } \frac{\partial T_{r=0}}{\partial r} = 0 \qquad (5)$$

2.2.2 Effective diffusion coefficient based on Arrhenius theory

The Arrhenius equation is often used for the temperature dependency of the effective diffusion coefficient D_{eff} :

$$D_{eff} = D_0 \exp(-\frac{E_a}{RT}) \qquad (6)$$

Simal and Rosselló [11] propose the extension of the Arrhenius equation for the cylindrical part of broccoli (stalks) by an extra term:

$$D_{eff} = 1.746 \times 10^{-5} \exp(-\frac{26155}{RT} + 1.383 \times 10^{-2} W) \qquad (7)$$

For the hemispherical part of broccoli (florets), Bon and Simal [2] and Simal and Rosselló[11] give:

$$D_{eff} = 8.04 \times 10^{-7} \exp(-\frac{20034.6}{RT}) \qquad (8)$$

With W the moisture content (kg water per kg dry matter), R the gas constant ($8.314 J.K^{-1}.mol^{-1}$) and T (K) the temperature. The Arrhenius equation is an empirical equation with its limitations in food products. Although it expresses the temperature dependency, above the glass transition temperature the state of the product matrix changes, resulting in changed diffusion properties. However, the Arrhenius equation is not able to predict the diffusion in porous media like the floret.

2.2.3 Effective diffusion coefficient based on Free Volume theory and Maxwell-Eucken theory

In porous media the effective diffusion coefficient depends on the diffusion properties of the dispersed phase (air) and continuous phase (product)[12]. By using the Maxwell-Eucken relationship, the diffusion coefficient for water in products is composed from the diffusion coefficient of water in the continuous phase (D_c) and in the dispersed phase (D_d):

$$D_{eff} = D_c \left(\frac{D_d + 2D_c + 2(1-\varepsilon)(D_d - D_c)}{D_d + 2D_c - (1-\varepsilon)(D_d - D_c)} \right) \qquad (9)$$

For moisture diffusion during broccoli drying, D_d is the water vapor diffusion coefficient in the air and D_c is the mutual diffusion coefficient of water molecules in food polymer chains. ε (-) is the porosity, which is low for the stalk and high for the porous floret. The water vapor diffusion coefficient in the air is given by Olek and Perre[13]:

$$D_d = 23 \times 10^{-6} \frac{98100}{P} \left(\frac{T}{273.15} \right)^{1.75} \qquad (10)$$

With P is the pressure (Pa), and T the temperature (K)

The mutual diffusion coefficient of water molecules in a food polymer matrix is a combination of the self-diffusivity of the water molecules (D_w) and the self-diffusivity of the solids (D_s). The mutual diffusivity for binary systems is given by the Darken relation[14]:

$$D_c = Q(\phi \cdot D_w + (1 - \phi)D_s \tag{11}$$

$$Q = 1 - 2\chi\phi(1 - \phi) \tag{12}$$

with ϕ (-) is the volume fraction of the solid phase, Q (-) is a thermodynamic factor, and χ (-) is the interaction parameter.

The self-diffusion coefficient of water (D_w) follows the free volume theory, which considers physical properties of the product, such as water molecule mobility and the glass transition temperature. The free volume theory predicts the effective diffusion coefficient for a whole range of moisture contents and temperatures. Vrents and Duda[6] showed the application for polymer diffusion system, while He and Fowler[10] used this theory for moisture transport in sugars.

The water self-diffusivity in a polymer matrix is given by:

$$\ln\frac{D_w}{D_0} = \frac{\Delta E}{RT} + \frac{y_1\hat{V}_1^* + \xi y_2\hat{V}_2^*}{y_1\left(\frac{K_{11}}{\gamma}\right)(K_{21} - T_{g,1} + T) + y_2\left(\frac{K_{12}}{\gamma}\right)(K_{22} - T_{g,2} + T)} \tag{13}$$

with ΔE the activation energy (J.mol^{-1}), D_0 the pre-exponential factor (m^2.s^{-1}), ς the ratio between molar volume of solvent versus solute (-), K_{ij} the free volume parameters (K), $T_{g,i}$ the glass transition temperature of component i (K), y_i the mass fraction (%), and $\hat{V}_i^*$ the critical volume of component i (ml.g^{-1}).

Free volume parameters of water are given by He and Fowler [10] (See Table 1). Sugars are the main building blocks in broccoli. The physical properties of sugars are close and therefore we choose the free volume parameters of sucrose as representative for the solids. These parameters are summarized in Table 2.

Table 1 Free volume parameters of pure water

Symbol	Value
$\hat{V}_1^*$ (ml.g^{-1})	0.91
$T_{g,1}$ (K)	136
D_0 (m^2.s^{-1})	1.39×10^{-7}
ΔE (J.mol^{-1})	1.98×10^{3}
K_{21} (K)	-19.73
K_{11}/γ (m.L.g^{-1}.K^{-1})	1.945×10^{-3}

Table 2 Free volume parameters of solid matrix of broccoli

Symbol	Value
$\hat{V}_2^*$ (ml.g^{-1})	0.59
$T_{g,2}$ (K)	360
K_{22} (K)	69.21
C1	11.01
C2	69.21
k (J.K^{-1})	1.38×10^{-23}
a (m)	1×10^{-9}

The remaining parameters are given by Vrentas and Vrentas[15]:

$$K_{22} = C_2 \tag{14}$$

$$\frac{K_{12}}{\gamma} = \frac{\hat{V}_2^*}{2.303 C_1 C_2} \tag{15}$$

where C_1 and C_2 are universal constants.

The self-diffusivity of the solids (D_s) follows from the Stokes-Einstein theory [16]:

$$D_s = \frac{kT}{6\pi\eta_{eff}} \tag{16}$$

With *a* the radius of the solid particle (m), η_{eff} the viscosity (Pa.s) and *k* the Boltzmann constant.

The sorption isotherm relationship is used in the boundary condition for mass transfer (equation 3). According to Mulet and Sanjuan[1] the sorption isotherm for broccoli is:

$$a_w = 1 - \exp(-5.18W^{0.93}) \tag{17}$$

Mulet and Sanjuan[1] observed also shrinkage during drying. Simal and Rosselló [11] suggested a shrinkage model which is based on a proportional change of the volume with the changes in moisture content:

$$\frac{V}{V_0} = 0.0649 + 0.0952W \tag{18}$$

According to their results, shrinkage only happens in radial direction.

2.2.4 Degradation of healthy components

As an indicator for components that contribute to health, vitamin C is considered. Despite of the different sample nature, experiments on potato and pineapple samples showed similar results for the vitamin C degradation rate constants[17,18]. These results are therefore also applied for broccoli. The degradation of vitamin C follows a first order degradation kinetics:

$$\frac{dC}{dt} = -kC \quad (19)$$

with C the concentration (kg/m^3) and k the rate constant (s^{-1}). The temperature dependency of k is given as:

$$k = k_0(-\frac{E_a}{RT}) \quad (20)$$

Mikshkin and Saguy[17] and Karim and Adebowale[18] found the following expressions for the rate constant and activation energy of vitamin C degradation during drying:

$$k_0 = \exp(P_1 + P_2W + P_3W^2) \quad (21)$$

$$E_a = P_4 + P_5W + P_6W^2 + P_7W^3 \quad (22)$$

With P_1-P_7 as constants and W the moisture content (see Table 3)

Table 3 Vitamin C degradation kinetic model parameter values for Eq. (21) and (22)

Parameter	**Value**	**Parameter**	**Value**
P_1	16.38	P_4	14831.0
P_2	1.782	P_5	241.1
P_3	1.890	P_6	656.2
		P_7	236.8

2.3 Results

2.3.1 Diffusion model for broccoli stalks

The free volume theory model was used to compute the effective diffusion coefficient during diffusion controlled drying of broccoli stalks. It is assumed that capillary water transport is neglectable to the diffusive transport. Simulations were done for cylindrical stalks of length 0.02m and radius 0.004m. he drying conditions and the sample sizes were the same as in the work of Simal and Rosselló [11]. They reported effective diffusion coefficient values at 90°C between 1.63×10^{-9} to 2.25×10^{-9} ($m^2.s^{-1}$) for different drying times (720s-2160s) and positions in the product by using the Arrhenius equation. The diffusion coefficient values based on the free volume theory range for these conditions from 1.56×10^{-9} to 3.20×10^{-9} ($m^2.s^{-1}$).

Further simulations with the free volume theory were done for the effective diffusion coefficient during drying of broccoli stalks. As the self-diffusion coefficient of water molecules is influenced by the moisture content, a full range of moisture contents was used. In Figure 2 (top) the effective diffusion coefficient is expressed as a function of moisture content during drying and different product temperatures. The figure shows that the obtained diffusion coefficients vary with temperature and moisture content and are comparable to the results of Simal and Rosselló [11]. Especially at moisture contents, below 0.5 kg water per kg dry matter, the results deviate from the literature values. Here, the free volume theory predicts a lower diffusion coefficient because of the lower mobility of the water molecules. For the diffusion coefficient a maximum value is found for a moisture content of 2 kg water per kg dry matter. Furthermore, the graph shows that, just like the Arrhenius equation, the diffusion coefficient increases with raising temperature.

2.3.2 Diffusion model for broccoli florets

Similarly, the effective diffusion coefficient of drying of broccoli florets was calculated. In the simulations, a diameter of 0.04m and an average porosity 0.2 was used for the florets. Mulet and Sanjuan[1] gave effective diffusion coefficients based on the Arrhenius theory for the temperature range 35-70°C. Their reported values of the effective diffusion coefficient were in the range of 3.00×10^{-8} to 6.23×10^{-8} ($m^2.s^{-1}$). The values of the effective diffusion coefficient according the free volume theory are lower and ranged from 0.86×10^{-8} to 1.67×10^{-8} ($m^2.s^{-1}$) over the temperatures range between 35-70°C.

Furthermore, the same simulations which have been done for broccoli stalks were also done for broccoli florets for a wide range of moisture contents and temperatures. The results are shown in Figure 2 (bottom). Again, the results are comparable with literature values [1], except for the low moisture content range where due to the lower water mobility the diffusion coefficient is low. Compared to the broccoli stalks, the simulations show for the broccoli florets a ten times higher value. This is result of the porous structure of the floret in which the air pockets enhance diffusion.

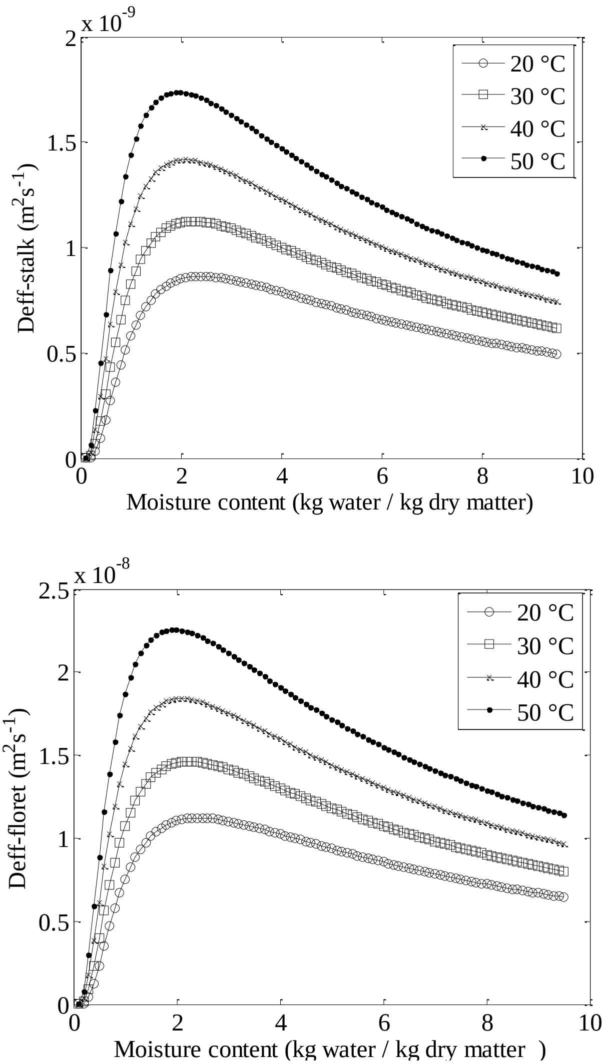

Figure 2 Simulation results of effective diffusion coefficient of water in broccoli at different temperatures. Top: broccoli stalk. Bottom: broccoli floret.

2.3.3 Drying simulation results

Dynamic drying simulations have been done in Comsol Multiphysics. A symmetric 2-D model was chosen according to the structure shown in Figure 1. The size of the simulation sample was 0.02m in radius for the broccoli floret, 0.01m in radius and 0.02m in height for the broccoli stalk. To ensure diffusion controlled drying, the air flow rate was set to 2.5 $m.s^{-1}$. Shrinkage of the sample was included as well (see equation 18). The initial moisture content was set to 9.6 kg water per kg dry matter and was uniform distributed throughout the whole sample. The initial temperature of the product was 20°C.

Figure 3 shows the moisture distribution in broccoli after ten hours of drying. The color surface gives the moisture distribution within broccoli. The temperature distribution was also calculated, but after ten minutes drying, the temperature profile was already equally distributed.

The figure shows that the moisture diffuses from the center to the outer surface in the direction of the arrows. At the surface, moisture evaporates due to the mass and energy exchange with the air and the surface dries first. Moisture content increases towards the center of the product. The product gradually shrinks during the drying process, and shrinkage is shown by comparing the current frame with the original frame.

Compared to the stalk, the moisture profile for the floret is more uniform. This is a result of the porous structure of the floret, which takes advantage of the diffusion properties of water in air. However, as the dimensions of the floret are larger than that of the stalk, drying of the floret takes more time.

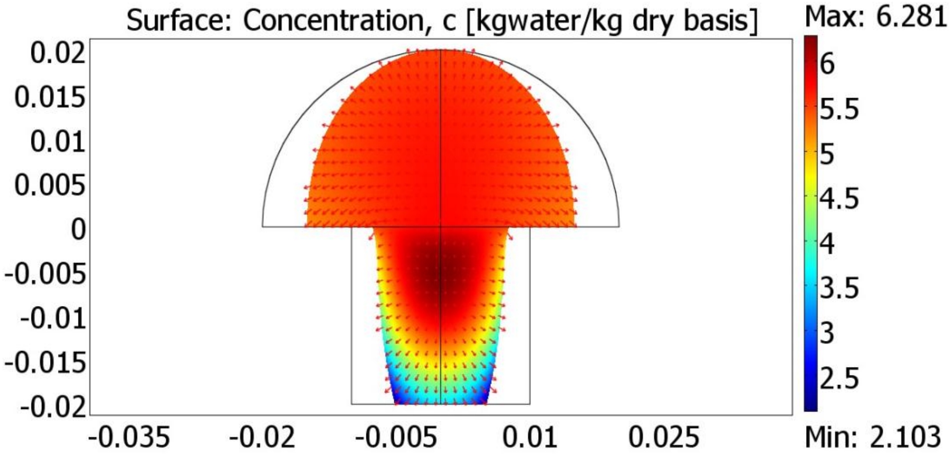

Figure 3 Spatial moisture distribution in broccoli at 10 hours of drying at 50°C. Drying starts at the outer frame which changes due to shrinkage to the colored frame. Coordinates in meters.

Simulation results for different positions in stalk and floret are given in Figure 4. The results concern different positions along the vertical axis (height) in the floret and stalk. Each curve in Figure 4 indicates the local moisture variation as a function of the drying time. The drying curves for the broccoli stalks differ for the positions, the outer surface dries faster than the center core, whereas, the drying curves for broccoli florets are close for the different positions.

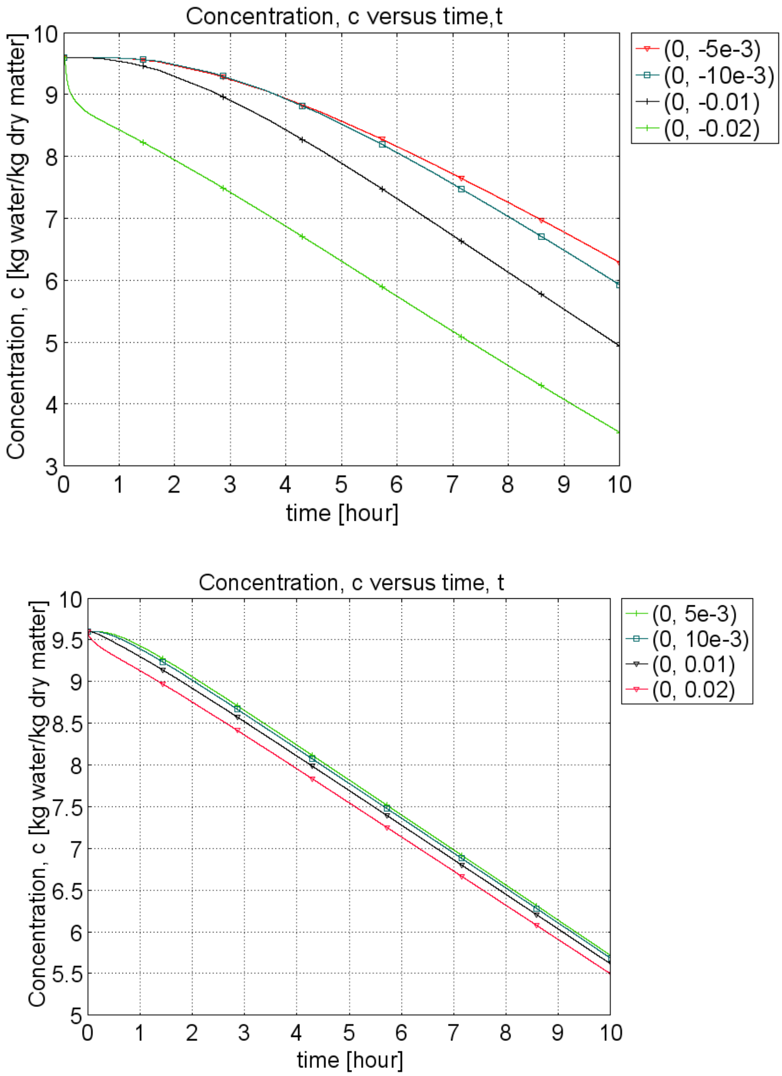

Figure 4 Top: Drying curves of broccoli stalk at different positions from top to bottom along the vertical axis in the stalk (m). Bottom: Drying curves of broccoli floret at different positions from bottom to top along the vertical axis in the floret (m)

2.3.4 Comparison the results from Free Volume theory and Arrhenius theory

Figure 5 shows the comparison between using the free volume theory and the Arrhenius equation for the effective diffusion coefficient. The drying curve for the average moisture content of the same piece of broccoli as considered in previous section. The graph shows that after one hour drying the curves starts to deviate. As the effective diffusion coefficient from the free volume theory is above that based on the Arrhenius equation (see Figure 2), drying is faster. During drying the differences in average moisture content increase. At low moisture contents, where the mobility of water decreases, the diffusion coefficient from the free volume theory falls below that of the Arrhenius equation. As a result, the drying curves approach and cross each other. As the degradation rate of healthy components is strongly coupled to the local moisture content, accurate moisture content prediction is important.

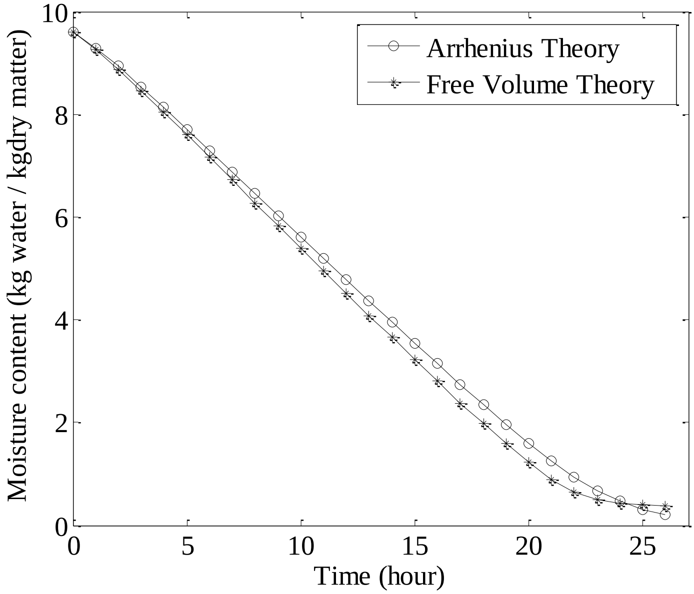

Figure 5 Comparison of average moisture content based on Free Volume Theory and Arrhenius theory

2.3.5 Degradation of healthy components

Figure 6 gives the degradation rate constant for vitamin C degradation for a range of moisture contents and temperatures. The degradation rate constant is a bell shaped curve; above 4 kg water per kg dry matter the degradation rate is constant and very low and there is a maximum value at moisture content of 2 kg water per kg dry matter. The rate constants increase with increasing temperature.

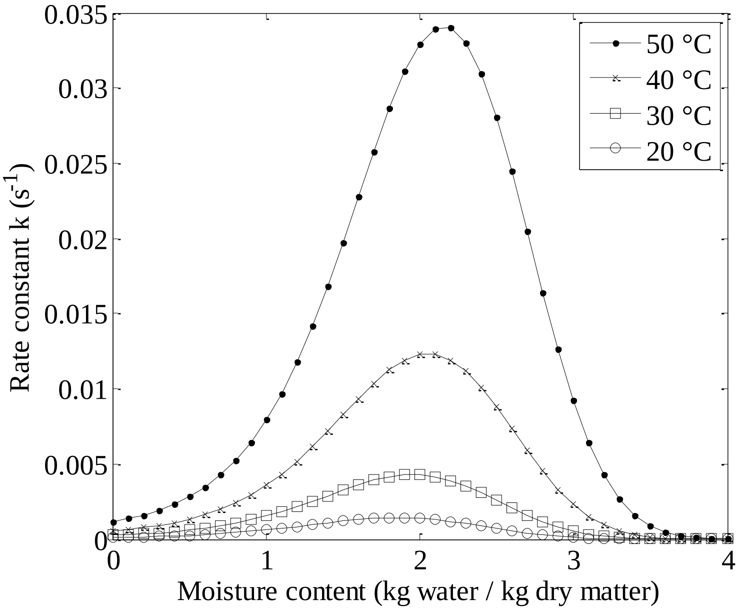

Figure 6 Vitamin C degradation rate constant as a function of moisture content and temperature.

The vitamin C concentration profiles resulting from drying are given in Figure 7. The top figure, for t=10 hour, shows that at this moment degradation starts at the bottom of the broccoli stalk. The floret and the major part of the stalk still have the initial concentration. Till this moment, the moisture content in the major part of the broccoli was above 4 kg water per kg dry matter, where vitamin C degradation hardly occurs. Figure 7 shows also the concentration profiles at 15 hour and 16 hour drying. In this period, the moisture content of the whole body reach values where the degradation rate constant increases rapidly. As a result of these conditions, the vitamin C concentration decreases fast. At 15 hours, vitamin C concentration in the stalk is already low and the concentration starts to decrease in the floret. At 16 hours, there is hardly any Vitamin C left.

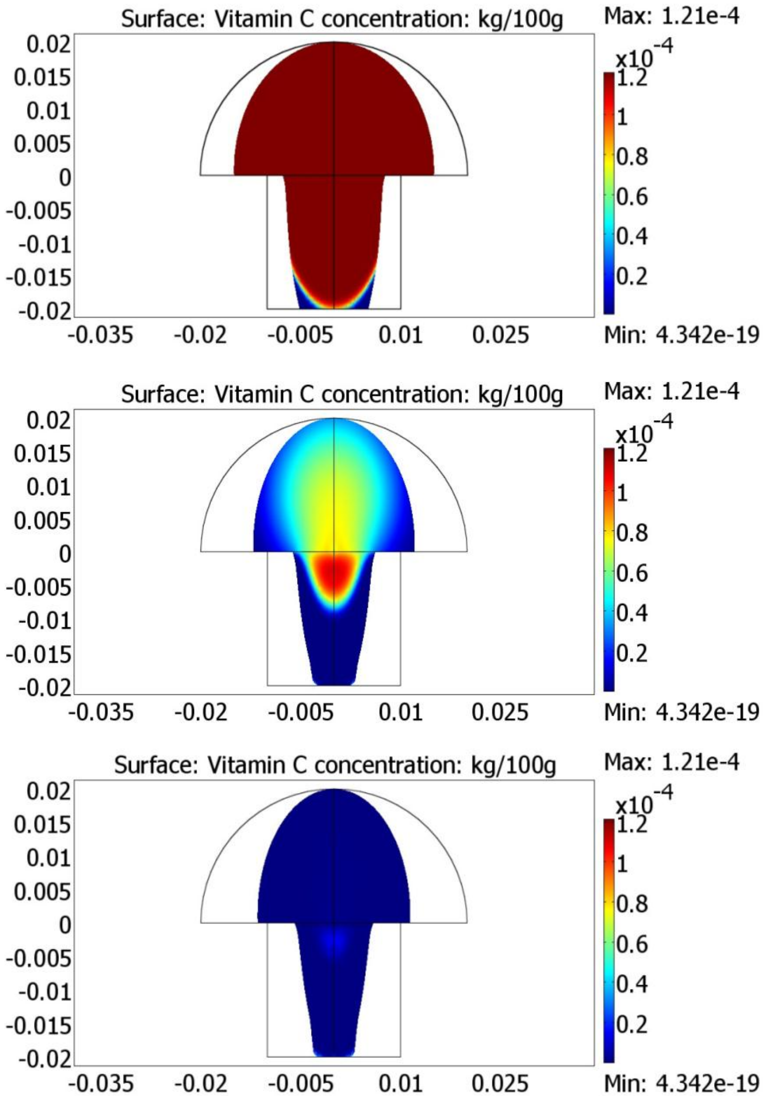

Figure 7 Vitamin C distributions throughout the sample. Top: after 10 hour drying, middle: after 15 hour drying, bottom: after 16 hour drying. Coordinates are given in meters

2.3.6 Analysis of drying behavior of different sizes of broccoli

In the previous simulations, a piece of fresh broccoli (as shown in Figure 1) is considered for drying. Due to the mild drying conditions and the large size of the sample, drying takes a long time. In order to reduce the energy requirement and to limit the size of drying equipment, the drying time should be lowered. Furthermore, to limit the degradation the nutritious components like vitamin C, the time with high values for the degradation rate constant (k; see Figure 6) should be as short as possible.

Instead of a full piece of broccoli, separate parts can be dried. Due to the branch structure of broccoli, the piece of broccoli from Figure 1 can be split up in smaller florets and remaining cylindrical pieces of stalk. Simulations are done for three sizes of florets, and four sizes of cylinders which are taken from the broccoli structure in Figure 8. The sizes are specified in Table 4.

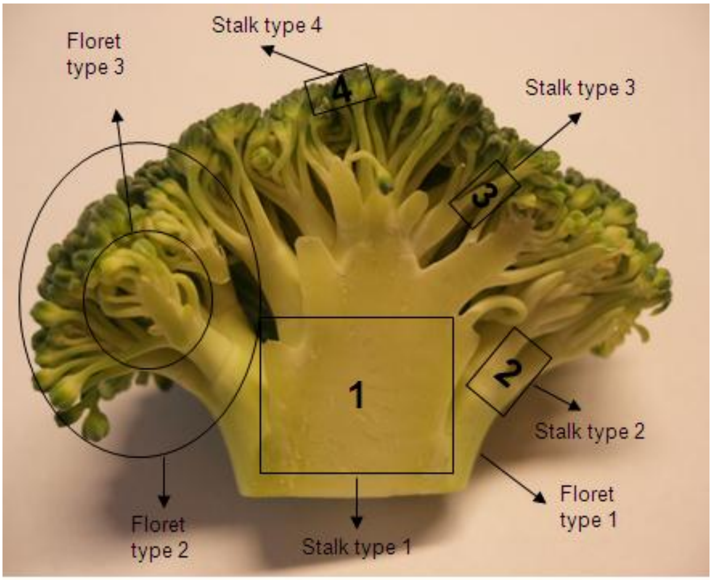

Figure 8 Cross section of a broccoli floret. Numbers refer to the different pieces to be dried.

Table 4 Size specification for the different types of broccoli florets (hemispherical and cylindrical part) and stalks (cylindrical part only). Unit: m

Florets	Diameter (semispherical)	Height (semispherical)	Diameter (cylindrical)	Height (cylindrical)
Type 1	0.04	0.02	0.02	0.02
Type 2	0.02	0.01	0.006	0.005
Type 3	0.005	0.005	0.002	0.002
Stalks	Diameter (cylindrical)	Height (cylindrical)		
Type 1	0.02	0.02		
Type 2	0.004	0.005		
Type 3	0.002	0.004		
Type 4	0.001	0.004		

The upper graph in Figure 9 shows the average moisture contents for the three types of broccoli florets. Drying of a small sample is much faster than that of the larger pieces. The smallest floret can be dried in a few hours, whereas the largest one will need at least 24 hours to be dried.

Simulations for the different cylinders are given in the lower graph of Figure 9. The difference in drying rates follows from the slopes of the curves and the time required to reach the final moisture content. Compared to the initially given structure, drying is much faster by splitting the sample into multi-cylinders and the smallest cylinder can be dried within one hour which could be an acceptable residence time in industrial dryers.

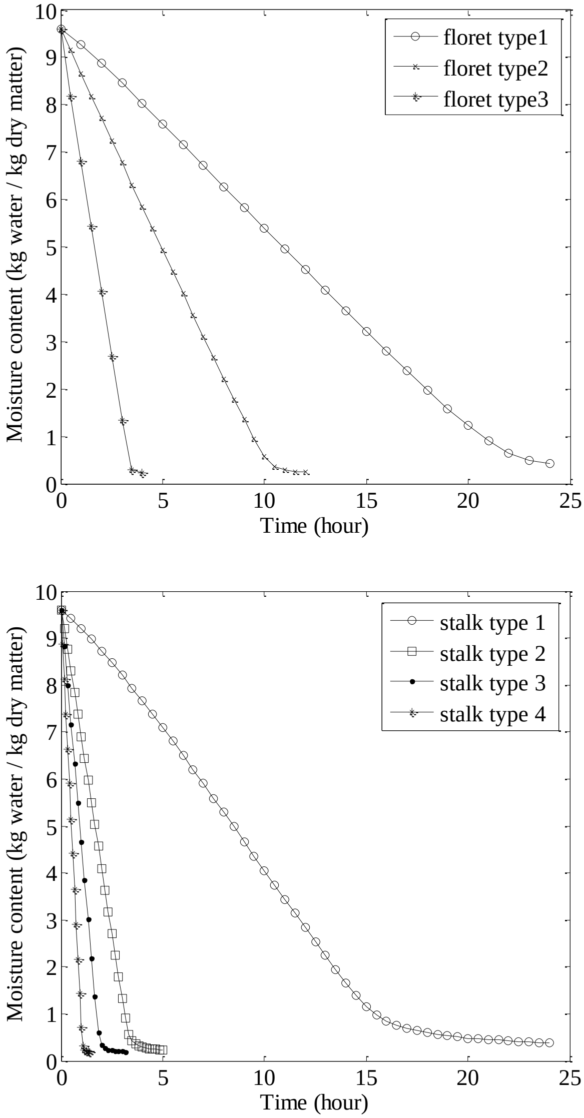

Figure 9 Average moisture content in different sizes of broccoli florets (top) and stalks (bottom) after 24 hour drying

2.4 Conclusions

In this paper, the free volume theory combined with the Maxwell-Eucken theory is used to predict the effective diffusion coefficient during drying of broccoli. The obtained values from the proposed model are close to the effective diffusion coefficient as given in the literature. Main advantage of the free volume theory is that the mobility of water molecules is taken into account and that the glass transition temperature is involved. As a consequence this model has the potential to predict the effective diffusion coefficient from general physical and chemical properties for a wide range of moisture contents and temperatures. The other advantage is that by combining the free volume theory with the Maxwell-Eucken theory, the moisture transport in the porous structure of a broccoli floret can be predicted as well.

The effective diffusion coefficient from the free volume theory varies with the product moisture content and temperature. As a consequence the drying curve deviates from models where the effective diffusion coefficient is only a function of temperature according to the Arrhenius equation.

By using a spatial model, temperature and moisture distribution, as well as shrinkage is presented by the 2-D color map and a moving mesh function. The temperature distribution in broccoli proved to be uniform after a relatively short time. During drying at 50°C the moisture distribution in the broccoli floret is homogeneous. The simulations show that a long drying time is required to bring the broccoli moisture content to a level of 0.2 kg water per kg dry matter which is the level for longer shelf life. However, by redefining the structures for drying, drying time can be enhanced significantly. The spatial calculations make it possible to estimate the content of healthy components (e.g. vitamin C) throughout the product and as a function of time. At high moisture contents (>4kg water per kg dry matter) the rate constant is very low and degradation hardly occurs. However, the degradation rate is high at a moisture content of 2 kg water per kg dry matter. So optimization towards optimal drying paths to limit degradation is required.

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Chapter 3

Moisture Sorption Isotherms of Broccoli Interpreted with the Flory-Huggins Free Volume Theory

Abstract

In this work, the Flory Huggins Free Volume theory is used to interpret the sorption isotherms of broccoli from its composition and using physical properties of the components. This theory considers the mixing properties of water, biopolymers and solutes and has the potential to describe the sorption isotherms for varying product moisture content, composition and temperature. The required physical properties of the pure components in food became available in recent years and allow now the prediction of the sorption isotherms with this theory. Sorption isotherm experiments have been performed for broccoli florets and stalks, at two temperatures. Experimental data shows that the Flory Huggins Free Volume (FHFV) theory represents the sorption isotherm of fresh and blanched broccoli samples accurately. The results also show that blanching affects the sorption isotherm due to the change of composition via leaching solutes and the change of interaction parameter due to protein denaturation.

Keywords: sorption isotherm, Flory Huggins Free Volume theory, glass transition, interaction parameter

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3.1 Introduction

Water is the main component in fresh food products. One of the most common ways for preservation of these products is removal of water by drying, such that the water activity is sufficiently low (typically below 0.3). During drying, mass transfer in the product is driven by (water) activity gradients. Moisture sorption isotherms define the relation between concentrations and activities, and give the boundary conditions for mass transfer. The measurement and estimation of moisture sorption isotherms of products is therefore an essential aspect for designing or modeling drying processes. Moreover, the moisture sorption properties are important for the sensory, physical, chemical and biological properties of dried products [1, 2].

Several (semi)-empirical expressions are known to adequately describe the moisture sorption isotherm; for example Henderson, Oswin, Halsey, Chung-Pfost equations, and the GAB equation, which has been adopted by the American Society of Agricultural engineers as a standard for describing moisture sorption isotherms [3-5]. The GAB equation is commonly used; its accuracy is high compared to other relations [6-11]. Furthermore, the GAB equation is recommended by the European project COST 90 on Physical Properties of Foods [12].

These relations are, however, from a physical point of view not appropriate for food materials. The GAB equation is an extension of the BET model, which describes (inert) gas adsorption on hard surfaces. In food, water is not absorbed on surfaces, but through molecular absorption inside the matrix. Thus, the phenomenon is more related to mixing of solvent (water), (bio) polymer, and other soluble solutes [13], which are commonly described by the Flory-Huggins theory. The FHFV theory extends the FH (Flory Huggins) theory by taking into account the structural (non-equilibrium) verification in the glassy state, and it uses the glass transition temperature as a parameter [14].

The glassy state is not an equilibrium state, and in principle the thermodynamic theory of Flory Huggins would not apply. Moreover, neither would any other sorption isotherm theory apply such as GAB and BET, because they also assume an equilibrium state. However, Leibler and Sekimoto show that the Free Volume theory does have some physical basis as the excess sorption in a glassy state (Free-

Volume contribution) is due to the elastic energy stored in the material [41]. In absence of any theory handling properly the non-equilibrium glassy state, we have opted for the FHFV theory. Earlier, the FHFV has been applied to predict the moisture sorption isotherm for carbohydrates [15] and hydrogen binding polymers [16] and recently it has been successfully applied to predict the sorption isotherm of meat proteins, starch, maltodextrins and water mixtures, as well as of ternary mixtures [17-20]. These applications showed that the sorption isotherm based on the FHFV theory is accurate over the full range of water activities ($0<a_w<1$), a wide range of temperatures, and can be extended to mixtures. The key parameters in the FHFV for mixtures are the interaction parameters (χ) for water to hydrophilic components that have hydrogen bonds, and the glass transition temperature (T_g), which can be obtained from independent measurements. Following the classification of Moreira et al. [21] and van der Sman [20] the interaction parameters for water-sugars (mono and di-saccharides), water-polysaccharides and water protein are subdivided for vegetables.

In this work, we apply the FHFV theory to interpret the sorption isotherm properties for broccoli based on the composition of broccoli. The composition varies throughout the parts of broccoli resulting in different moisture sorption behavior. Therefore, distinct parts of broccoli are considered.

Plant tissue is generally compartmentalized: different components are located in different parts of the cellular tissue, such as sugars in vacuoles, protein and fibers in cytoplasm organelles. The compartmentalized plant tissue can be viewed as a phase separated system. The vacuole phase contains all the solutes (mono, disaccharides) and water; while the other phase contains all the biopolymers, from the cytoplasm, and cell wall materials. Due to the permeability of the membranes between them, water can diffuse between the two phases. At local equilibrium, water activities in two phases are equal. In the theory for fresh vegetables, we will acknowledge the fact of this compartmentalization, treating the tissue as a phase separated system.

Processing methods may have a big effect on the structure, as cell membranes may loss permeability and the phase separated system becomes a mixed system, by which the moisture sorption isotherms may change significantly. Blanching changes the cellular structure [22-24], and consequently changes the organization of the cell structure. Leaching of soluble solids [25] changes the composition, while protein denaturation increases the interaction parameter of water-protein, and changes consequently the sorption isotherm.

Although several studies concern the influence of blanching on the progress of drying and the quality attributes [26-28], knowledge on the influence of blanching on the sorption isotherm is still limited.

In this work, we therefore also evaluate the effect of blanching and composition changes on the moisture sorption isotherm relations. The evaluation is based on the product composition and physical properties, by which we aim to quantify the effect of blanching on the sorption isotherm for broccoli.

3.2 Materials and Methods

3.2.1 Sample preparation

Samples were taken from freshly harvested broccoli. Moisture sorption isotherm measurements were performed with fresh, blanched and oven-dried samples. The fresh broccoli samples were obtained by cutting florets (height 0.5 cm and diameter 0.5 cm) and stalks (height 1 cm and diameter 1 cm) from the fresh pieces of broccoli. The blanched samples were obtained by blanching in excess of water at 90°C for 3 minutes. Then samples were divided into the categories florets and stalks. To reduce the measurement time for the moisture sorption isotherm measurements, all samples were pre-dried in an oven at 50°C for about 12 hours. This treatment might affect the cell structure, but Gonzalez et al. [29] reported a minor reduction of cell viability for onion treated at for 30 min at 50°C in water. Also Sanjuan et al. [30] and Wu and Chang [31] reported a heat treatment of broccoli at 40-70°C during 30 minutes didn't affect the texture of broccoli. Therefore, it was assumed that the texture was not affected by the pre-drying procedure.

3.2.2 Moisture sorption isotherm measurement

A 24-sample analyzer (SPSX-S3-EU01508 Sorption test instrument, Project Messtechnik, 2008) was used for moisture sorption isotherm measurements. All measurements started at low moisture content, 0% relative humidity, going up stepwise (10%) to 90% and going down again to 0%. The change of sample weight was recorded every five minutes, the measurements for each level of water activity were minimal 250 minutes and if necessary they were continued until equilibrium. The equilibrium was determined when the weight change was less than 0.01% in three consecutive measurements. The sorption isotherms were measured at 25°C and 50°C.

3.2.3 Glass transition temperature measurement

Broccoli samples were dried in an air drier at 50°C (see sample preparation). Samples with different moisture content were then taken for glass transition temperature measurement, which were carried out in duplicate in the Modulated Differential Scanning Calorimeter-MDSC (TA Instruments). MDSC can increase the sensitivity and resolution of complex thermal events [43]. Instead of the linear temperature program, it is modulated by a sine wave with specified amplitude and frequency. The ability of the sample to follow the imposed modulation depends on the chosen period. The fastest modulation rate depends on the heat capacity and thermal conductivity of the sample. Most samples will easily follow modulation periods of 50 seconds or greater, at which heating rate of 2°C/min with amplitude of 0.5°C is a reasonable value to use [44].

Therefore, for the measurement, Samples of about 20 mg were weighted in aluminum measuring cups which were hermetically sealed. The temperature scan in modulated mode was performed by increasing the temperature from -60°C till +160°C with a rate of 2°C/min and an oscillating temperature with an amplitude of 0.5°C and a period of 100 seconds. During this scan the reversible and irreversible heat flow were measured. Glass transition temperature is in the reversible heat flow. It is identified as the midpoint between $T_{g,onset}$ and $T_{g,endset}$.

3.2.4 Moisture content measurement

For the T_g measurements, only part of the sample was used; the rest was put in the oven for moisture measurement. The moisture content was determined gravimetrically by oven drying (105°C, 24 h).

For the moisture sorption isotherm was assumed that the equilibrium moisture content of a sample that resides at 0% RH equals to zero. The measured value at this condition is used to calculate the moisture content for other relative humidity conditions.

3.2.5 Glucose content measurement

Fresh and blanched samples were prepared according the procedure given in section 2.1. All samples were frozen in liquid nitrogen and milled into powder. The glucose content was determined enzymatically. D-Glucose in presence of adenosine-5’-triphophate (ATP) is phosphorylated by the enzyme hexokinase (HK) to glucose-6-phosphate (G-6-P) with the simultaneous formation of adenosine-5’-diphosphate (ADP). Only D-glucose is converted and fructose is not involved in the reaction.

$$D - Glucose + ATP \xrightarrow{HK} G - 6 - P + ADP \quad (1)$$

The enzyme glucose-6-phosphate dehydrogenase (G6PDH) in presence of nicotinamide-adenine dinucleotide phosphate (NADP+) catalyzes the G-6-P oxidation in gluconate-6-phosphate with the formation of reduced nicotinamide-adenine dinucleotide phosphate (NADPH).

$$G - 6 - P + NADP^{+} \xrightarrow{G6PDH} gluconate - 6 - phosphate + NADPH + H^{+} \quad (2)$$

The amount of NADPH formed in this reaction is stoichiometric with the amount of D-Glucose. NADPH is measured by the increase in absorbance at 340nm.

3.3 Theory and Modeling

3.3.1 Moisture sorption isotherm prediction: mixed system

According the Flory-Huggins Free Volume theory [20], the activity of water in a mixture is:

$$ln a_w\left(\phi_\mathrm{w}, \chi_{eff}, N_{eff}\right) = \ln(\Phi_\mathrm{w}) + \left(1 - \frac{1}{N_{eff}}\right)(1 - \phi_\mathrm{w}) + \chi_{eff}(1 - \phi_\mathrm{w})^2 + F(\phi) \quad (3)$$

in which a_w is the water activity (-), ϕ_w is the volume fraction of water, χ_{eff} is the effective interaction parameter, N_{eff} is the effective ratio of molar volume of water versus solutes, and $F(\phi)$ is the free volume term.

The free volume term $F(\phi)$ is given as

$$F(\phi) = 0 \qquad T \geq T_{glas}$$

$$F(\phi) = M_w y_w^2 \frac{\Delta C_{p,s}}{RT} \frac{dT_g}{dy_s} \frac{T - T_g}{T_g} \qquad T < T_{glas} \quad (4)$$

in which M_w is the molecular weight of water (g.mol^{-1}), y_w is the mass fraction of water (kg water/kg product), y_s is the mass fraction of the solid matrix(-), $\Delta C_{p,s}$ (kJ.kg^{-1}.K^{-1}) is the change in the specific heat capacity at the glass transition of pure water, T_g is the glass transition temperature of the product (K), and T the actual product temperature (K).

The glass transition temperature T_g follows from Couchman and Karasz relation, which is based on the entropy continuity condition at T_g and the volume continuity condition [32]:

$$T_g = \frac{y_w \Delta C_{p,w} T_{g,w} + y_s \Delta C_{p,s} T_{g,s}}{y_w \Delta C_{p,w} + y_s \Delta C_{p,s}} \quad (5)$$

In which $T_{g,w}$ and $T_{g,s}$ are the glass transition temperatures of pure water and the solute. In the case of broccoli, the product matrix, being a mixture of fibers, sugars, and proteins, is considered as the solute. $\Delta C_{p,w}$ (1.83 kJ/kg/K) and $\Delta C_{p,s}$ (0.42 kJ/kg/K) are the differences in specific heat of water or solute between rubbery and glassy state which has the same value for all polysaccharides, sugars, and proteins [17-20]. y_s and y_w are the mass fractions of solids and water.

Differentiation of Equation 5 gives:

$$\frac{dT_g}{dy_s} = \frac{\Delta C_{p,w}\Delta C_{p,s}y_w(T_{g,w}-T_{g,s})}{\left(y_w\Delta C_{p,w}+y_s\Delta C_{p,s}\right)^2} \quad (6)$$

The effective ratio of the molar volume of water versus that of the solutes (N_{eff}) can be computed via the volume-averaged relation as well:

$$\frac{1}{N_{eff}} = \frac{\sum_i \phi_{i/}N_i}{\sum_i \phi_i}$$ (mono (i=1), di (i=2), poly (i=3)) saccharides, protein (i=4)) (7)

For monosaccharides and disaccharides, the ratios of molar volumes $\frac{1}{N_i}$ are 0.160 and 0.084 respectively. For long chain polymers like proteins and polysaccharides, the effective ratio is zero.

The volume fraction is calculated according to the mass fraction, and the density of the components (Table 1), with the assumption that the partial molar volumes are constant:

$$\phi_i = \frac{\frac{y_i}{\rho_i}}{\sum\frac{y_i}{\rho_i}} \quad (8)$$

Table 1 the effective density of the components[33]

Component	Density (kg/m3)
Water	1000
Ash	2440
Protein	1330
Carbohydrate	1550
Fat	930

The above constants are based on the assumption that the partial molar volumes are constant in rubbery and glassy state. As stated in other papers [20, 42], in the rubbery state, the specific volume of carbohydrates and water mixtures follow the rule of ideal mixing. However, in the glassy state, the specific volume may deviate from the ideal mixing rule which is due to the pore formation in the glassy state. Therefore, we assume that in the glassy state there are two phases: pore phase and solid phase. In the solid phase, it is assumed to follow the ideal mixing rule. In the pore phase, pore space can be occupied by water in the gas phase whose density is negligible compared to other compounds. Thus, in glassy state, we assume that ideal mixing is still valid [20].

Table 2 Composition data of broccoli floret and broccoli stalk (USDA data extended with data from Wageningen University)

Component	Broccoli floret (%)	Broccoli stalk (%)
Water	89.3	90.7
Ash	0.87	0.92
Protein	2.82	2.98
Fat	0.37	0.35
Total Carbohydrates	6.64	5.24
Monosaccharaides	1.5	1.17
Disaccharides	0.60	0.39
Polysaccharides	3.2	2.34

The remaining parameter in the moisture sorption isotherm relationship (equation 4) is the effective interaction parameter χ_{eff}, which depends on the composition. In broccoli monosaccharides (glucose, fructose), disaccharides (sucrose, lactose, and maltose), polysaccharides (fibers), and proteins are the main building blocks that influence the moisture sorption behavior (Table 2; extended USDA data for broccoli). It was assumed that glucose and fructose are present in a ratio of 1:1 [40], and because the contribution of ash is low it is not taken into account.

A volume averaged relationship leads to the effective interaction parameter between water and the matrix with all of its components:

$$\chi_{eff} = \frac{\sum_i \phi_i \chi_i}{\sum_i \phi_i} \quad \text{, (mono (i=1), di (i=2), poly (i=3)) saccharides, protein (i=4))} \qquad (9)$$

Here χ_{eff} is the effective interaction parameter of the mixture, χ_{iw} is the interaction parameter between component i and water, and ϕ_i is the volume fraction of component *i*. For monosaccharides and disaccharides, the interaction parameters with water are constant at the values of 0.27 and 0.53, respectively. For polymers (fibers and protein), the interaction parameter follows from the composition:

$$\chi_i = \chi_{i,I} + (\chi_{i,II} - \chi_{i,I})(1 - \phi_{w,eff})^2 \text{ , with } \quad \phi_{w,eff} = \phi_w \frac{\phi_{i(i=3,4)}}{\sum \phi_i}$$

(mono (i=1), di (i=2), poly (i=3)) saccharides, protein (i=4)) (10)

In which $\chi_{iw,I}$ equals 0.5 for a fully hydrated polymer, and $\chi_{iw,II}$ is the interaction parameter with the dry polymer *i*. For water-insoluble fibers $\chi_{3,II}$ is constant at 0.8, for protein, depending on the degree of denaturation, $\chi_{4,II}$ is in the range 0.8-1.4. For fully denatured protein $\chi_{4,II}$ is equal to 1.4, a value that has been reported for meat, mushroom and carrot [19, 20]. The parameters are summarized in Table 3.

Table 3 Interaction parameter of all components (van der Sman, 2012, 2013)

Component	symbol	value
Monosaccharides	χ_1	0.27
Disaccharides	χ_2	0.53
Polysaccharides	$\chi_{3,I}$	0.50
	$\chi_{3,II}$	0.80
Protein	$\chi_{4,I}$	0.50
	$\chi_{4,II}$	0.8-1.4

3.3.2 Moisture sorption isotherm prediction: phase separated system

For fresh products, the plant tissue is generally compartmentalized: soluble solids such as sugars (mono, disaccharides) are contained in vacuoles, which have their own cell membrane that is impermeable to solutes. Protein and fibers (polysaccharides) are found in cytoplasm and the cell wall material. These phases are separated by membranes (plasmalemma), which is permeable for water. Therefore, for fresh product, water is partitioned by two compartments to obtain local equilibrium, where the water activities of the two compartments are equal.

$$a_{w,1}(\phi_{\mathrm{w},1},\phi_1,\phi_2,\phi_{3,4}=0)=a_{w,2}(\phi_{\mathrm{w},2},\phi_3,\phi_4,\phi_{1,2}=0\,) \qquad (11)$$
$$\text{with } \phi_{\mathrm{w}}=\phi_{\mathrm{w},1}+\phi_{\mathrm{w},2}$$

Water activities in two phases have to be calculated separately via equation 3. The parameters in equation 3 such as glass transition temperature (T_g), volume fraction (ϕ_i), effective ratio of the molar volume of water versus that of the solutes (N_{eff}), interaction parameter (χ_{eff}) have to be determined via the composition for two phases. The fraction of water in two phases has to be determined via minimization procedures that solves the water partitioning that adheres the condition $a_{w,1}=a_{w,2}$.

The structure and compartmentalization in fresh vegetables is affected by heat treatments, which may result in complete mixing of the two phases present in the fresh vegetables. Therefore for the blanched samples and the samples for which the sorption isotherm measured at higher temperatures (>50°C) the vegetable is considered as a homogeneous mixture.

3.4 Results and Discussions

3.4.1 Glass transition temperature of broccoli

Since water acts as a plasticizer, the glass transition temperature at which the structure changes between glass and rubber state depends on the water content [34, 35]. Pure water has a glass transition temperature of 134K while for fresh food with a mass fraction of water in the range of 0.8-0.9; the glass transition temperature is about 150K [36]. The measurement range of common glass transition temperature measurement devices is above 250K and only broccoli samples with moisture content below 17% fall in this range. Therefore, our measurements concern dried samples in the range of 3-17% (%kg water/kg product). The results are given in Table 4.

Table 4 Glass transition temperature measurements of broccoli with different water contents

Water content (% kg water/kg product)	T_g (K)
16.5	269.3
8.25	288.3
6.62	307.5
3.05	320.8

Using $T_{g,w} = 134K$ for pure water and the change in specific heat capacity $\Delta C_{p,w} = 1.83\ kJ.kg^{-1}.K^{-1}$, equation 6 was fitted against experimental data. The fit resulted in $T_{g,s} = 359K$ and $\Delta C_{p,s} = 0.42\ kJ.kg^{-1}.K^{-1}$ for broccoli. Figure 1 gives the curve and as a validation the figure includes the product glass transition temperature measured by Sanjuan et al. [37, 38] which coincides with the fitted curve.

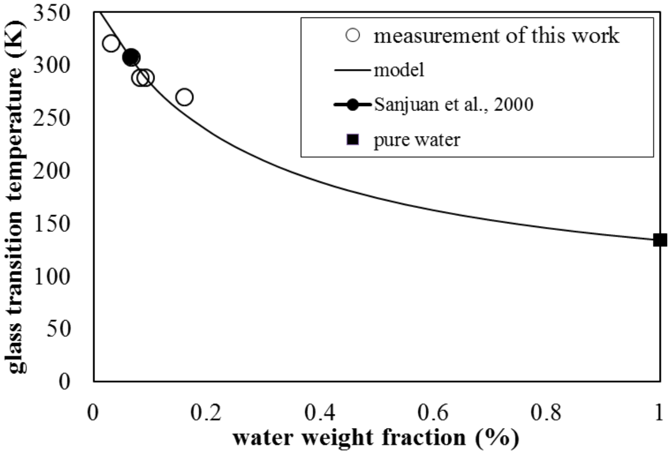

Figure 1 Results for the glass transition temperature (Tg) measurements and comparison with literature data

3.4.2 Adsorption-desorption hysteresis

The Flory Huggins Free Volume theory concerns the molecular properties of materials which are being mixed and presents therefore the absorption isotherm. For modeling drying processes the desorption isotherm is more relevant than the absorption isotherm. All the adsorption-desorption curves, obtained from the DVI-measurements, showed that the adsorption-desorption hysteresis is minimal (an example is given in Figure 2). Hence, the desorption isotherm also interpreted with the FVFH theory.

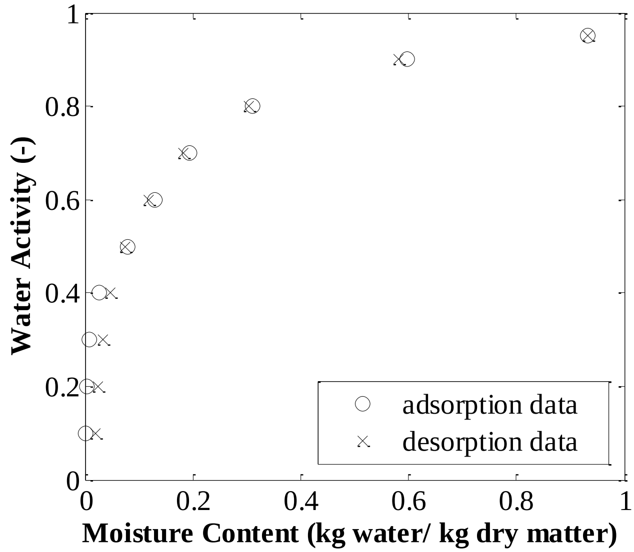

Figure 2 Comparison of desorption and adsorption isotherm curve for broccoli stalks at 25°C

3.4.3 Fresh broccoli moisture sorption isotherm

Fresh broccoli sorption isotherm measured at 25°C, phase separated FHFV was applied. Monosaccharaides, disaccharides, and water ($y_{w,1}$) are in the vacuole phase, while protein and polysaccharides and water ($y_{w,2}$) are in the cytoplasm organelles. The interaction parameters of water-monosaccharide χ_1 , water-disaccharideχ_2, water-polysaccharide χ_3 and water-protein χ_4 from table 3 were applied to calculate the fresh broccoli moisture sorption isotherm data at 25°C. At equilibrium, water activities at two phases are equal. Water is partitioned in the two phases. Water mass fraction in the vacuole phase was found to be linear with total moisture content for both floret and stalk.

$$y_{w,1} = 0.349X + 0.0066 \tag{12}$$

with X the moisture content (kg water/kg dry matter). This implies that the water partitioning between the two phases is nearly constant, which explains the similarity between the two predictions in figure 3.

Our calculations show little difference in the predictions of the sorption isotherm using FHFV theory for both the phases-separated system and the completely mixed system. Both predictions show good comparison with experimental data, as indicated in Figure 3.

It was expected that temperature have a minor effect on the interaction parameter of water-(poly) saccharides. For 50°C measurements, however, for broccoli with a considerable amount of protein in the dry matter, denaturation of protein results in a higher value of χ_4 and as a consequence the contribution of $\chi_{eff}(1-\Phi_{\mathrm{w}})^2$ increases compared to the free volume term $F(\Phi)$.

The FHFV was fitted to the measured values at 50°C with $\chi_{4,II}$ (protein-water) as a fitting parameter. The fitted value for $\chi_{4,II}$ was 1.4 (see Table 5 and Figure 3), which is the same value as for fully denatured protein [17, 18]. The complete denaturation is probably caused by the relative long residence time in the DVS sorption measurement equipment (about 80 hours).

Table 5 Estimated interaction parameters of protein for fresh broccoli florets and stalks

	Interaction parameter χ_4	RMSE floret	R^2 floret	RMSE stalk	R^2 stalk
25°C mixed theory	0.8	0.054	0.970	0.038	0.984
25°C Phase separated	0.8	0.060	0.984	0.039	0.985
50°C	1.4	0.026	0.992	0.072	0.937

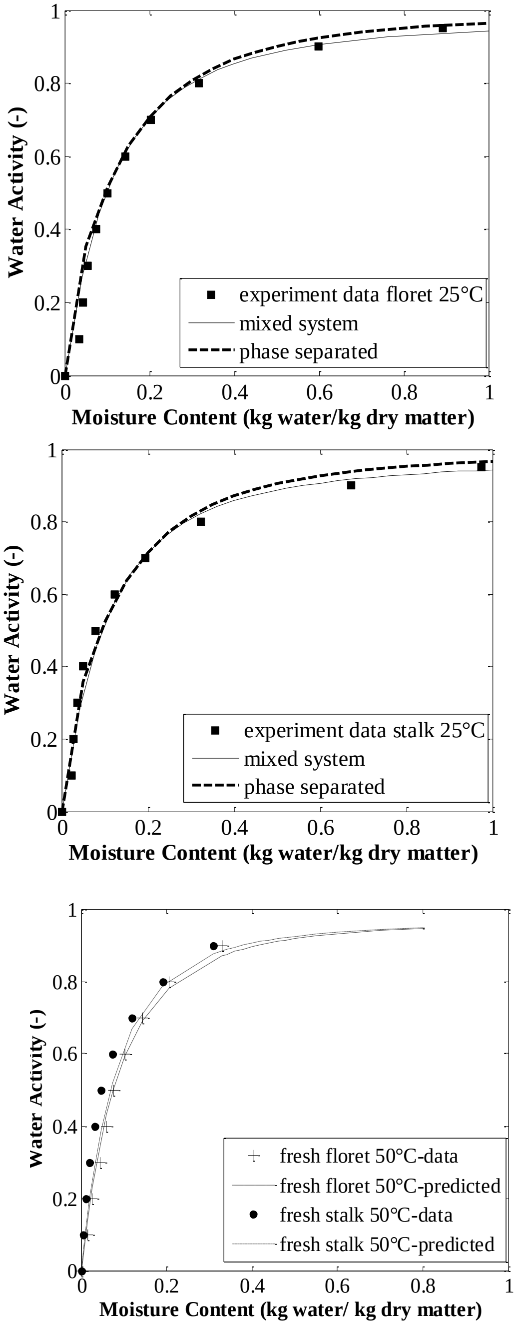

Figure 3 Desorption isotherm data and Flory Huggins Free Volume Theory curves for fresh broccoli at 25°C and 50°C

3.4.4 Blanched broccoli

During blanching in water soluble solids leach into the water. Mate et al. [39] used the glucose content as an indicator for the change of soluble solids in the matrix during blanching. The loss in glucose content in blanched samples (compared to fresh samples) is given in Table 6. The relative loss is stronger for florets stronger than for stalks and this affects the moisture sorption isotherms through equation 4, equation 8 and equation 10, by lower values of ϕ_i in the FHFV theory.

Table 6 Relative glucose loss in broccoli due to blanching

Broccoli	Glucose loss (%）
floret	49.8
stalk	28.5

Although the composition changes were taken into account, the moisture sorption isotherms of blanched product were not correctly predicted by using the values in table 3. Therefore, the FHFV was fitted to the data with χ_4 as fitting parameter. The results for the blanched broccoli are given in Figure 4, and the estimated values for the interaction parameters χ_4 in Table 7. The interaction parameter for (poly) saccharides in blanched broccoli has the same value as in the fresh samples. The proteins in broccoli denature partly during short-time blanching and this results in a higher value of the protein interaction parameter (χ_4=0.9). The protein interaction parameter at 25°C and 50° differ also (respectively 0.9 and 1.4). The value χ_4=1.4 obtained at 50°C is in line with our previous observation for fresh broccoli and shows the continuation of protein denaturation during the residence time of sample in the moisture sorption isotherm measurement device.

Table 7 Estimated interaction parameters of protein for blanched broccoli

	Interaction parameter χ_4	RMSE floret	R2 floret	RMSE stalk	R2 stalk
25°C	0.9	0.039	0.984	0.034	0.988
50°C	1.4	0.055	0.951	0.054	0.953

To demonstrate the effect of composition and the role of heat treatments, all the obtained sorption isotherms for fresh broccoli and blanched broccoli florets and stalks are plotted for the two temperatures in Figure 5. The effects of the heat treatments on the sorption isotherms are clear. With the intensive heating, cell walls were broken down and protein was denatured, resulting in an enhanced release of bounded water. Therefore, at the same temperature, the sorption isotherms of blanched broccoli are below that of fresh broccoli. Similarly, Figure 5 shows the differences in the sorption isotherms for the measurements at different temperatures for fresh and treated samples.

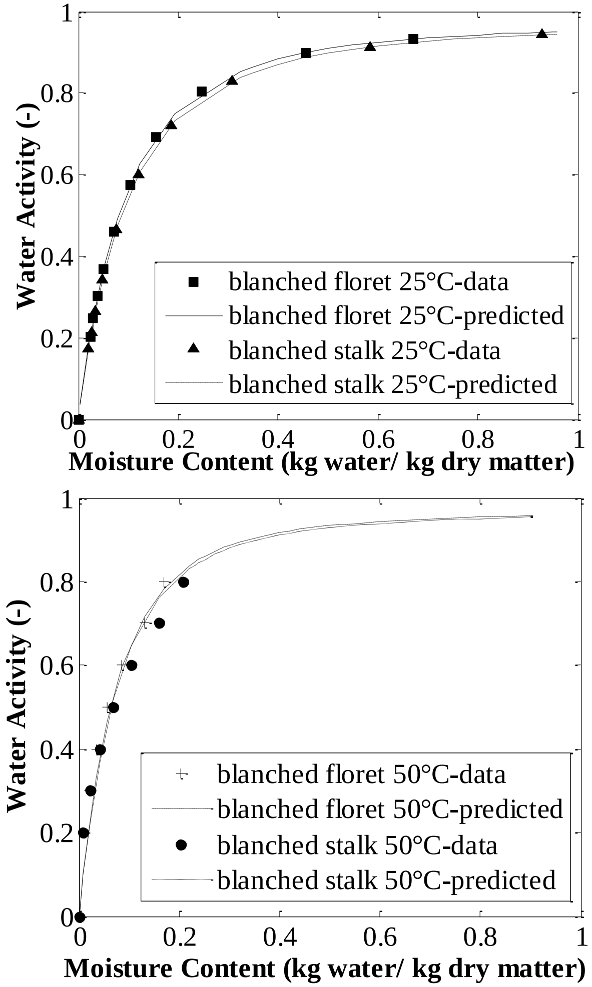

Figure 4 Desorption isotherm curves at 25°C and 50°C for blanched broccoli florets and stalks.

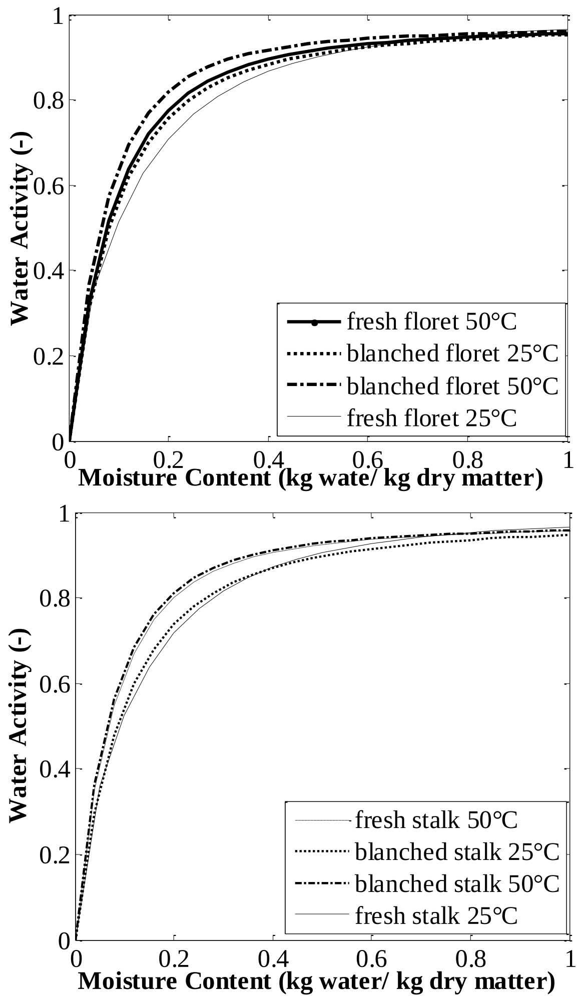

Figure 5 Comparison of fresh and blanched broccoli floret and stalk at 25°C and 50°C

3.5 Conclusions

Sorption isotherms expressions, like Oswin, Henderson, GAB, are derived from gas adsorption properties to solid surfaces. Food products, however, are a matrix with a mixture of water and several components with polymer properties. For these systems, the Flory-Huggins Free Volume (FHFV) theory is more appropriate to describe the moisture sorption isotherms. The FHFV allows prediction of the sorption isotherms from the products composition and the physical properties of the components. In this work, the use of the FHFV is applied to interpret the moisture sorption isotherms of broccoli.

For both fresh broccoli florets and stalks we have applied the FHFV theory for phase separated systems, with soluble solids contained in the vacuole. The water partitioning between vacuole phase and biopolymer phase remained about constant. Using FHFV interaction parameters from earlier and independent studies on pure components (monosaccharaides, disaccharides, polysaccharides, and protein) resulted for the moisture sorption isotherm at 25°C in good agreement of prediction and experimental data.

The moisture sorption isotherm of 50°C showed that the interaction parameter for protein has been changed to that of fully denatured protein during the long time the sample resides in the moisture sorption isotherm device.

Blanching has a significant influence on the moisture sorption behavior. This is caused by 1) loss of soluble solids (leaching of carbohydrates), and 2) protein denaturation. Taking the changed composition into account it was found that for the 25°C moisture sorption isotherm the interaction parameter for protein increased because of the denaturation during blanching. For 50°C the protein interaction parameter was equal to fully denatured protein like for the isotherm for fresh broccoli ate 50°C.

The Flory-Huggins Free Volume theory (FHFV) has a sound theoretical basis for water-polymer interactions and can well describe the moisture sorption isotherm relation for food products like broccoli. We do expect that the theory will perform similarly for other products. Most parameters in the FHFV can be found in literature and if the state of protein is known, the FHFV predicts the moisture sorption isotherm well. If the state of protein is not precisely known, the water-protein interaction is the only parameter to be estimated. This is in contrast to traditional moisture sorption isotherms relationships, which need 3-5 parameters to be estimated (like the GAB, Henderson, Oswin and other relations). The obtained values make physical sense, which implies that predictions of the sorption isotherms are possible when good information about the components and their state is available.

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Chapter 4

Anomalies in Moisture Transport during Broccoli Drying Monitored by MRI?

Abstract

Magnetic Resonance Imaging (MRI) offers unique opportunities to monitor moisture transport during drying or heating of food, which can render unexpected insights. Here, we report about MRI observations made during drying of broccoli stalks indicating anomalous drying behaviour. In fresh broccoli samples the moisture content in the core of the sample increases during drying, which conflicts with Fickian diffusion. We have put the hypothesis that this increase of moisture is due to the stress diffusion induced by the elastic impermeable skin. Pre-treatments that change skin and bulk elastic properties of broccoli show that our hypothesis of stress-diffusion is plausible.

Keywords: MRI, Drying, Broccoli, moisture transport, stress diffusion

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4.1 Introduction

Magnetic resonance imaging (MRI) is an established technique for studying the internal states in biological systems. When coupled to in-situ thermal treatments MRI can be viewed as a rather novel enabling technology that yields unprecedented insights into the physical transport phenomena that occur during food processing.[1-6]

In this work, we apply MRI to investigate the changes in moisture distribution in time observed during in-situ drying of broccoli which apparently violates Fick's law.

Convective drying of vegetables is mostly considered as a diffusion-controlled process.[7] Traditionally in food science, diffusion is described by Fick's law in which the mass flux is linear with the gradient in moisture content. A few papers in food science report deviations of moisture transport from Fick's law. Johnson et al. (1998)[8] reported an increased moisture content in the product centre during drying of plantain but without further explanation. Arnaud and Fohr (1988)[9] observed that the intra-kernel moisture content gradient increases during drying and decreases during tempering. Courtois et al. (2001)[10] and Toyoda (1988)[11] have considered the internal structure of products as a reason for deviation. In rice and corn there are internal regions with different moisture transport properties. Other deviations from Fick's law are reported for cooking of starch-rich products with moisture transport against the moisture gradient.[12,13] The deviations are said to be caused by gelatinization of starch during heating, which results in changes of local water holding capacity and water activity in the heterogeneous product. Different degrees of starch gelatinization result in different potential maximum moisture contents (ceiling moisture content). Therefore, the moisture transport during rice cooking is driven by the difference of local moisture content and the ceiling moisture content. Watanabe et al. (2001)[14] proposed the so called "water demand" model to describe this transport phenomenon, which is not captured by Fick's law.

Furthermore, Wählby et al. (2001)[15] observed during experiments an increased moisture content in the product centre during cooking of beef without clear explanation. Transport against the gradient in moisture content is thermodynamically possible if gradients in swelling pressure arise. Van der Sman (2007)[16] modelled swelling pressure-driven moisture transport (based on the Landau expansion of the Flory-Rehner theory) caused by protein denaturation near the product surface during cooking of meat. In that model, the elasticity properties of the product play an important role and result in moisture transport in directions opposite to the moisture gradient. Recently, it has been shown that the full Flory-Rehner theory, indeed, holds for cooked meat.[17]

Another example is from the field of polymer physics where during drying the formation of a skin at the polymer surface resulted in water transport against the gradient in the moisture content. Okuzono and Doi (2008)[18] have called this phenomenon stress diffusion, and they formulated a generalized Fick's equation with an elastic term to describe the stress diffusion. In view of the preceding cited analysis and observations of non-Fickian moisture transport, we pose that the observed non-Fickian behaviour during broccoli drying is due to elastic stresses.

To test this hypothesis, we applied pre-treatments (blanching, freezing and peeling) which change the product structure and thus its textural and elastic properties. Experiments have been done in a MRI device with continuous and controlled in-situ hot air supply; the acquired MRI images provide data about moisture transport and shrinkage during drying. The different pre-treatments have been compared in terms of drying rates, shrinkage and moisture content profiles, via which the validity of our hypothesis are analyzed.

4.2 Materials and Methods

4.2.1 Materials

For all measurements parts of the broccoli stalk were used. The sizes of the samples were about 0.01 m in height, 0.01 m in radius. Figure 1 gives an example of a fresh broccoli sample.

4.2.2 Pre-treatments

In total six different pre-treatments were applied. An overview of the samples and pre-treatments is given in Table 1. After all pre-treatments, the free water at the sample surfaces was removed at room temperature with tissue paper.

Figure 1 Cross section of a broccoli stalk sample

4.2.3 Drying in the MRI device

The sample was fixed by a stick on a sample supporter and inserted into a drying chamber in the MRI measurement device. The size of the drying chamber was 0.032 m in diameter and 0.2 m in length. A continuous flow of temperature-controlled air was supplied. The air temperature was controlled at 30°C or 50°C, the air velocity at 1.0m/s and the relative humidity at 10%.

Drying was continued until the moisture content of the samples was constant. Depending on the material properties, the experimental time for the fresh broccoli stalks ranged from 12 to 48 hours. Initial and final product moisture contents (M0, Mi) were determined by oven drying (105°C, 24 hours).

Table 1 Overview of pre-treatments and experiments

Pre-treatment	Procedure
Peeling	1.0mm-1.5mm skin was removed
Blanching	90°C water, 3 minutes
Freezing	-25°C, 48 hours
Experiment	pre-treatment
1	Non treated
2	Peeled
3	Non-peeled, blanched
4	Peeled, blanched
5	Non-peeled, frozen
6	Peeled, frozen

4.2.4 MRI imaging equipment

All measurements were performed on a 3 T (128 MHz for protons) MRI system (Bruker, Karlsruhe, Germany), consisting of an Avance console, a superconducting magnet with a 0.5 m vertical free bore (Magnex, Oxford, UK), a 1 T/m gradient coil, and a birdcage RF coil with an inner diameter of 0.04 m.

4.2.5 MRI imaging

3D images were obtained using a Turbo Spin Echo (TSE) MRI sequence[19], a repetition time TR of 2 s, an effective spin echo time TE of 3.35 ms and a spectral bandwidth SW of 50 kHz. Only 16 echoes were acquired in the TSE train to avoid T2-weighting. Odd and even echoes were separately phase-encoded forming two different images to avoid Nyquist ghost's artefacts, so the turbo factor was 8. Two acquisitions were averaged to improve image quality. The Field-Of-View (FOV) was 35×35×35 mm^3 with a matrix size of 64×64×64 resulting in a spatial resolution of 0.55×0.55×0.55 mm3. The interval time between measurements was 34 minutes.

T2 mapping was done using a Multi Spin Echo (MSE) imaging sequence20, a TR of 2 s, a TE of 3.59 ms and a SW of 50 kHz. Per echo train 128 echoes were acquired; 16 acquisitions were averaged to improve image quality. The FOV was 35×35 mm2 with a matrix size of 64×64 resulting in an in-plane resolution of 0.55×0.55 mm2. The slice thickness was 3 mm. The interval time between measurements was 34 minutes.

4.2.6 Numerical methods and data analysis

MRI-measurement data handling for graphical interpretation and analysis was performed with home-built software written in IDL (RSI, Boulder, CO). For shrinkage calculations, pixels with an intensity value above 0.75 (with the maximum value of 11.42 per pixel) were counted and for each pixel a volume of 0.16mm3 was assigned. By summing up the volume of all counted pixels the instantaneous volume (Vt) of the sample was calculated.

The degree of shrinkage is defined as the ratio of the reduced volumes (V_0-V_t) to the initial volume (V_0):

$$S_V = \frac{V_0 - V_t}{V_0} \tag{1}$$

and the fraction of moisture removed from the initial product is:

$$S_m = \frac{M_o - M_t}{M_0} \tag{2}$$

Where M_0, the initial moisture content, was measured by the oven method and M_t is the moisture content at different sampling time t.

4.2.7 MRI data calibration

For wet samples, the signal intensity is assumed to be linear with moisture content.[21] However, for nearly dry samples the intensity images are weak and deviate from the linear relationship. The minimum detectable liquid water concentration is about 20 kg.m^{-3}.[22,23]

Hence, to establish the extent of linearity between MRI signal intensity and moisture content, we have plotted the shrinkage data as a function of the fraction of removed moisture. Assuming incompressibility of the solid and water present in broccoli, and absence of air, the reduced volume must be attributed to the loss of moisture. In Figure 2 we show this relation, which also indicates the accuracy of the interpretation of signal intensity to moisture content. It shows that below S_m=0.85 shrinkage is more or less linear with the fraction of removed moisture, whereas in the last phase of drying (S_m >0.85) there is a deviation from linearity. In this region, with product moisture content below 0.3 kg water/kg dry matter, the measured values might be lower than the actual values.

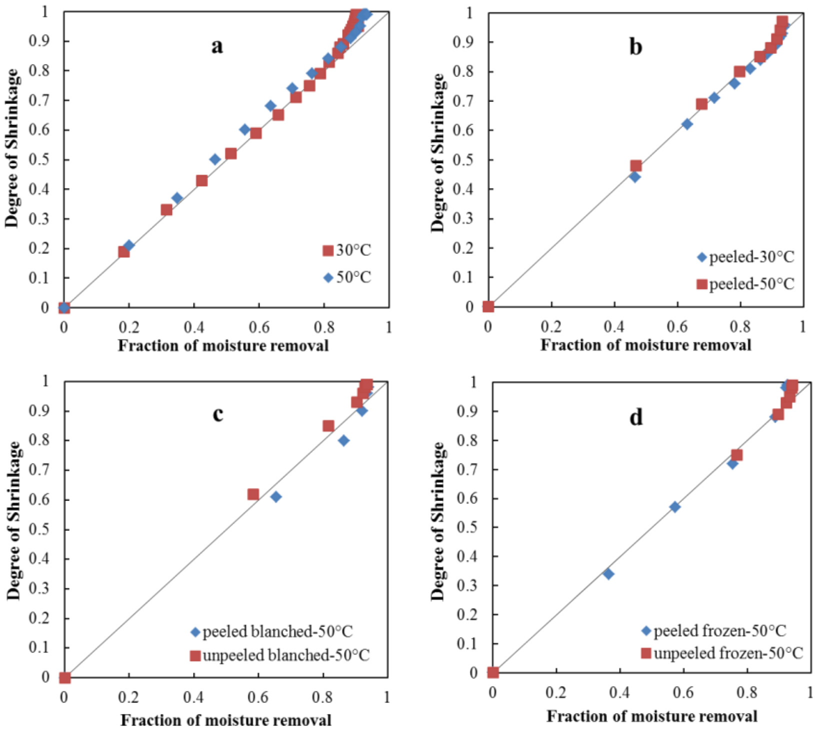

Figure 2 Shrinkage as a function of the fraction of moisture removal. a: unpeeled fresh samples at 30 and 50°C drying; b: peeled fresh samples at 30 and 50°C drying; c: peeled blanched samples and unpeeled blanched samples dried at 50°C; d: peeled frozen samples and unpeeled frozen samples dried at 50°C.

4.3 Results and Discussions

4.3.1 Drying pattern of fresh broccoli stalks

Figure 3 presents the MRI measurements for the central cross-section of fresh broccoli samples dried at 30°C and 50°C. Differences in brightness indicate the distribution of moisture throughout the sample; the brighter the color, the higher the moisture content. The bar in the figures provides a relative scale for the moisture content. The gap at the bottom of each image indicates the hole made by the stick which supports the sample. In the first image of both figures slightly higher moisture content is observed at the edges. It indicates that there is still some free water at the surface, which is the consequence of cutting.

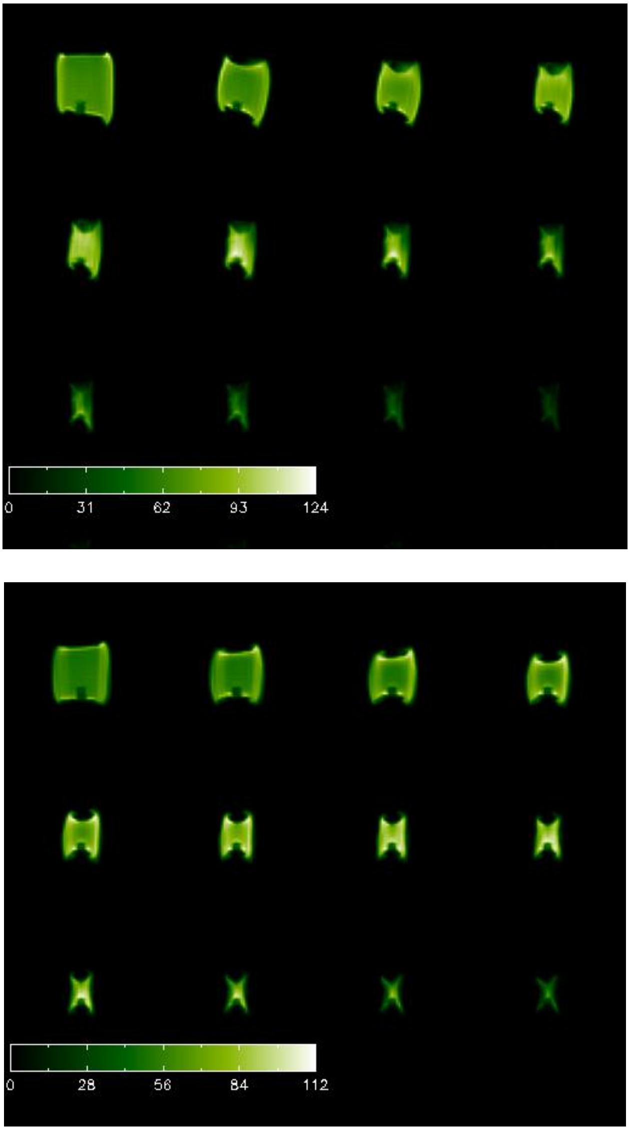

Figure 3 Series of MRI intensity of the middle slice of fresh broccoli samples in time. Top: drying at 30 °C; time interval between samples 272 minutes, total time 50 hours. Bottom: drying at 50 °C, time interval between samples 68 minutes, total time 12.5 hours.

Figure 3 shows an anomalous drying behaviour for both the 30°C and 50°C drying experiment for fresh and non-treated samples: after several hours of drying the moisture in the centre has been increased for the sample dried at 30°C the brightness at the center of the images of row 2 is above that of row 1, and for 50°C drying the brightness of the first image of row 2 is above that of the initial image.

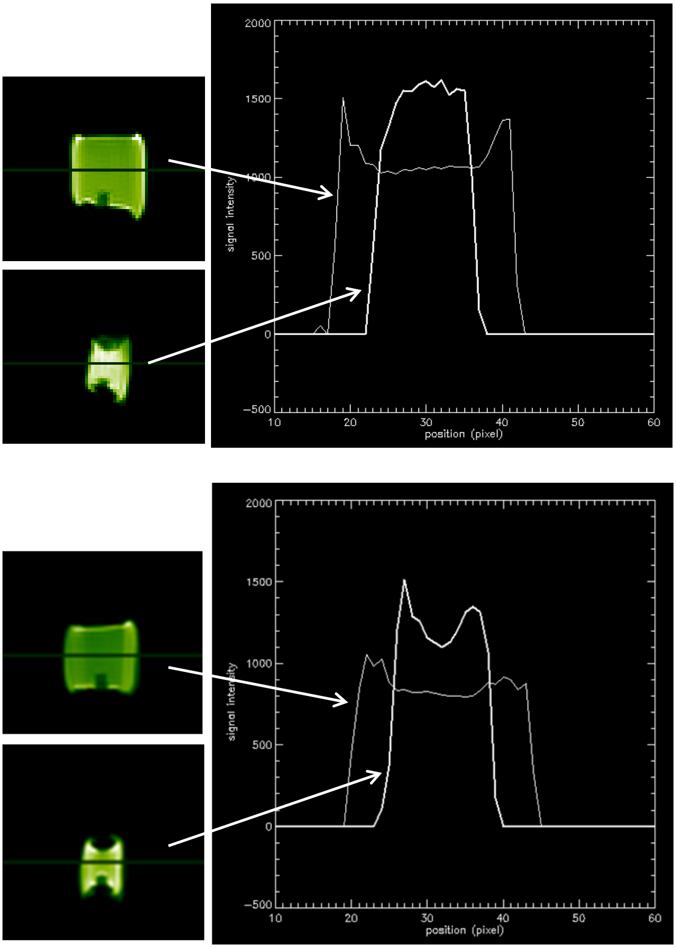

Figure 4 MRI intensity values for a cross-section (given by the horizontal lines). Top: drying at 30 °C; initial sample and at 18.1 hours. Bottom: drying at 50 °C; initial sample and at 6.8 hours. In both cases, the moisture content in the centre of the samples surpasses the initial sample.

Figure 4 gives the intensity (proportional to moisture content) for the cross-section of the image at start of drying and at 18.1 hours for drying at 30°C, and at 6.8 hours for drying at 50°C. We observe clearly that during drying, the moisture content in the centre rises far above the initial moisture content at any location of the sample. Compared to its initial value, the moisture content in the centre increases by 50-60%. This anomaly in drying behavior evidently deviates from the standard Fickian diffusion. According to the work of van der Sman (2007)[16] and Okuzono and Doi (2008)[18], shrinkage and deformation of the skin cause an internal pressure gradient, which results in a temporarily pressure-driven moisture transport towards the center of the product.

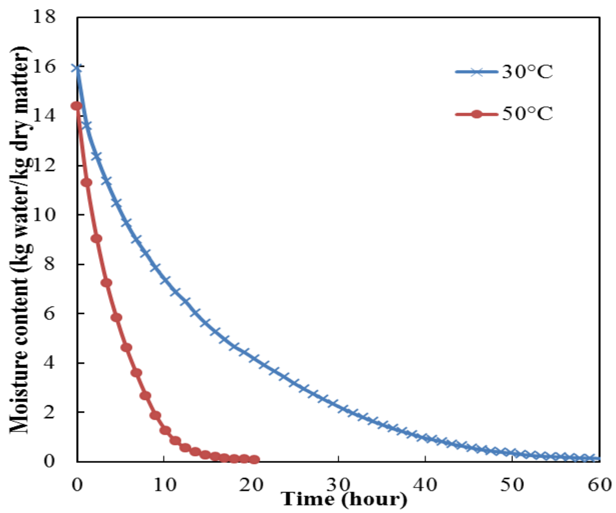

Figure 5 Drying curves of fresh broccoli stalks at different drying temperatures (30 and 50°C drying).

Despite the increasing moisture content in the centre of the product, the drying curves for the full samples, which are given in Figure 5, show monotonic decreasing moisture content.

Furthermore, the MRI images in Figure 3 show the decreasing size of the samples due to shrinkage during drying. Figure 2a shows the shrinkage quantitatively. The drawn lines in Figure 2 correspond to the situation where shrinkage is equal to moisture removal. The data points for drying at 50°C are above that for drying at

30°C which indicates that shrinkage at 50°C is stronger than at 30°C (Figure 2a). This result can be explained by the relation of elasticity and moisture content. Krokida et al. (1998)[24] reported that in the high moisture content region, elasticity decreases with decreased moisture content, whereas in the low moisture content region, elasticity increases while moisture content decreases. During drying , the skin dries fast and due to the low moisture content the skin is more elastic and causes a centre-directed moisture transport.[16] Moreover, the skin forms a significant barrier for moisture transport and therefore moisture removal takes place in the longitudinal direction of the sample. It results in an early stage of drying in a "butterfly" shape.

The cross-sections in Figure 4 also show that shrinkage differs for the height and width direction. For isotropic shrinkage of a cylindrical shape, the ratio (V_t/V_0) between the diameter at time t (d_t) and the initial diameter (d_0) is equal to the square root of the volume ratio $(V_t/V_0)^{0.5}$ (with V_t the volume at time t , and V_0 the initial volume).

However, for the broccoli samples in Figure 4, (V_t/V_0)=0.52, while $(V_t/V_0)^{0.5}$=0.22. The anisotropic shrinkage is caused by the impermeable and elastic structure of the skin and causes internal stress in the samples. From these results it is hypothesized that by applying pre-treatments that break down the wall structure the anomalies in drying behaviour could be reduced or even be cancelled.

4.3.2 Drying patterns after pre-treatments

To verify the hypothesis that the centre directed moisture transport is induced by the elastic properties of the product structure, product treatments were applied to break down the wall structure. The product treatments are 1) peeling: to remove the skin, 2) blanching: to soften the total tissue, both skin and core, thus to level out the elasticity differences between skin and center[25], and 3) freezing and thawing: to break down the internal structure, and to change the elasticity of the internal structure.[5]

4.3.2.1 Peeling

The results for two drying temperatures are shown in the images of Figure 6. Compared to Figure 3, the increased moisture content hardly occurs which confirms the role of elastic properties and the transport barrier of the skin. The first images also show increased moisture content at the surface, which is a result of moisture release at the surfaces where the skin was removed by cutting.

MRI images in Figure 3 and Figure 6 show different forms of shrinkage during drying. The peeled samples keep their original form for a long time, but towards the end of drying when the edge of the product approaches the glassy state, these samples also end with the “butterfly” shape. Figure 2b presents the degree of shrinkage as a function of the fraction of removed moisture for the peeled samples at 30 and 50°C. For a fraction of removed moisture below 0.85, shrinkage is linear to the fraction of removed moisture. For both temperatures the results coincide with the drawn line, which indicate the absence of an elasticity contribution to drying (see section 3.1).

4.3.2.2 Blanching

Blanching results in tissue-softening and can level out the differences in mechanical properties between the core and the skin.[26] For the blanched samples only a small difference in drying behavior between the peeled and unpeeled sample is found in Figure 7. So, the barrier for mass transport by the skin is removed by only blanching. Not only the structure of the skin is softened, the internal matrix is also softened by blanching and as a result, differences in elastic properties are leveled out resulting in standard Fickian moisture transport. The drying time is reduced to about 4.5 hours. The drying rate of both samples is nearly equal, but the shrinkage of the peeled blanched sample is below that of the non-peeled sample (Figure 2c).

4.3.2.3 Freezing

During freezing, ice crystals are formed in the tissue. Upon thawing, individual ice crystals merge into large complexes which both break the structure and increase the internal pore size. With the destruction of internal structure, elasticity is lowered. However, freezing is not effective enough to break down the barrier by skin. Results for peeled and non-peeled samples are given in Figure 8. Due to the internal stress, the product shrinks easily during drying. The images in Figure 8 show a strong “butterfly” form for the non-peeled frozen sample. The skin remains a mass transfer barrier. Drying occurs mainly along the longitudinal direction, and there is moisture accumulation just below the skin where the highest moisture content was detected.

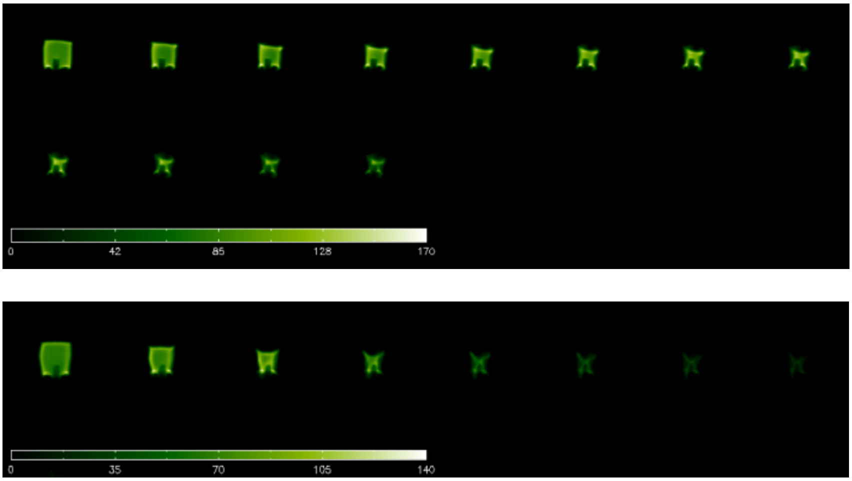

Figure 6 Series of MRI intensity of the middle slice of peeled broccoli stalks in time. Top: drying at 30 °C; Bottom: drying at 50 °C. Total drying time respectively 12.5 and 9.0 hours

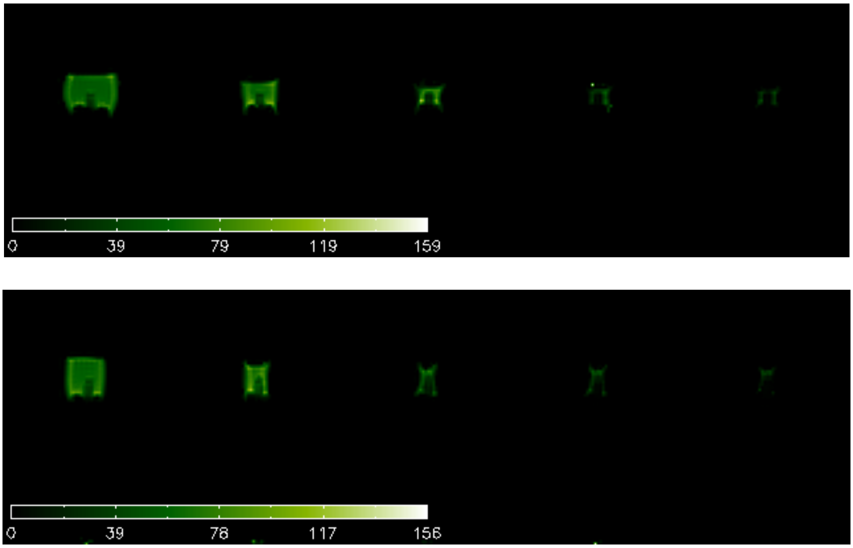

Figure 7 Series of MRI intensity of the middle slice of blanched broccoli stalks in time. Samples are dried at 50°C. Top: fresh unpeeled sample is blanched before drying. Bottom: sample first peeled then blanched before drying. Total drying time 4.5 hours.

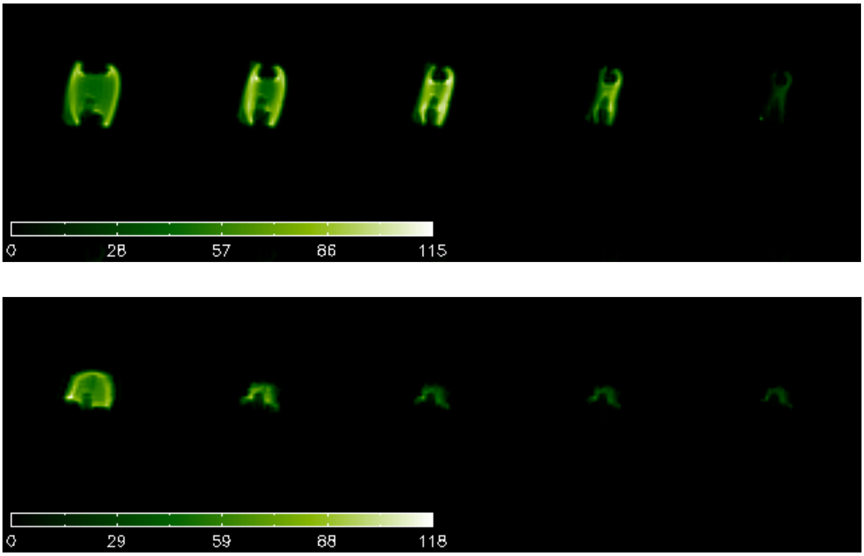

Figure 8 Series of MRI intensity of the middle slice of frozen broccoli stalks in time. Samples are dried at 50°C. Top: fresh sample frozen before drying. Bottom: sample first peeled then frozen before drying. Total drying time 4.5 hours.

The barrier for mass transport is absent for the peeled sample and therefore the peeled frozen sample does not have elastic stress-driven diffusion, and dries uniformly and the shape remains during drying and the moisture content in the center decreases in time. For both samples, shrinkage was equal to the volume of lost moisture (see Figure 2d). The change in the structure due to the freezing and thawing advances drying significantly and drying is completed within 4.5-5 hours.

4.4 Conclusions

From this investigation using in-situ MRI imaging of drying broccoli, and above cited earlier reports, it is observed that moisture transport in foods can be due to moisture concentration gradients and gradients in elastic stress. In our case of pre-treated broccoli, the gradients in elastic stresses are probably induced by inhomogeneity in elastic properties of the skin compared to the core. During drying of broccoli, the internal stress gradient can achieve a level that results in moisture transport against the gradients in moisture concentration. These observations are confirmed by pre-treatments which breakdown the internal structure and that of the product skin. Removing the skin of the broccoli sample by peeling results in a uniform product with drying behavior closed to Fickian diffusion. Blanching as a pre-treatment softens the skin and core of the product and creates uniform properties throughout the material to be dried. In this case drying can, indeed, be considered as a diffusion-driven process. Freezing and subsequently thawing as pre-treatment of fresh broccoli does not change the inhomogeneity of the elastic properties of the product during drying. In addition, we have observed that the pre-treatments peeling, blanching and freezing all enhance the drying rate significantly.

It is also likely that the skin (cuticle) of fresh products forms a barrier for moisture transport, which amplifies the effects of the internal stress gradients. This leads to anisotropic shrinkage, and subsequent moisture transport towards the centre of product. Drying of fresh products no longer follows the standard Fick's law of diffusion. Drying models must be extended and the observed results show that stress-driven diffusion term must be included, similar to the work of Okozuno and Doi (2008)[18].

According to thermodynamics, it is even more proper to relate the moisture transport to gradients in chemical potential (or equivalently water activity or swelling pressure). If formulated in terms of the proper thermodynamic potential, there exists no anomaly. The formulation of transport in terms of gradients of thermodynamic potential is customary in the field of soft matter physics[18,27], and food science can take advantage of this in adapting their framework.

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Chapter 5

Quantifying Broccoli Drying Rates from MRI Measurements

Abstract

The distribution of the internal moisture content during drying of broccoli is monitored by MRI imaging with controlled airflow and temperature. The measurements concern fresh broccoli florets with a porous structure and stalk samples as well as pre-treated (blanched and peeled) samples. The drying behaviour in the MRI device is compared with the behaviour in a pilot installation.

The Free Volume theory describes the variation of the effective diffusion coefficient throughout the rubbery and glassy states that occur during drying of food products. The Free Volume theory is validated on the average moisture content from the MRI experiments. The fitting parameters were the mass transfer coefficient and the self-diffusion coefficient for solids.

The results of MRI measurements showed that pre-treatments increase the drying rate of pre-treated products, which is result of an increased mass transfer coefficient and self-diffusion coefficient for solids due to the removal of a transport barrier or opening the cell structure. With the estimated parameter values the Free Volume theory reveals how the effective diffusion coefficient varies with moisture content. Drying curves from the MRI experiments for a single particle represent the drying behaviour of a batch of particles in the pilot plant.

Keywords: diffusion properties; MRI; convective drying; moisture profiles

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5.1 Introduction

Models to describe the mass transport driven by concentration gradients during drying of food are based on Fickian diffusion (Mulet et al., 1999). In these representations the diffusion coefficient is set to be a function of temperature according to the Arrhenius equation. However, due to the interaction between the product matrix and water, drying of food products behaves in a more complex way, and consequently, often a mismatch between the outcome of diffusion based drying models and the data is observed. An important reason for the deviation is that during drying the product passes through rubbery and glassy states, resulting in changes of water mobility and consequently in a moisture dependent effective diffusion coefficient. The varying diffusion properties within each state and between the different states may not be ignored. Therefore, a model that reflects the physical changes by a varying effective diffusion coefficient is required.

In previous work (Jin et al., 2011, Sman and Meinders, 2013) the Free Volume theory for moisture transport is proposed to predict the moisture transport during drying of broccoli. This theory includes water mobility and involves the glass transition temperature to distinguish between different moisture transport in rubbery and glassy states. The potential of this model to predict moisture transport was illustrated by simulation studies on a spatially distributed model and comparison with literature information. The first aim of this work is to validate a spatial distributed drying model based on the Free Volume theory from experimental data.

The validation of a spatially distributed drying model is difficult with traditional methods. The most used methods to examine the internal moisture distribution in foods during drying are destructive methods (e.g. by taking slices from the sample) or non-destructive methods (e.g. γ ray densitometry). Drawbacks of these methods are the requirements on the size of the sample, the limited resolution and that they can only be applied in a one-dimensional direction (McCarthy et al., 1991, Ruiz-Cabrera et al., 2005, Chen, 2007).

Magnetic Resonance Imaging (MRI) is a non-destructive technique to examine the interior of food products. It provides the opportunity to investigate the internal moisture distribution and transport of food products during in-situ heating. Nott et al., (2000) applied the technique to monitor the phase transition and temperature distribution in food during microwave heating. Watanabe et al., (2001) applied this technique to monitor moisture transport during rice cooking. Other examples of the application of MRI to food products are given by Schrader and Litchfield (1992), Foucat, et al. (2002) and McCarthy et al. (1991). In contrast to these examples, in this work MRI is used for in situ monitoring of the moisture content and its distribution during drying and to derive characteristic parameters in the Free Volume theory.

The cell structure in plant tissue has also a main role in moisture transport. The density of the cell structure increases from the centre towards the surface. Especially the surface and the layers just below the surface form a high resistance to moisture transport. Blanching affects the cell membranes and equalizes the resistance for moisture transport throughout the tissue (Sila et al., 2005, Gomez et al., 2004, Galindo et al., 2005). Another method to equalize the resistance is the removal of the outer layer by peeling (Xanthopoulos et al., 2012, Prachayawarkorn et al., 2010). In our previous work, the effect of pre-treatments on the internal moisture distribution and shrinkage behaviour during drying was investigated with MRI (Jin et al., 2012). In that work, it was shown that pre-treatments prior to drying significantly increase on the drying rate, but it was not studied quantitatively. Hence, the second aim of this work is to quantify the drying rate from experimental MRI data. For that purpose, we fit moisture profiles in broccoli during drying from MRI imaging data to simulations of a drying model using the Free Volume theory. Influences of different pre-treatments (peeling, blanching) on drying rate of broccoli are quantified by characterizing parameters: the mass transfer coefficient and the self-diffusion coefficient for solids

In the MRI installation only one broccoli particle can be dried at a time. These results can differ to that of a large scale dryer. The third aim of this work is to compare the drying behavior of a single particle in the MRI installation and that of multiple particles in a pilot dryer.

5.2 Theory and Modeling

At constant temperature, Fick’s second law for diffusion-controlled particle drying is given as:

$$\frac{\partial W}{\partial t} = \frac{\partial}{\partial r}\left(D_{eff}\frac{\partial W}{\partial r}\right) \qquad (1)$$

with *Deff* the effective diffusion coefficient(m2.s-1), *W* the moisture content (kgwater.kgdry matter-1), *r* the position in the diffusion direction (m) and *t* the time(s).

According the Maxwell-Eucken relationship, the diffusion coefficient for water in porous products is a combination of the diffusion coefficient of water in the continuous phase (*Dc* ; product) and in the dispersed phase(*Dd* ; air):

$$D_{eff} = D_c\left(\frac{D_d+2D_c+2(1-\varepsilon)(D_d-D_c)}{D_d+2D_c-(1-\varepsilon)(D_d-D_c)}\right) \qquad (2)$$

with ϵ is the porosity (-) (estimated as 0.3 for broccoli florets and 0 for stalks from image processing), *Dd*(m2.s-1) the water diffusion coefficient in air which is given by Olek (2003), :

$$D_d = 23\times 10^{-6}\ \frac{98100}{P}\left(\frac{T}{273.15}\right)^{1.75} \qquad (3)$$

where P is the pressure(Pa), and T the temperature(K).

Dc (m2.s-1) is the water diffusion coefficient in the solid matrix, and follows from the Darken relation (Hahn et al., 1986, Sman,and Meinders,2013):

$$D_c = Q(\phi D_w + (1-\phi)D_s) \qquad (4)$$

$$Q = 1 - 2\chi\phi(1-\phi) \qquad (5)$$

with *Dw*(m2.s-1) is the self-diffusion coefficient of water molecules, D_s(m2.s-1) the self-diffusion coefficient of solid particles, ϕ(-) the volume fraction of the solid phase, *Q*(-) the thermodynamic factor, and χ (-) the interaction parameter (Jin et al., 2013)

The self-diffusion coefficient of water molecules D_s(m2.s-1), is given by the Free Volume theory (Vrentas and Duda, 1977):

$$ln\left(\frac{D_w}{D_0}\right) = \frac{\Delta E}{RT} - \frac{y_1\hat{V}_1^{\,*}+\zeta y_2\hat{V}_2^{\,*}}{y_1\left(\frac{K_{11}}{\gamma}\right)(K_{21}-T_{g,1}+T)+y_2\left(\frac{K_{12}}{\gamma}\right)(K_{22}-T_{g,2}+T)} \qquad (6)$$

with y_1 and y_2 respectively the mass fraction of water and solids in the product. These mass fractions are related with the volume fraction ϕ. The free volume parameters for water and product are given in Table 1. The Free Volume parameters sucrose in Table 1 holds for a large range of food ingredients. In contrast to Vrentas and Duda (1977) the glass transition temperature of sucrose is used instead of that of the product.

Table 1 Universal parameters for the Free Volume theory

Water properties	Value		Product properties	Value
$\hat{V}_1^*$ (ml.g-1)	0.91		$\hat{V}_2^*$ (ml.g-1)	0.59
$T_{g,1}$ (K)	136		$T_{g,2}$ (K)	360
$D_{0,w}$ (m2.s-1)	1.39×10-7		K_{22} (K)	69.21
ΔE (J.mol-1)	1.98×103		k (J.K-1)	1.38×10-23
K_{21} (K)	-19.73		a (m)	1×109
K_{11}/γ (m.L.g-1.K-1)	1.945×10-3			

Because of the varying composition and physical properties of the solids, the self-diffusion coefficient Ds is used as a fitting parameter.

To solve equation 1, symmetry in the product is assumed. At the centre of the product there is no mass transfer and at the surface where r=R, the boundary condition for mass transfer is:

$$k_c\left(C_{surface} - C_{air}\right) = D_{eff}\rho_p \frac{\partial W_{r=R}}{\partial r} \qquad (7)$$

with kc the overall mass transfer coefficient (m.s-1), $C_{surface}$ and C_{air} are respectively the vapour concentration at the product surface and air (kg.m-3) and ρ_p the product density (kg.m-3). Using uniform Fickian diffusion for product implies that the resistance for mass transport in the surface layer is now added to the mass transfer coefficient.

$$C_{surface} = \frac{M_w a_w P_{sat}}{RT} \qquad (8)$$

The sorption isotherm relationship is used in the boundary condition for mass transfer (equation 9). According to our previous work (Jin et.al. 2013, van der Sman and Meinders, 2011, van der Sman 2012), the sorption isotherm is given by Flory-Huggins Free Volume theory (FHFV). The relation is described as:

$$ln a_w = ln(1 - \Phi) + \left(1 - \frac{1}{N_{eff}}\right)\Phi + \chi\Phi^2 + F(\Phi) \qquad (9)$$

With a_w the water activity (-), ϕ the solid volume fraction (-), χ the interaction parameter (-), N (-) the molar volume ratio of polymer and solvent (see Appendix A). The interaction parameter is a function of the physical properties of the components (Jin et.al. 2013).

5.3 Materials and Methods

5.3.1 Materials

Fresh broccoli was cut in florets and stalks. The dimensions for the florets were about 0.01 m in height and 0.01 m in radius. Each floret includes a stalk part of 0.005 m in height and 0.005 m in radius. The mass of the florets was around 1.5 gram.

The dimensions of the stalks were 0.01m in height and 0.01m, the mass of these stalk was about 2.5 gram.

5.3.2 Pre-treatments

For all the samples, different pre-treatments were applied (Table 2). After all pre-treatments, the free water at the sample surfaces was removed at room temperature with tissue paper before further processing.

Table 2 Overview of pre-treatments and experiments

Pre-treatment	procedure
Peeling	1.0mm-1.5mm skin was removed
Blanching	90°C water, 3 minutes
Experiment	pre-treatment
1.	Fresh
2.	Peeled
3.	blanched

5.3.3 Drying chamber (MRI)

The sample was fixed by a stick on a sample supporter and inserted into a drying chamber in the MRI measurement device. The size of the drying chamber was 0.032 m in diameter and 0.2 m in length. A continuous flow of dry conditioned and temperature controlled air was supplied. The air temperature was 30°C and 50°C, respectively, the air velocity 1.0 m/s and the relative humidity 10%.

Drying was continued until the moisture content of the samples was constant. Depending on the material properties, the experimental time for the fresh and pre-treated broccoli ranged from 12 to 48 hours. Initial and final product moisture contents were determined by oven drying (105°C, 24 hours).

During drying in the MRI drying chamber a large flow of air is applied for only one particle. As a result, particle temperature decline in air and product due to evaporation is small and it is reasonable to assume that the particle dries at isothermal conditions in time.

5.3.4 Drying chamber (pilot dryer)

Product was dried in a drying chamber fed by temperature and zeolite dehumidified air (Atuonwu et al., 2013). Samples were placed on a grid (0.2×0.2m, mesh size 0.0025×0.0025m), which is connected to a scale (Mettler Toledo PM2500). This scale measured the mass of product in the dryer continuously. For every drying experiment, 100 grams of samples were placed at the grid. Temperature and airflow rate are controlled.

5.3.5 MRI imaging

All measurements were performed on a 3 T (128 MHz for protons) MRI system (Bruker, Karlsruhe, Germany), consisting of an Avance console, a superconducting magnet with a 0.5 m vertical free bore (Magnex, Oxford, UK), a 1 T/m gradient coil, and a birdcage RF coil with an inner diameter of 0.04 m.

5.3.6 MR Imaging

3D images were obtained using a Turbo Spin Echo (TSE) MRI sequence (Scheenen et al., 2000), a repetition time TR of 2 s, an effective spin echo time TE of 3.35 ms and a spectral bandwidth SW of 50 kHz. Only 16 echoes were acquired in the TSE train to avoid T2-weighting. Odd and even echoes were separately phase encoded forming two different images to avoid Nyquist ghost's artefacts, so the turbo factor was 8. Two acquisitions were averaged to improve image quality. The Field-Of-View (FOV) was 35×35×35 mm^3 with a matrix size of 64×64×64 resulting in a spatial resolution of 0.55×0.55×0.55 μm^3. The interval time between measurements was 18 minutes.

5.3.7 Numerical methods and data analysis

MRI-measurement data handling and analysis was performed with home-built software written in IDL (RSI, Boulder, CO). To solve Equation 1-9, the structure of broccoli is configured in COMSOL and the equations are defined for each part of the structure.

5.3.8 MRI data calibration

Monitored intensity values above 0.75 counts/pixel were used for conversion to moisture content. Above this value, the MRI signal intensity is linear with moisture content (McCarthy et al., 1991). However, for nearly dry samples the MRI intensity might deviate from the linear relationship. Jin et al. (2012) discuss the use of the MRI intensity signal at low moisture content. The same procedure is followed here.

5.3.9 Moisture calculations

The average intensity from the MRI follows by the summation of all intensity values above the threshold 0.75 counts/pixel divided by the number of pixels above the threshold. The average moisture content is then derived from the average intensity and the initial and final moisture content of the product measured by 24 hours oven drying at 105°C. These values are used to convert the intensity signal to average moisture content.

Similarly the average moisture content in the pilot dryer is derived from the initial and final weight of the batch of samples.

5.3.10 Parameter estimation

The trajectories for the average moisture content in a sample were simulated by using COMSOL (Jin et al. 2011). As there was no suitable procedure for parameter estimation for the used model in COMSOL, the drying trajectories from COMSOL were imported to MATLAB to calculate the sum of squared errors (SSE) and R^2. Subsequently a decision was made to adapt the parameters, and the model in COMSOL was simulated again with the new parameters. This procedure was followed until the improvement of sum of squared errors was below 2% of its value.

5.4 Results and Discussions

5.4.1 MRI moisture profiles

Figure 1 gives the 3D image measurements for the cross section at the center of the broccoli floret sample. The intensity of the color indicates the moisture content distribution within the sample; the brighter the color, the higher local moisture content. The outer surface of the floret has a dark color, whereas the stalk in the floret has a bright color, which corresponds to the faster drying at the surface and slower drying in the center. The size of the sample corresponds to the size of each image and demonstrates shrinkage. After some time, the signal for the surface is too weak to interpret progress of drying by visual observation, but the changes in moisture content can still be recorded from the MRI signal.

Figure 2 gives an example of the 3D image measurements for the cross section at the center of blanched broccoli stalk. Blanching breaks the cell structure and softens the entire tissue and as a result moisture transport is enhanced. The drying time for blanched broccoli is therefore significantly shorter than that for untreated broccoli. Anomalies due to shrinkage, elasticity and stress diffusion as observed in untreated broccoli stalks do not occur for blanched broccoli (Jin et al., 2012).

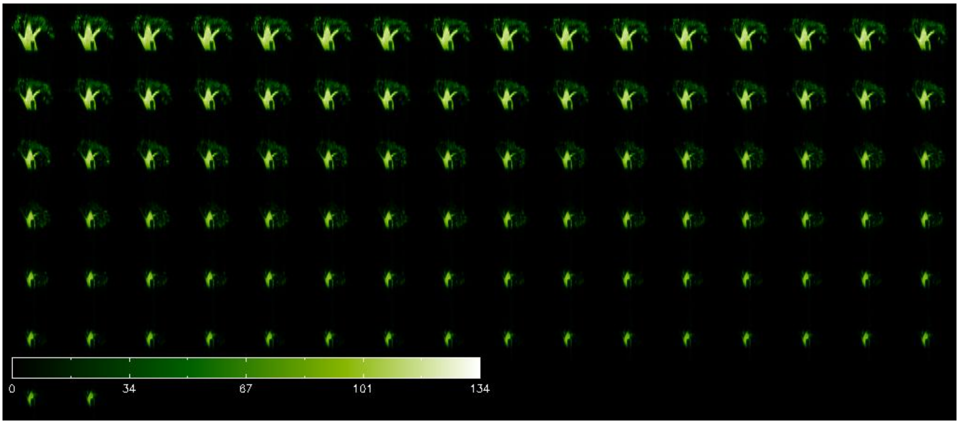

Figure 1 Series of MRI intensity in the centre of a fresh floret sample during drying at 30°C. Progress during drying is given in the pictures at the succeeding rows. The interval time is 18 minutes. Total drying time 14 hours

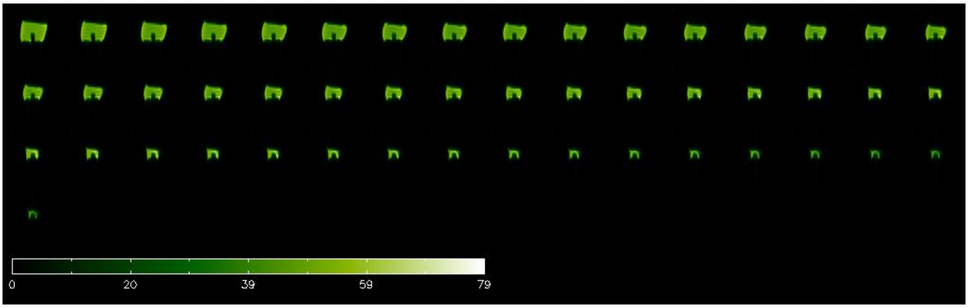

Figure 2 Series of MRI intensity in the centre of blanched broccoli stalks during drying at 30°C. The interval time is 18 minutes. Total drying time 10 hours

5.4.2 Moisture profiles and diffusivities

Figure 3 gives the average moisture content in florets derived from the MRI intensity. The moisture content is given as the moisture ratio

$$MR = \frac{W-W_e}{W_0-W_e} \tag{10}$$

With W_0 the water content at the start of drying ($kg_{water}.kg_{drymatter}^{-1}$), W_e the water content at the end of drying ($kg_{water}.kg_{drymatter}^{-1}$) and W the water content during drying ($kg_{water}.kg_{drymatter}^{-1}$).

The figures show the normal pattern for drying of vegetables. The average moisture content from the MRI intensity is fitted to the spatially distributed model based on the Free Volume Theory (equation 1-8). The dimensions and form used in the COMSOL model were close to the samples used in MRI experiments.

Universal constants and water properties are used in equation 6. The universal constants follow from sugar properties and are given in Table 1. Only two parameters remain for fitting; these are the self-diffusion coefficient of solids in broccoli (D_s) and the mass transfer coefficient (k_c). Results for these parameters are given in Table 3.

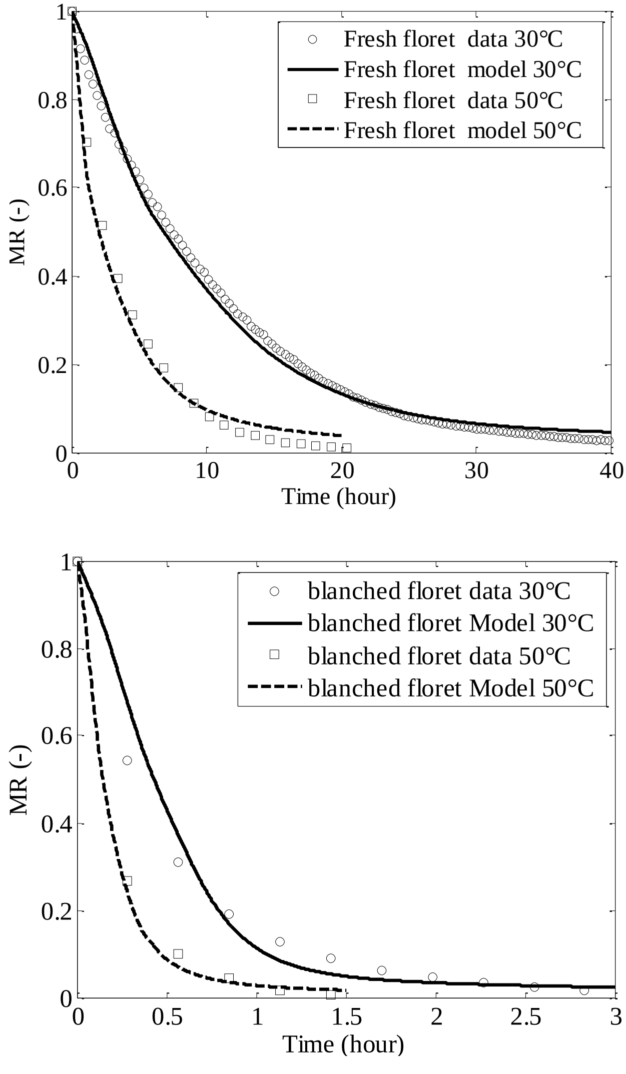

Figure 3 Measured and estimated drying curves expressed as moisture ratio (MR) of fresh and blanched floret at different temperatures. Top: drying of fresh broccoli florets at 30 and 50°C. Bottom: drying of blanched florets at 30 and 50°C.

Rossello et al. (1992) state that the initial stage of drying is governed by the mass transfer coefficient as the most important parameter. This stage is followed by a period of both mass transfer and diffusion control drying. In the last stage of drying, the drying rate is diffusion controlled.

The results obtained from figure 4 yield similar mass transfer coefficients for broccoli florets at 30 and 50°C (Table 3). In the initial stage, drying at 50°C is, however, faster than at 30°C, which is caused by improved diffusivity. So, according to Rossello et al. (1992), the start of broccoli drying is both mass transfer and diffusion controlled.

For the blanched samples, it was found that the mass transfer coefficient increased dramatically, and values for self-diffusion coefficient of solids are ten times higher than for fresh dried broccoli florets. This increase is due to the tissue softening and breaking down of cell walls.

The values for the self-diffusion coefficient are, except for the blanched floret at 50°C in line with literature values for gels which are in the range of 1e-9 to 1e-10 m^2s^{-1} (Amsden 1998, Masaro and Zhu 1999, Wu et al., 2009, Kvarnström et al., 2009). The noticeable result for the blanched floret at 50°C is possibly caused by a deviation in the used porosity. It has been reported that for drying of broccoli, shrinkage is equal to moisture removal which indicates that the volume substituted by air is minimal (Jin et al., 2012). Therefore, the porosity should be constant during drying, except for the last phase of drying (glassy state) with a small derivation from the linearity (Jin et al., 2012). The Free Volume model is sensitive to the chosen value of the porosity (see equation 2,4,5). For the broccoli florets a porosity of 0.3 was derived from image analysis of the cross sectional areas. However, occasionally higher porosity values were found. Using a porosity value 0.4 for the blanched floret at 50°C brings the self-diffusion coefficient for that sample in the expected range.

The obtained mass transfer coefficients (see Table 3) are rather high, but comparable to those for drying of other crops (Temple et al., 1999, Crip and Woods, 1994, and Patil et al., 1992). The high values can be result of two aspects. The first is that in the simulation with COMSOL a smooth outer surface is used, while the surface of the actual sample is non-smooth and has a higher surface area. The second reason is that the mass transfer coefficient is an effective coefficient, which also includes the resistance of the skin layer. As moisture transport is considered as diffusion in a uniform product, the resistance for moisture transport in the surface is included in the mass transfer coefficient for boundary layer. Pre-treatments affect the surface layers and the change of the resistance is reflected by the mass transfer coefficient (compare the differences in mass transfer coefficient for peeled and blanched stalks). The effect of blanching on the total drying time is significant; the drying time is reduced to about 2-3 hours, whereas for fresh broccoli floret the time was at least 15-20 hours.

Results for broccoli stalks are given in figure 4. For peeled and blanched stalks, the mass transfer coefficients at the different temperature levels are also the same. With the removal of the mass transfer barrier by peeling, drying enhanced significantly at both 30 and 50°C and drying curve is comparable to blanched broccoli stalks with intact skin (see Jin et al, 2012).

Table 3 Results of data fitting. Mass transfer coefficient (k_c) and self-diffusion coefficient of solids (Ds)

sample	k_c (m.s^{-1})	D_s (m^2.s^{-1})	RMSE (-)	R^2
Fresh floret (30°C) ε = 0.3	0.025	1E-10	0.16	0.99
Fresh floret (50°C) ε = 0.3	0.026	5E-10	0.21	0.99
Peeled stalk (30°C)	0.073	1E-11	0.45	0.96
Peeled stalk (50°C)	0.075	1E-10	0.41	0.99
Blanched floret (30°C) ε = 0.3	0.38	1E-9	0.46	0.92
Blanched floret (50°C) ε = 0.3	0.40	1E-8	0.10	0.99
Blanched floret (50°C) ε = 0.4	0.4	5E-9	0.11	0.99
Blanched stalk (30°C)	0.074	3E-11	0.37	0.99
Blanched stalk (50°C)	0.076	3E-10	0.22	0.99

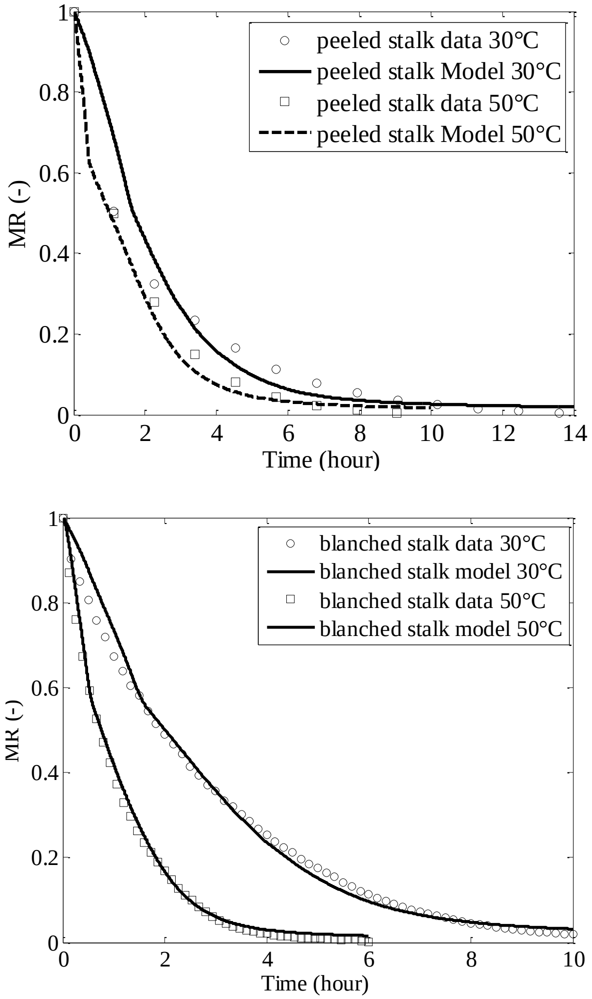

Figure 4 Measured and estimated drying curves expressed as moisture ratio (MR) of peeled and blanched stalks at different temperatures. Top: drying of peeled stalks at 30 and 50°C. Bottom: drying of blanched stalks at 30 and 50°C.

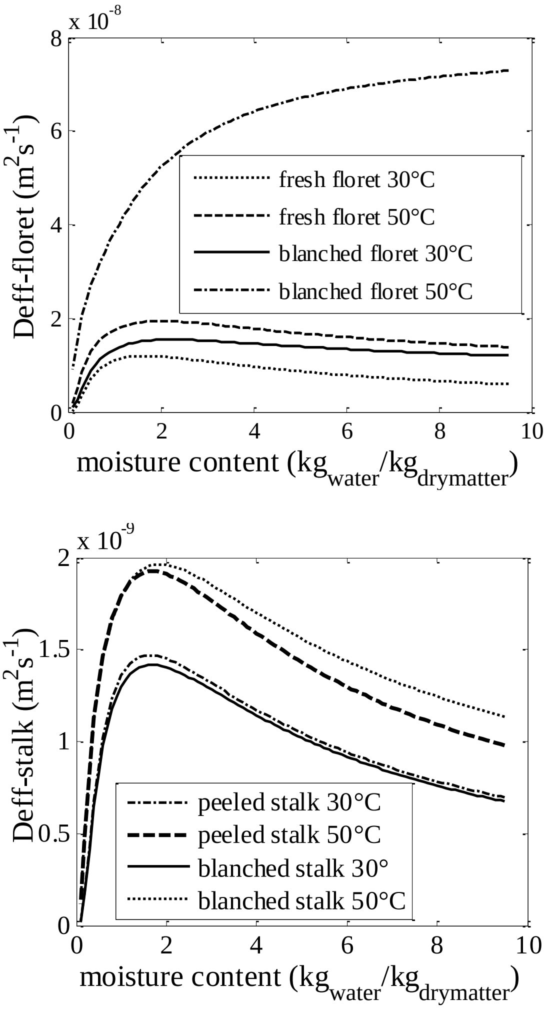

Figure 5 Effective diffusion coefficients for broccoli florets (top) and stalks (bottom) as a function of the moisture content at 30°C and 50°C

Figure 5 shows the resulting effective diffusion coefficient as a function of moisture content for florets and stalks. The effective diffusion coefficient has for both products a maximum value and decreases with lower moisture contents. At low moisture contents the product approaches the glass transition temperature, which causes a lower mobility of the water molecules. The decreased mobility gives a lower self-diffusivity (D_w) for the water molecules in equation 6. The lower self-diffusivity is consequence of the changing water mass fraction (y_1) and solid mass fraction (y_2) during drying. The maximum value for D_{eff} is the result of the varying value of the volume fraction during drying (Φ , related with y_1 and y_2) in the Darken relations (equation 4 and 5). Similar results are reported for the mutual diffusion coefficient of water in gelatine (Yapel et al., 1994), and for drying of starch rich products (Karathanos and Vegenas, 1991). For the blanched floret at 50°C, the maximum in the curve is absent. This is due to much higher effective diffusion coefficient and D_w and D_s values in the same order of magnitude. This also can be explained by the possibly high porosity of the floret. It must also be noted that this sample has an exceptional value for the self-diffusion coefficient in table 3.

5.4.3 Comparison of single MRI particle drying and pilot drying

The drying model and MRI drying experiments consider drying of a single particle of broccoli; floret or stalk. Experimental results from MRI drying data were compared to results of a pilot plant batch dryer. In the MRI drying chamber, dried conditioned air was supplied and for the comparison zeolite-dehumidified air was used in the pilot dryer. In Figure 6The results of the pilot dryer fall, regardless of noise, together with the MRI drying curve. From the comparison, we conclude that for the same drying conditions the single broccoli-drying model is representative for drying of a batch of samples in a pilot dryer.

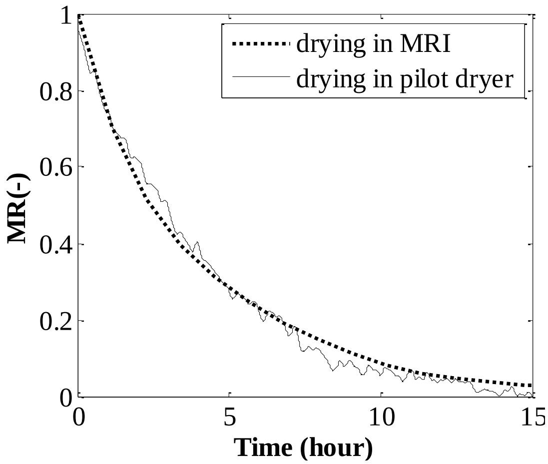

Figure 6 Comparison of drying curves obtained in the MRI system and in the pilot dryer (with ambient and dehumidified air).

5.5 Conclusions

MRI imaging offers the potential to study the internal moisture distribution of food products during processing. The moisture distribution obtained by MRI imaging of broccoli stalks and florets enables a model-based characterization of moisture transport during drying. From the time trajectories of the average moisture content, the effective diffusion coefficient and the mass transfer coefficient are successfully derived.

The effective diffusion coefficient depends, like in other food products, on the mobility of water in the food matrix. The mobility of water in food is described by the Free Volume theory. The Free Volume model uses a number of universal constants and leaves the self-diffusion coefficient of solids as fitting parameter. This parameter is derived for different pre-treated broccoli products.

The results show that the effective diffusion coefficient is a function of the product moisture content, and varies thus during drying. Compared to fresh products, pre-treatments increase the mass transfer coefficient for moisture either by removing the transport resistance of the skin (peeling), or by disruption of the cell structure (blanching). Disruption of the cell structure by blanching of stalks increases the effective diffusion coefficient only slightly, while the effect for florets is significant.

MRI experiments of a single particle proved to be representative for drying experiments in a conventional pilot dryer. This supports the use of drying models derived from MRI data to predict and optimize drying in larger scale units.

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Chapter 6

Drying Strategies to Retain Nutritional Components in Broccoli

Abstract

This work concerns the combined optimization of the retention of bioactive components and energy efficiency during drying of vegetables like broccoli. Kinetics for the degradation of glucosinolates, vitamin C and drying of broccoli are used to calculate optimal drying trajectories for the control variables air flow rate and temperature. It is shown from plots of the optimal drying trajectories in moisture-temperature state diagrams with degradation and drying rates, that areas with high degradation rates are circumvented. The drying strategies allow for halving the energy consumption and a significant increase of vitamin C content.

Keywords: broccoli, drying, dynamic optimization, glucosinolates, vitamin C retention, energy efficiency

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6.1 Introduction

Food quality is the main performance indicator in food processing. Besides the visible quality aspects (shape, color, sensory etc.), nutritional impact has become a major aspect for quality. Among the nutritional aspects, antioxidant properties of bioactive components are considered as a key for human health especially due to the anti-cancer effect. For example, glucosinolates, present in brassicaceae, have significant anti carcinogenic properties in colorectal cancer (Verkerk, 2009). Vitamin C, the most abundant in water soluble antioxidant, is a basic component for health and reduces the risk for cancer and heart diseases (Tribble, 1999, Byers and Perry, 1992). These components are, however, heat sensitive and the availability in processed food is reduced during heat treatments like cooking and drying.

Convective drying is most applied for preservation of food products over long periods. It also provides opportunities for the production of convenient food. Convective drying is a heat intensive treatment which results in degradation of heat sensitive bioactive components. Goula and Adamopoulos (2006), Zanoni et al. (1998) reported that for conventional drying of vegetables under constant drying conditions vitamin C retention is below 50% or even not detectable. Similar results are available for other nutritional components such as glucosinolates, which degrade at drying temperatures above 60°C (Oliviero et al., 2012).

In convective drying moisture is removed from the product by vaporization. The heat required for vaporization makes drying one of the most energy intensive industrial processes. The energy efficiency of convective dryers is often below 50% (Kemp, 2005) and drying accounts for at least 10% of industrial energy demand (Kudra, 2004). To retain as much as possible of the nutritional components in vegetables, mild drying conditions are recommended. Under these conditions energy efficiency is even below the level as mentioned by Kemp (2005). With the current price level for energy and the need for sustainable operations, industries that process food are now facing two challenges: 1) to retain nutritional components, and 2) to reduce the energy demand for drying. Therefore, in recent years, lots of efforts have been paid to increase energy efficiency and to lower the energy consumption by the development of advanced dryers (Menshutina et al., 2004, Dufour, 2007, Djaeni 2007, Nagle et al., 2010).

Energy efficiency and product quality seem conflicting demands, but at the other hand developing drying methods that meet both needs is regarded as a challenge (Mujumdar, 2004). In this work we consider the possibilities of dynamic optimization to find optimal drying trajectories that increase both energy efficiency and product quality. The optimal trajectories are calculated for drying of broccoli where we aim to retain both vitamin C and glucosinolates in combination with high energy efficiency. To interpret the results, the optimal drying trajectories are given in moisture-temperature state diagrams which also present the degradation kinetics and the drying rate kinetics.

The results of this study give information for the design and operation of dryers in which bioactive compounds in food products can be retained. In addition, the moisture-temperature state diagram provides a basis to understand how to deal with multiple objectives.

6.2 Theory and Modeling

6.2.1 Mass and energy balances

The mass balances for the moisture content in a product particle during the time (t) the particle resides in a dryer and for the moisture content in the air around the particle are given by (single phase model, Law and Mujumdar, 2007):

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

$$0 = F_a\left(X_{a,in} - X_a\right) + M_p * \frac{dX}{dt} \quad (2)$$

With X is the moisture content (kg water.kg dry matter^{-1}), X_e is the equilibrium moisture content (kg water.kg dry matter^{-1}), k is the drying rate constant (s^{-1}), F_a is the air mass flow rate (kg.s^{-1}.m^{-2}), X_a is the moisture content of air (kg water.kg dry air^{-1}), $X_{a,in}$ is the moisture in inlet air (kg water.kg dry air^{-1}), and M_p is the weight of dry matter (kg.m^{-2}).

The Biot number for heat transfer for broccoli particles of 1×1 cm is below 1 which indicates that the time scale for heating is much faster than the time scale for moisture transport during drying. This is confirmed by our previous simulations

(Jin et al., 2011), which showed for broccoli particles a time constant for heat transfer in the range of 3-5 minutes. Therefore we assumed that product and air have the same temperature, and experimental data also confirmed that. As a result, the combined energy balance for product and air is given by (single phase model, Law and Mujumdar, 2007):

$$M_p C_{pp} \frac{dT}{dt} = F_a\left(C_{pa} + X_{a,in} * C_{pv}\right)(T_{in} - T) - F_a * \Delta H_{vap}\left(X_a - X_{a,in}\right) \quad (3)$$

With T is the product temperature (°C), T_{in} is the air inlet temperature (°C), C_{pp} is the specific heat capacity of product (kJ.kg^{-1}.K^{-1}), C_{pa} is the specific heat capacity of air (kJ.kg^{-1}.K^{-1}), C_{pv} is the specific heat capacity of water vapor (kJ.kg^{-1}.K^{-1}), ΔH_{vap} is the latent heat of vaporization (kJ.kg^{-1}).

The energy efficiency is defined as the energy used for moisture evaporation (E_{ev}) to the total energy supplied to the dryer (E_{in}):

$$\eta = \frac{E_{ev}}{E_{in}} \quad (4)$$

The heat used for moisture evaporation is:

$$E_{ev} = M_p \left(\frac{dX}{dt}\right) \Delta H_{vap} \quad (5)$$

And the energy supplied to the dryer:

$$E_{in} = F_a C_{pa}(T_{in} - T_{amb}) \quad (6)$$

With T_{amb} is the ambient temperature (°C).

6.2.2 Degradation kinetics

Experiments on a range of product samples showed common results for the vitamin C degradation rate constants (Mishkin et al., 1984, Karim and Adebowale, 2009). These kinetic results are here applied for broccoli. The degradation of vitamin C follows a first order degradation kinetics:

$$\frac{dC}{dt} = -k_c C \quad (7)$$

With C the concentration of vitamin C (g.kg^{-1} product) and k_c is the degradation rate constant (s^{-1}) for which the temperature dependency is given by:

$$k_c = k_{c0}\left(-\frac{E_{ca}}{RT}\right) \tag{8}$$

With R the gas constant (J.mol^{-1}.K^{-1}), E_a the activation energy (J.mol^{-1}) and k_{c0} the pre exponential factor.

Mishkin and Saguy and Karim and Adebowale reported the following expressions for the degradation rate constant and activation energy for vitamin C as a function of the moisture content:

$$k_{c0} = exp(P_1 + P_2X + P_3X^2) \tag{9}$$

$$E_{ca} = P_4 + P_5X + P_6X^2 + P_7X^3 \tag{10}$$

The values for P1-P7 are given in Table 1.

Table 1 Model parameter values for vitamin C degradation kinetics

Parameter	Value	Parameter	Value
P_1	16.38	P_4	14831.00
P_2	1.78	P_5	241.10
P_3	1.89	P_6	656.20
		P_7	236.80

Glucoraphanins is a group of abundant glucosinolates in broccoli and most important as a nutritional component. Thermal degradation of glucosinolates (GL) follows a first order reaction model, and the temperature dependency of the degradation rate constant is given by the Arrhenius equation (Oliviero et al., 2012):

$$\frac{d[GL]}{dt} = -k_d[GL] \tag{11}$$

$$k_d = k_{G0} exp\left(-\frac{E_{Ga}}{RT}\right) \quad (12)$$

With T the product temperature (K), k_d is the degradation rate constant (min^{-1}), k_{ref} is the degradation rate constant at reference temperature (min^{-1}), T_{ref} (K) is the reference temperature, E_a the activation energy (J.mol^{-1}).

According the experimental results of Oliviero et al. (2012) the moisture dependency of $k_{G0}$and E_{Ga} is given by (see also Table 2):

$$k_{G0} = exp(u_1 + u_2 X) \quad (13)$$

$$E_{Ga} = u_3 + u_4 X + u_5 X^2 \quad (14)$$

Table 2 Model parameter values for glucosinolates degradation kinetics

Parameter	Value	Parameter	Value
u_1	25.21	u_3	91741.97
u_2	8.29	u_4	133.60
		u_5	32606.35

6.2.3 Specification of product and drying system

The calculations concern uniform pieces of broccoli stalks that pass a dryer system. The product and drier properties are specified in Table 3.

Table 3 Dryer and product properties used for calculations and optimization

Parameter	Value
M_p	1.00 ($kg.m^{-2}$)
T(t=0)	25°C
C_{pa}	1.00 ($kJ.kg^{-1}.K^{-1}$)
C_{pv}	1.93 ($kJ.kg^{-1}.K^{-1}$)
C_{pp}	0.837+1.256X($kJ.kg^{-1}.K^{-1}$) (Hussain and Dincer, 2003)
ΔH_{vap}	2500-2.386T ($kJ.kg^{-1}$) (Henderson-Sellers, 1984)
T_{amb}	20 (°C)
k	$0.22exp(-\frac{19403}{8.314T})$ (s^{-1}) (derived from Jin et al., 2011)
$X_{a,in}$	0.007 (kg water/kg dry matter)

6.2.4 Degradation and drying rates in the moisture-temperature state diagram

The total losses of components depend on both time and degradation rate at a moment during drying. To illustrate the optimal drying strategies we use moisture-temperature state diagrams in which contour lines of equal degradation rate (for vitamin C and glucosinolates) and the drying rates are plotted (see Figure 1). The color bar indicates the values of these constants, the darker of the lines, the higher the constant values.

The total degradation of vitamin C and glucosinolates and total drying depends on a combination of rate and time. A short stay in a region with an elevated degradation rate can result in a similar degradation of vitamin C as a long stay in a region with a lower degradation rate. Although the time is missing in the state diagram, the diagram still can help to explain the drying strategies (as will be shown later). A first conclusion from the diagram is that in the considered temperature range (20-60°C), the degradation rate of glucosinolates is very low and loss of glucosinolates can be considered as a minor aspect. The degradation rate constant for vitamin C is neglectable for moisture contents above 3.5 kg water.kg dry matter^{-1}, and below 1 kg water.kg dry matter^{-1}. Degradation rates of vitamin C are the strongest in the moisture range of 1.0-3.0 kg water.kg dry matter^{-1}. When passing this moisture range during drying the product temperature be reduced to retain vitamin C or the time in this moisture range should be short. Outside the heat sensitive range the drying path hardly affects the vitamin C content.

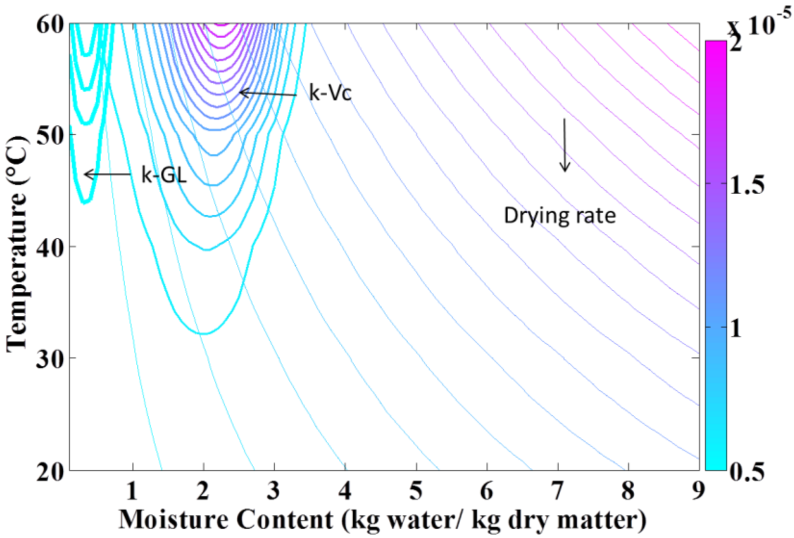

Figure 1 Moisture-temperature state diagram of fresh broccoli stalks with contour lines for the degradation rate constant of vitamin C (k-Vc) and glucosinolates (k-GL) and the drying rate

6.2.5 Optimization objectives and boundaries

The objective is to minimize the loss of the nutritional components vitamin C and glucosinolates. The control variables considered were temperature of the inlet air and air flow rate. The control variables are constrained by:

$$30\ °C \leq T_{in} \leq 60\ °C$$

$$0.005\,\frac{kg}{s} \leq Fa \leq 0.1\,\frac{kg}{s} \tag{15}$$

The restriction on the control variable air temperature affects the degradation rate constants. The degradation rate constant of glucosinolates in this temperature range is very low (see also Oliviero et al., 2012). Therefore we included only vitamin C and energy efficiency in the objective function. Both are relative values and it is intended to bring them at the end of the drying time as close as possible to 1. This aim is reflected in the objective function (J) by the first two terms:

$$J\ = w_1\left(\frac{C}{C_0} - 1\right)^2 + w_2(\eta - 1)^2 \tag{16}$$

With $\frac{C}{C_0}$ the retention ratio (-) of vitamin C compared to its initial concentration, w_1 and w_2 weight factors for respectively vitamin C retention and energy efficiency. Vitamin C retention and energy efficiency in equation 17 are in the same range (0-1), and therefore the weight factors $w_1 = 1$ and $w_2 = 1$ were applied.

Three final drying times (8,10 and 12 hours) at which a given final product moisture content must be achieved were considered. The total optimization problem is then defined as:

$$min\,J = w_1\left(\frac{C}{C_0} - 1\right)^2 + w_2(\eta - 1)^2$$

$$with\ respect\ to\ eq\ 1 - 15$$

$$x(tf\ = 8{,}10{,}12\ hours) = 0.1\ \frac{kg\ water}{kg\ product}$$

$$30\ °C \leq T_{in} \leq 60\ °C$$

$$0.005\frac{kg}{s} \leq Fa \leq 0.1\frac{kg}{s}$$

Drying trajectories can be calculated as continuous functions (Bryson, 1999) or by discrete functions like piecewise constant and piecewise linear functions. Discrete functions are most suitable for realization in batch or continuous drying of vegetables; each function can represent a drying stage. The calculation of the trajectories in this work is therefore based on optimization for piecewise constant and piecewise linear functions. The time intervals/drying stages were chosen to be equally.

In a first instance, a comparison is made between piecewise linear and piecewise constant functions for the temperature in combination with a constant flow rate. To obtain the best results, the required number of drying stages is increased until the improvement is no longer significant.

The results are compared to a reference with the best results for constant conditions over the whole drying time. Next, drying trajectories are calculated with both air flow rate and air temperature as control variables.

6.3 Results and Discussions

6.3.1 Comparison of piecewise linear and piecewise constant control profiles

Optimization results for comparison of piecewise linear and piecewise constant control profiles obtained with the Matlab function fmincon are listed in Figure 2. In these optimizations, the inlet air temperature trajectory was optimized, air mass flow rate was set to at 0.1 $kg.s^{-1}.m^{-2}$, and the drying time was 10 hours.

The top figure in Figure 2 shows for piecewise linear functions that the retention of vitamin C increased significantly by increasing the control stages for inlet air temperature. The improvement between 8 and 10 stages is still significant, but beyond 10 stages there is only a minor effect. The entire multistage controlled drying processes yield an improved energy efficiency (up to 42% at 10 or more stages) compared to the reference case with optimal constant drying temperature (28%), and an improved vitamin C retention (up to 60% at 10 or more stages) compared to the reference case (32%).

Figure 3 represents a plot for the drying strategies in state diagram. The drying trajectories for piecewise linear functions for 8 and 10 stages show in Figure 3 a different strategy. The 8 stages drying trajectory starts with a lower drying rate for the wet product and needs a higher drying temperature at the end of the drying. As a result vitamin C degradation occurs in the last drying stage during a relative long time. The 10 stage dryer passes at a moisture content of 2 kg water/kg product a region of higher degradation rates, but compensates the loss by a shorter stay in this region and low loss in the late drying stages.

For the optimization of piecewise linear functions with given length of each interval the number of parameters to be optimized are equal to "$number\ of\ stages + 1$" . That yields for the dryer with 10 stages 11 parameters to be optimized. Optimization problems with different aspects in the objective function (vitamin C retention and energy efficiency) and a high number of parameters often have local minima. Starting the optimization at different conditions, however, always resulted in similar outcomes for vitamin C retention and energy efficiency.

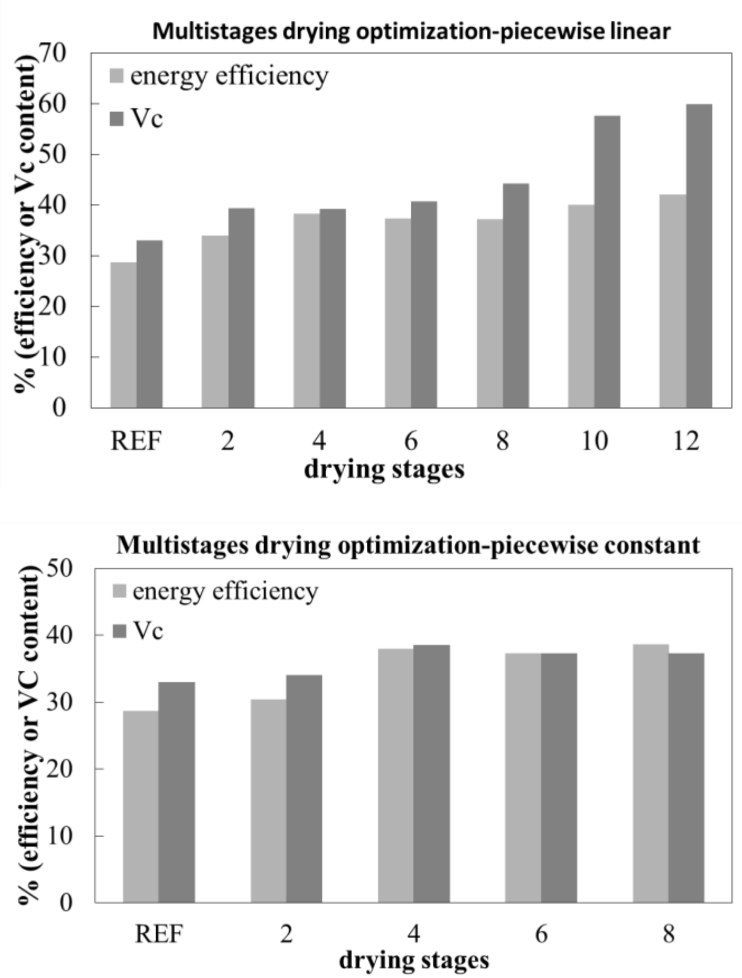

Figure 2 Comparison vitamin C retention (relative to the initial concentration) and energy efficiency by applying piecewise linear and piecewise constant control variables for air temperature. REF: optimal constant conditions for temperature and flow rate

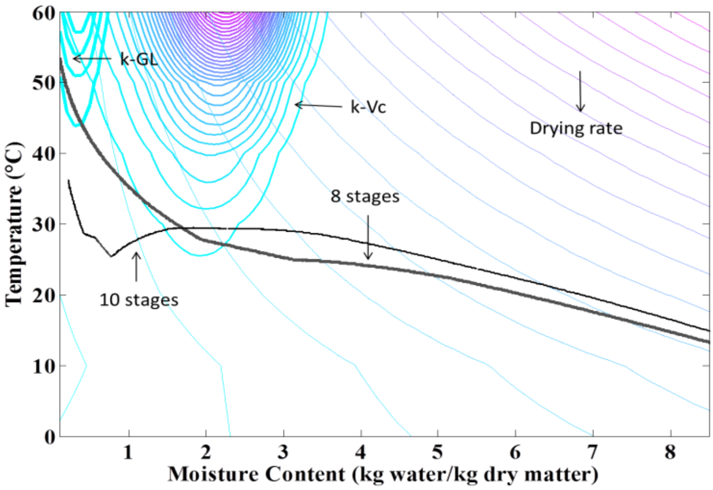

Figure 3 Product temperature trajectories in the state diagram for 8 stages and 10 stages with piecewise linear controlled air temperature

The results for piecewise constant functions for the inlet air temperature in Figure 2 show that the improvement is only significant when increasing the number of stages from two to four. Comparing both methods shows that piecewise linear functions yield the highest energy efficiency around 42%, and vitamin C retention around 60%, whereas with piecewise constant function the highest vitamin C retention is only about 40%.

The temperature trajectories of piecewise linear functions with ten stages, and piecewise constant function with four stages (the best results for each methodology) are given in the state diagram in Figure 4. In the first drying stage with a high drying rate, moisture evaporation is high enough at relative low temperatures. At the end of the first stage the product enters the region of vitamin C degradation and the piece wise constant controlled dryer responds by decreasing the temperature. The ten stage piecewise linear controlled dryer the product can easily avoid the region of vitamin C degradation. To satisfy the final moisture content constraint the four stage piecewise constant controlled dryer cannot avoid the region, which results in more vitamin C degradation.

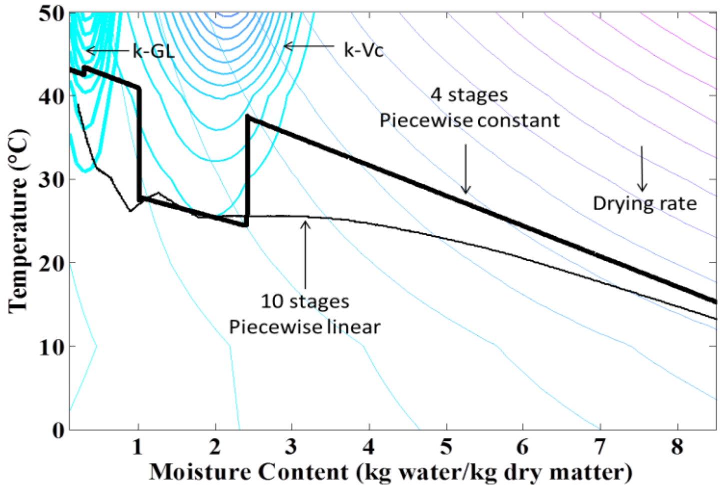

Figure 4 Product temperature trajectories in the moisture-temperature state diagram for comparison of best results from piecewise linear and piecewise constant controlled variables

6.3.2 Trajectories for air temperature and air flow rate

Following the results from previous section the piecewise linear functions were applied for the calculations of the trajectories of both air temperature and flow rate. The results in Figure 5 show that using the air flow rate as an extra control variable yields both a better energy efficiency and better vitamin C retention. Increasing the number of stages from two to four gives a significant improvement, while above four stages the improvement for energy efficiency and vitamin C retention is marginal. The energy efficiency increases to 65% and is combined with vitamin C retention around 55%. The loss in vitamin C is in the objective function compensated by gain in energy efficiency. The achieved energy efficiency is more than 100% better than the results for the reference case. In other words the energy consumption is halved. Note: by applying a higher weight factor for vitamin C in the objective function (equation 17), vitamin C retention can be improved.

For piecewise linear controlled inputs for air temperature and flow rate it satisfies to apply four stages. This number is also to be preferred from a numerical point of view. Only 10 parameters need to be optimized, while the number of parameters for an 8 stage system equals to 18. A lower number of parameters reduce the risk for ending in a local minimum.

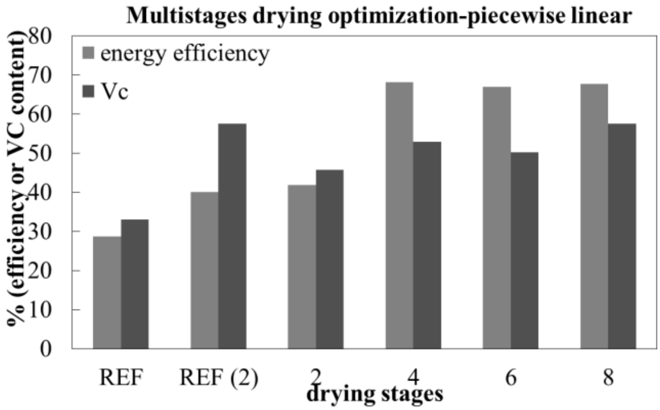

Figure 5 Optimization results with piecewise linear control variables for both air temperature and air flow rate. REF: optimal constant conditions for temperature and flow rate, REF(2): best result from piecewise linear optimization of temperature with 10 stages.

The optimized trajectories for air temperature and flow rate in the four stages dryer are given in Figure 6. In the initial stage of drying moisture is released easily from the product and don't need a high temperature. The moisture is then energy efficient removed by a high flow rate in combination with a moderate temperature. In the later stages of drying, the drying rate is not that high and then a low air flow rate satisfies, but to enhance drying in this phase a higher temperature is applied.

Again the drying strategy is represented in the state diagram (bottom figure, Figure 6). Due to the low product temperature degradation of the nutritional components is absent in the initial stage of drying. In the later stages of drying the trajectory just reaches low values for vitamin C degradation. To satisfy the constraint on the final moisture content, the product temperature increases to 45°C in the end stage of drying. Because of the low moisture content the vitamin C degradation rate is low in this stage. The improved energy efficiency is result of the decreasing air flow rate throughout the drying time. In the initial period of drying the drying rate is high and combined with an high air flow rate. With falling moisture content the drying rate reduces and the air flow rate can decrease accordingly to realize energy savings (bottom figure, Figure 6)

Because of the mild drying conditions (to retain vitamin C all temperatures remain below 60°C) degradation rate of glucosinolates is low. Glucosinolate retention is above 90%.

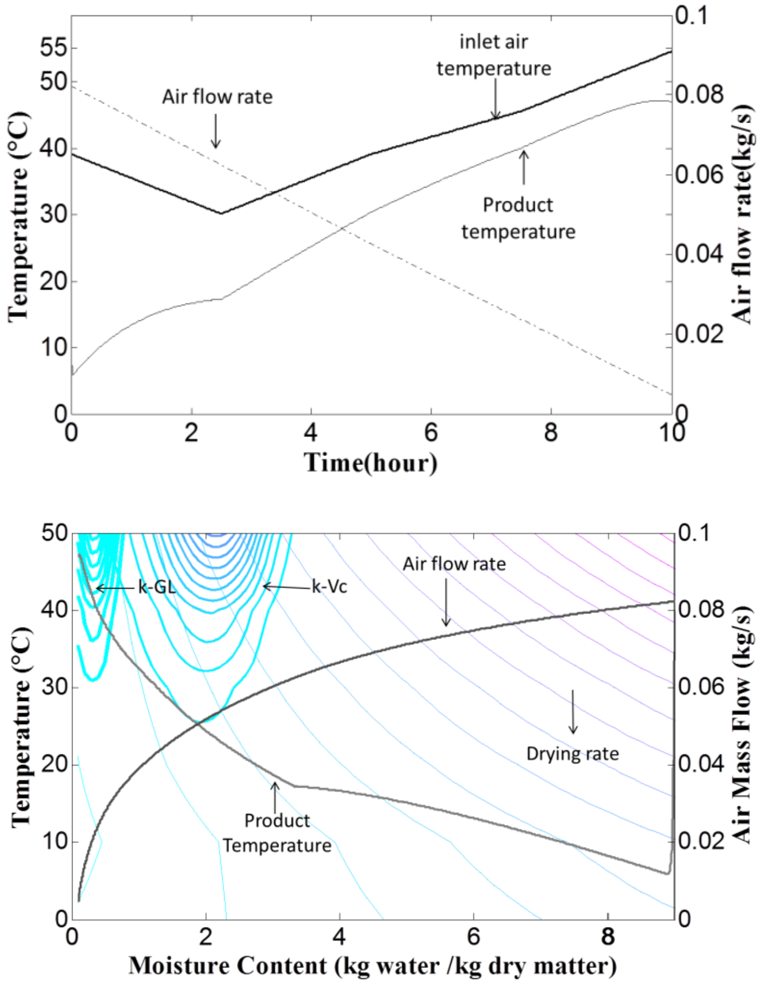

Figure 6 Temperature trajectories of the inlet air temperature, product temperature, and air flow rate as a function of time (top), and trajectories presented in moisture-temperature state diagram (bottom)

6.3.3 Effect of drying time

Figure 7 shows the effect of the drying time on the vitamin C retention and energy efficiency. Compared to 10 hours of drying, 12 hours of drying results in only a slight improvement of vitamin C retention. Although the distance for the product temperature trajectory to the region of vitamin C degradation increases (see Figure 8), the total beneficial effect is only small due to the longer residence time during which degradation occurs. There is no further improvement in energy efficiency. A shorter drying time (8 hours) requires a more intensive heating to satisfy the constraint on the final product moisture content. The increased heating results in a significant loss of vitamin C and a lower energy efficiency. In order to achieve the same final moisture content the product is forced to pass through a region of high drying rates which fall together with a higher degradation rate for vitamin C.

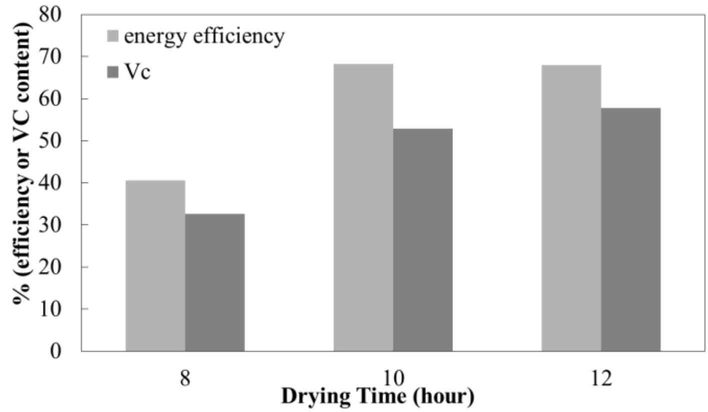

Figure 7 Optimization results with piecewise linear control variables for both air temperature and air flow rate at different drying times (8, 10, 12 hours)

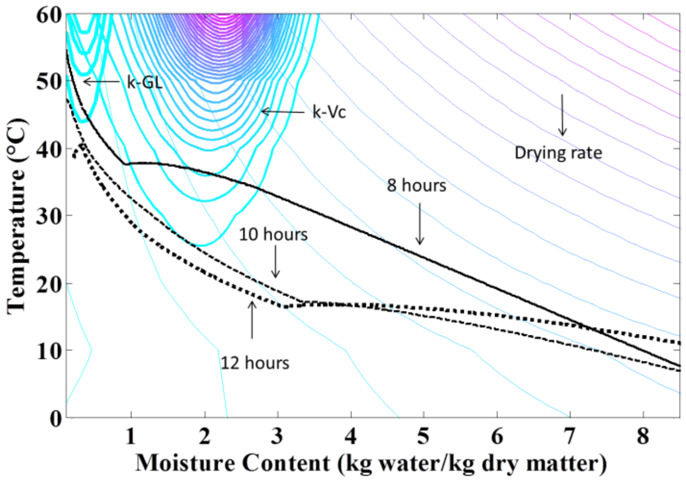

Figure 8 Product temperature trajectories in the moisture-temperature state diagram for air temperature and flow rate as control variables for different drying times (8, 10, 12 hours)

6.3.4 Sensitivity of the drying strategies for the drying rate

The role of the drying rate constant is also investigated. Products with a higher drying rate constant can be dried in a shorter time, while products with a lower drying rate constant need more time to be dried. Table 4 gives the results for the drying time for variations of the drying rate constant, while keeping the same result for the objective function. A 20 and 50% higher drying rate constant reduces the drying time from 10 to 8 and 6 hours respectively. For the considered cases, the optimized trajectories pass the areas of high vitamin C degradation in a comparable way. This means that the most sensitive component (Vitamin C in this case) in the state diagram is most essential for the trajectory.

Table 4 Effect of drying rate constant on drying time, vitamin C retention and energy efficiency

Drying rate constant	Drying time (hr)	Vc retention	Energy efficiency
k see table 3	10	55%	65%
1.2×k	8	55%	62%
1.5×k	6	60%	59%

6.4 Conclusions

Convective drying is an energy intensive operation in food processing which causes a high heat load to heat sensitive components. Most of the heat sensitive components have, however, an important contribution to the nutritional value of food products. To retain these components mild drying is often applied which results in a low energy efficiency. This work showed the development of drying strategies that meet both aims: high energy efficiency and a high retention of heat sensitive components.

To compromise between both objectives, optimal drying trajectories for the control variables air temperature and air flow rates are calculated. Representation of the trajectories in moisture-temperature state diagrams showed that the strategies avoid temperature- moisture content regions where degradation of the nutritional components occurs, or that the product resides only a short time in such region. To satisfy the objective for high energy efficiency, the conditions are also chosen in such way that the air flow rates are linked to the drying rate. Moisture-temperature state diagrams can also be used for other applications to obtain an overview of the possible pathways and to support the optimization results.

Piecewise linear and piecewise constant functions are used for the optimization for the controlled inputs. Piecewise linear functions resulted in the best performance with 55% for vitamin C retention and 65% for energy efficiency. These results are superior to a dryer with the best constant settings of the controlled variables: 32% retention for vitamin C and 28% of energy efficiency. In other ways, the energy consumption can be halved and the retention of nutritional components increased with 70%. These results show the impact of using optimized drying strategies instead of constant drying conditions.

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Chapter 7

Mechanistic driven modeling and optimization for drying of healthy foods: Retrospectives and Perspectives

7.1 Energy efficient drying of healthy food products

Food products with a high level of nutritional components are considered as healthy products and have gained a lot of attention in the food market. Freshly harvested food products have a high level of nutritional components, but their shelf life is limited. To prolong the shelf life fresh food can be dried, but during the heat treatment the nutritional components deteriorate. Therefore, retention of nutritional components during drying of food has become a challenge for research.

Drying is an energy intensive process and it is expected that in the near future the global economy will consume more energy. Considering the global energy shortage and global warming there is a need for highly energy efficient processes. Governments of several countries and food industries agreed with covenants to reduce the energy consumption and the CO_2-exhaust. The food drying industry faces two challenges at the same time: retention of heat sensitive nutritional components for healthy food products and decreasing the energy consumption while maintaining profitability.

Retention of quality and increasing the energy efficiency of drying are conflicting objectives. High energy efficiency is realized at high drying temperatures but results in a significant degradation of quality attributes, whereas a high retention of quality attributes asks for low drying temperatures which have low energy efficiency. The primary research question as stated in Chapter 1 was:

1. Can the optimization problem for mild, sustainable drying of healthy vegetables be solved by use of mechanistic modeling?

The problem of apparent conflicting demands concerning mild, sustainable drying has been resolved (in Chapter 6) by formulating it as a model-based dynamic optimization problem to develop drying strategies that seek the best compromise between energy efficiency and retention of healthy components. In order to apply this technology, kinetic models for the degradation of nutritional components had to be combined with novel mechanistic drying models.

In a food matrix moisture transport does not always follow the standard diffusion laws. The mobility of water changes with the state of the product and the interaction between moisture and the product matrix varies. Therefore it was essential to investigate the moisture transport behavior on the basis of an advanced mechanistic drying model for moisture transport. This part of the research (Chapters 3 -5) represents the answers to the following two secondary research questions:

2. How to describe the drying rate and moisture sorption isotherm by models based on physical properties related to the product matrix?
3. How to validate moisture transport models and how to detect moisture transport phenomena non-destructively, qualitative and quantitatively?

The mechanistic driven modeling and optimization approach for the production of dried healthy foods was implemented to drying of broccoli. Details on the concept of this approach, the major findings, some comments on limitations and issues, and the main contribution are discussed in the following retrospective section, whereas expectations on the impact on drying research and the potential for the drying industry are given in the perspectives section.

7.2 Mechanistic driven modeling and optimization for drying of healthy foods: Retrospectives

Vegetables contain water, carbohydrates, proteins, fats, and ash. All these components are often well organized in the cellular matrix. Drying of vegetables involves simultaneous heat and mass transfer, physical and chemical changes, and changes of the properties of the cellular matrix. State of the art models for moisture transport during drying include empirical or semi-empirical aspects. In this thesis, the emphasis was put on the use of a drying model based on physical concepts for the empirical and semi-empirical aspects and to use that model for optimization. The setup and implementation of this systematic approach is the main contribution of this thesis work. The original scheme as envisaged in Chapter 1 is shown in Figure 1. It includes the development of a mechanistic model, model validation, mechanistic assisted optimization, and the implementation and evaluation of the optimized drying trajectory. This approach has been applied to drying of broccoli. Prior to discussing element-by-element the main achievements of this thesis according to the proposed approach it is appropriate to provide the entire project context first.

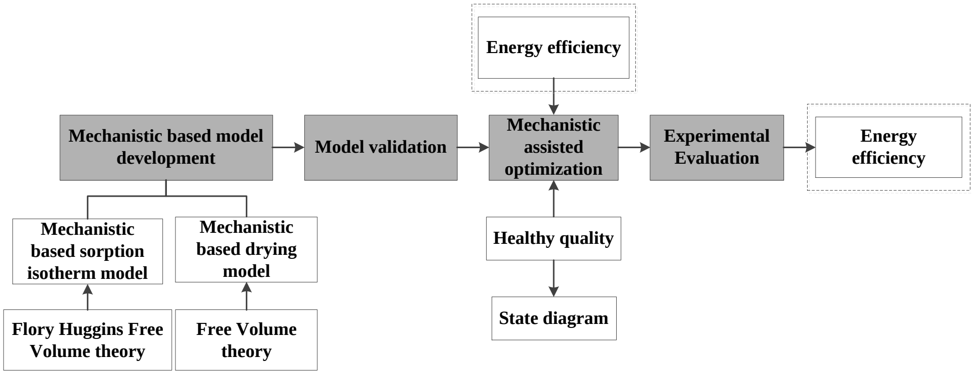

Figure 1 Mechanistic modeling and optimization to produce healthy foods.

7.2.1 The project "Energy efficient drying of healthy food products"

The total research project concerned 3 parallel projects:

1. Influence of drying technology on stability and availability of glucosinolates in broccoli (T. Oliviero),
2. Drying of healthy foods: from mechanism to optimization (this thesis),
3. Energy-efficient low-temperature drying using adsorbents (J. Atuonwu).

The topic of this thesis is to integrate findings of sub-projects 1 and 3. It is clear that to solve the central question of this thesis, knowledge about kinetics and assumptions about energy consumption are needed. However, as the projects were running in parallel, it was unavoidable that a full integration at this stage was not yet possible, and certain limitations had to be accepted.

In this thesis the degradation kinetics was obtained from project 1. In Chapter 6 the kinetics for vitamin-C and glucosinolates were used, but a complete picture requires also the kinetics of myrosinase inactivation. Although preliminary trajectory optimizations were done for the complete set of healthy components considered in the project, and the envisaged experiments as shown in Figure 1 were performed, the analysis results were not yet available for this thesis.

In project 3, it was shown that with the application of adsorbents and energy recovery the energy consumption in low temperature drying can be more than halved. The proposed adsorbent system can be combined with traditional dryers as an add-on. In line with these findings, in the current thesis (in Chapter 6) the energy efficiency is treated in the traditional way without considering an adsorption add-on system. This does not invalidate the approach, as it can be applied to any drying equipment.

7.2.2 Mechanistic drying model

In this thesis work the sorption isotherm and moisture transport are modeled and validated by using the physical properties of the components in the product and by using the state of the food matrix. Two forms of free volume models, i.e. the Free Volume theory for moisture transport and the Flory Huggins Free Volume theory for sorption isotherms, are used in this work. To assess the effective diffusion coefficient in Fick's law the Free Volume Theory replaces the Arrhenius equation (see Chapter 2). The main advantage of this model is that the parameters are based on the physical properties of the components. Also variations in moisture mobility that occur when the product passes during drying through the rubbery and glassy state are involved. By combining the Free Volume theory with the Maxwell-Eucken theory, the moisture transport in a porous broccoli floret is well predicted. The validation work for the model showed how the effective diffusion coefficient varies with moisture content and temperatures during drying.

Another important contribution is the application of a mechanistic model for the sorption isotherm for fresh and pre-treated vegetables. It was demonstrated that the Flory Huggins Free Volume (FHFV) theory predicts the sorption isotherm for broccoli accurately, not only for fresh samples but also for blanched samples with a changed composition compared to the fresh product. Changed sorption properties due to pre-treatments are hardly mentioned in literature. The main advantage is that the FHFV theory, just as the Free Volume theory for moisture transport, is based on product composition and physical properties. The consequences of changed composition due to pre-treatments like blanching on the sorption isotherms can therefore be predicted by using the FHFV theory.

7.2.3 Spatial modeling of products during drying

The degradation of the nutritional components in a product depends on the local time varying temperature and moisture content rather than on the average values. Therefore, in this work a spatial distributed model (COMSOL multi-physics) is used to illustrate the impact of temperature and moisture distribution, and shrinkage by a 2D color map (Chapters 2 and 5). Calculations with this spatial modeling reveal how the nutritional components degrade throughout the product as a function of time. Spatially distributed moisture and temperature profiles are desired for the evaluation of the quality degradation over the whole product.

7.2.4 Non-destructive validation and detection of drying phenomena

Moisture transport during drying is monitored non-destructively with MRI. While MRI was used before in the context of drying, this is the first time it was applied to broccoli. With fresh broccoli stalks anomalous moisture transport was observed, which seemed to conflict with Fickian diffusion. The internal stress developed during drying and the elastic impermeable skin were the source of the anomalies. Pre-treatments such as peeling or blanching change the skin and bulk elastic properties of broccoli and support the hypothesis of stress-diffusion for fresh products. Fickian drying behavior occurs only if the significant moisture transport resistance in the skin of fresh food products is removed by a pre-treatment. This thesis work shows that besides coupled heat and mass transfer, other physical phenomena such as stress development, elasticity changes etc., are involved in drying. Multi-physics modeling should be used to explain the complex moisture transport during drying.

7.2.5 Optimization of drying trajectories and the isokinetic state diagram

Model based optimization of the dynamics during drying is a powerful tool to find optimal drying trajectories to retain nutritional components and to increase the energy efficiency. However, while 2-D analysis and CFD were used in the detailed analysis of Chapters 4 and 5, the direct use of COMSOL in conjunction with dynamic optimization was simply not possible because of the computational burden. Instead, in Chapter 6, a lumped moisture and temperature model was used. This model was calibrated against the 2-D results. However, the lumping of temperature and moisture will result in a homogeneous degradation rate, whereas in reality the degradation rate is a distribution over the spatial dimension, with spots with higher than average, and spots with lower than averaged rates. The effect on the actually observed degradation is yet to be investigated. This experience with 2-D dynamic modeling shows that the scheme of Figure 1 must perhaps be expanded with a model reduction step.

Assuming that the overall quality degradation will not be too different from the degradation at lumped calibrated temperatures and moisture contents, this thesis shows that with the optimized drying trajectories the retention of nutritional components can be doubled, and the energy consumption can be halved compared to the conventional drying methods. State diagrams are combined with contour lines of equal degradation rate constants. These isokinetic state diagrams give a good motivation for the optimal trajectories; the product avoids regions with high degradation rates as much as possible. This thesis shows that isokinetic state diagrams are a powerful tool for optimization and understanding processing methods for high value food products. This concept can also be applied to other food products and processes.

7.3 Mechanistic driven modeling and optimization for drying of healthy foods: Perspectives

In this thesis, moisture transport and sorption isotherm models were successfully built by using underlying physical mechanisms. The models are experimentally investigated for an extended range of moisture contents and temperatures. Because of the mechanistic background of the used theories, extrapolation outside the experimental validation range is allowed.

The application of MRI offered the possibility for non-destructive monitoring of the drying mechanism in time. The MRI images showed anomalous moisture transport caused by stress assisted diffusion. The MRI results also show that drying of vegetables is a multi-physics process rather than purely mass and heat transfer process.

By using optimized drying trajectories, obtained by dynamic optimization, the energy consumption can be halved and the retention of nutritional components can be improved significantly. The isokinetic moisture-temperature state diagram explains the result of the optimization procedure. The effectiveness of the optimized process trajectories is realized minimizing the time during which the product resides under conditions which result in high degradation rates for qualities. The impact of the proposed research approach ‘mechanistic driven modeling and optimization for drying of healthy foods’ on drying research and potential for further work are discussed in the following sections.

7.3.1 Spatial distribution of quality in product and on dryer

In this work the spatial quality distribution in the product was calculated via a CFD-model. With this model it is possible to predict the spatial distribution of moisture and quality in time. The predictions for moisture are validated by monitoring the moisture distribution during drying non-destructively with MRI. Validation of the quality distribution is still an open question. Furthermore, calculation of the optimized drying trajectories to retain heat sensitive components and its validation is based on an averaged moisture and quality model and data. The computational efficiency of the CFD model in COMSOL multi-physics in combination with the optimization procedures was insufficient to allow full integration of the spatial model with the dynamic optimization. Further development of software that can realize dynamic optimization of spatial distributed models is recommended.

Vegetables are normally dried with belt dryers. Particles at different height on the belt have a different temperature-moisture content profiles and consequently different qualities. This aspect has not yet been discussed in this thesis. Future work is recommended to investigate the role of the spatial distribution within a dryer and to develop drying strategies either for a uniform quality distribution throughout the dryer, or to cope with the distribution in the final product.

7.3.2 Impact of adsorption drying on drying efficiency and quality

Although not extensively investigated in this work it is expected that the adsorbent system can also be combined as an add-on with the drying strategies as proposed in this thesis. Experimental results for drying of broccoli with ambient air and zeolite dehumidified air also showed that with dehumidified air the drying rate can significantly be enhanced in the first drying period. Quality degradation during drying depends on temperature and moisture content and residence time. Applying dehumidified air reduces the residence time of product in a dryer and it there are possibilities to reduce the residence times in regions of high degradation rates. This aspect has not yet been studied in this work. It may be worthwhile to do further work along the lines of this thesis to investigate quality retention in combination with zeolite dehumidified air.

7.3.3 Application to other food products and processes

A mechanistic driven modeling and optimization approach to dry healthy foods was proposed and applied in this thesis work. It includes four steps: model development, validation, optimization and implementation. Foods, either in its natural or processed form, with various ingredients such as moisture, carbohydrates, fat, protein and ash are complex soft matter. Processing of foods includes besides coupled heat and mass transfer also physical and chemical changes. All these changes affect the development of food quality during processing.

Optimization needs a good transport model and a good quality model. Empirical and semi-empirical models are limited in the extrapolation to conditions outside the validated range. Empirical models in the literature are often based on single response models which don’t include effect of varying multiple conditions that arise during food processing. For example the Arrhenius equation gives only the temperature dependency of the rate constants and the role of the changing composition is not included. Mechanistic drying models can overcome these limitations. Therefore they have the potential to be applied for a large range of processing conditions.

The case study in this thesis concerned drying of broccoli. Both the drying and sorption isotherm model are mechanistic and use the composition and physical properties of the components based. The experimental validation proved that the models are valid in a wide range of moisture contents and temperatures. With the isokinetic temperature-moisture content state diagram, optimized drying trajectories are designed which avoids temperature-moisture content regions with a high degradation rate.

This approach is a fundamental approach based on applied physics and can be applied to other food products and processing methods to dry healthy foods. The isokinetic temperature-moisture content state diagram is especially helpful to understand the drying trajectories for multi-objective problems and to obtain an overview of pathways that retain heat sensitive healthy components.

The optimal trajectories can be realized in batch dryers by varying the temperature settings in time. In continuous dryers the optimal trajectories can be realized by applying drying sections with distinct air temperatures for each section.

Summary

Convective drying is an effective post-harvest method to the extend shelf life of vegetables and to reduce the mass for transportation. The heat load during drying, however, affects the quality attributes negatively. Today, consumers in the industrialized world pay a raised attention on food quality, and especially to the nutritional value of food. This increased demand on quality has become a challenge for drying research, and to retain the nutritional value, mild drying conditions must be applied. However, at these conditions the energy efficiency to remove the water from the product by evaporation is low; often below 50%. Moreover, due to the growing global market for dried products, drying contributes more and more to the global energy consumption and CO_2-emission. Hence, there is a need for high energy efficient drying methods with low CO_2-emission. A straightforward solution to increase drying energy efficiency is high temperature drying, but these conditions are conflicting with the aim to retain nutritional components. To combine these two aims, i.e. energy efficient drying and retention of nutritional components, is a challenge for drying research.

In this thesis work, the conflict between quality retention and energy efficiency is investigated for the drying of broccoli. The approach in this work is based on mechanistic driven drying modeling and optimization. The approach includes three crucial elements: 1) mechanistic driven model development, 2) model validation, and 3) mechanistic model assisted optimization.

In the first parts of the thesis advanced mechanistic drying models are introduced. These are the Free Volume theory for moisture transport (**Chapter 2**), and the Flory-Huggins Free Volume theory to describe sorption isotherms (**Chapter 3**). The strength of these theories is that the mobility of water is based on the changes in physical state during drying (from rubbery to glassy state) and the mixing properties of water, biopolymers and solutes. These mechanistic models allow the extrapolation of the drying behavior to not experimentally validated conditions. Moreover, the model parameters have a physical basis and can directly be related to material properties. The drying behavior in broccoli is represented by 2D color maps to visualize the spatial distribution of moisture content, the progress of

degradation of nutritional components in the product and shrinkage during drying. The influences of pre-treatments are also incorporated in the models.

The second part of the thesis concerns experimental validation of the models from **Chapter 2** and **Chapter 3**. In **Chapter 4** moisture transport during drying of broccoli is monitored with MRI (Magnetic Resonance Imaging) as a non-destructive technique. The results show the spatial distribution of moisture content, shrinkage and drying rate of differently pre-treated samples during drying. The images revealed non-Fickian diffusion behavior for fresh stalks. The non-Fickian diffusion is caused by the moisture transport resistance of the stalk skin which creates, together with shrinkage, center directed stress driven moisture transport. This phenomenon was absent in pre-treated broccoli samples for which the resistance for moisture transport in the skin was reduced.

The drying rates for broccoli florets and stalks are derived from MRI data in **Chapter 5**. The Free Volume theory for moisture transport is validated on the average moisture content from the MRI experiments. The fitting parameters are the mass transfer coefficient and the self-diffusion coefficient of solids. The results quantify the enhanced drying rates of fresh and pre-treated samples due to the removal of the transport resistance in the skin and the changed cell structure. The influence of pre-treatments on the drying rate is in line with the results of **Chapter 4**. Comparison of experiments in a pilot dryer showed a good agreement with the drying behavior in the MRI device.

Chapter 6 concerns dynamic optimization to derive optimal drying trajectories that increase both energy efficiency and retention of nutritional components during drying of broccoli. For this step it was necessary to derive, from the spatial model, a drying model for the average moisture content and average value of the nutritional components. The kinetics for the degradation of glucosinolates and vitamin C (obtained from a parallel project) and the drying rate of broccoli are applied to calculate optimized drying trajectories for the control variables of temperature and air flow rate. The results have shown that with optimal trajectories the energy consumption can be halved, the vitamin C retention can be increased significantly, and the influence of drying on the degradation of glucosinolates is reduced to nearly zero. The optimized drying trajectories are plotted in an isokinetic temperature-moisture content state diagram which shows that the product areas with high degradation rates are circumvented.

Finally, in **Chapter 7** the contribution of the thesis work and the impact on drying research and the perspectives are discussed. The mechanistic driven drying modeling and optimization approach to produce healthy dried food is regarded as a fundamental approach which uses physical and chemical properties of the product. The advantage of the approach is the potential for application to a large range of processing conditions. The isokinetic temperature-moisture content state diagram, which gives a direct overview of possible pathways to retain heat sensitive components, is a powerful tool to support decision making in multi-objective problems in food process design. This thesis work is an important step in mechanistic modeling and optimization, but the end of this approach is not yet reached. Further adoption of the proposed methodology of monitoring and modeling transport phenomena and degradation of micronutrients in food matrices is believed to advance the quality of food products.

Samenvatting

Convectief drogen met verwarmde lucht is een effectieve manier om de houdbaarheid van levensmiddelen te verbeteren. Het beperkt ook de kosten van transport door het kleine productvolume en de lage productmassa. De warmtebelasting tijdens het drogen heeft echter een negatieve invloed op kwaliteitseigenschappen. De eindgebruikers in de geïndustrialiseerde wereld stellen steeds hogere eisen aan kwaliteit van gedroogde producten en met name aan de gezondheidseigenschappen. Het bereiken van betere gezondheidseigenschappen is daarom een belangrijk aspect in de ontwikkeling van droogtechnologie waarbij het toepassen van milde droogcondities centraal staat.
Echter, bij milde droogcondities is de energie-efficiëntie voor het verwijderen van water laag; in het algemeen beneden 50%. Omdat de wereldmarkt voor gedroogde producten nog altijd groeit, draagt drogen steeds meer bij aan de wereldwijde energieconsumptie en de CO_2-uitstoot. Daarom is het ontwikkelen van energiezuinige droogmethoden met lage CO_2-uitstoot van groot belang. Verhogen van droogtemperaturen is een eenvoudige methode om de efficiëntie van droogprocessen te verhogen, maar dat conflicteert met het streven naar milde droogcondities voor het behoud van gezondheidseigenschappen. Het combineren van de twee doelen, 1) energiezuinig drogen en 2) het behoud van gezondheidseigenschappen in gedroogde producten is daarom een van de grootste uitdagingen voor het huidige droogonderzoek.

In dit proefschrift wordt de conflicterende vraag voor behoud van kwaliteit en energie-efficiëntie onderzocht voor het drogen van broccoli. Het onderzoek maakt gebruik van het modelleren en optimaliseren van het droogproces op basis van mechanistische kennis. De aanpak is gebaseerd op de volgende elementen: 1) mechanistisch modelleren, 2) model validatie en 3) modelgebaseerde optimalisatie.

In het eerste deel van dit proefschrift worden geavanceerde mechanistische modellen geïntroduceerd. Dit betreft de Free Volume theorie voor watertransport in groenten die gedroogd worden (**hoofdstuk 2**), en de Flory-Huggins Free Volume theorie voor de beschrijving van sorptie-isothermen (**hoofdstuk 3**). In deze theorieën is de verandering van de mobiliteit van water in de productmatrix, welke tijdens drogen van de rubber- naar de glasstatus gaat, meegenomen. Verder gebruiken deze theorieën de mengeigenschappen van water, biopolymeren en opgeloste componenten. De modelparameters in deze mechanistische modellen hebben een fysische achtergrond en volgen uit materiaaleigenschappen. Daarmee wordt de mogelijkheid voor extrapolatie van het drooggedrag naar niet-experimenteel gevalideerde condities sterk uitgebreid. Het drooggedrag is weergegeven in 2D kleurengrafieken die de ruimtelijke verdeling van water in het product, de afbraak van micronutriënten en de krimp tijdens het drogen weergeven. Het effect van behandelingen die voorafgaan aan het drogen is in deze modellen meegenomen.

Het volgende deel van dit proefschrift betreft experimentele validatie van de modellen uit **hoofdstuk 2** en **hoofdstuk 3.** In **hoofdstuk 4** wordt het vochttransport in broccoli tijdens drogen gemonitord via MRI (Magnetische Resonantie Imaging). Het voordeel van deze methode is dat het product intact blijft tijdens het meten waardoor er geen neveneffecten optreden. De metingen geven de ruimtelijke verdeling van het vochtgehalte, de krimp en droogsnelheid voor verse en voorbehandelde broccoli in de tijd weer. Uit de resultaten blijkt dat het drogen van verse broccoli sterk afwijkt van de gebruikelijke Fick-diffusie. Deze afwijking wordt veroorzaakt door de weerstand voor watertransport in het oppervlak van het product, door de krimp en door stress ontstane naar binnen gericht watertransport. Dit verschijnsel was sterk gereduceerd of afwezig bij voorbehandelde producten.

In **hoofdstuk** 5 worden de droogsnelheden voor broccoliroosjes en -stelen afgeleid uit MRI data (**hoofdstuk 4**). De Free Volume theorie voor watertransport is gevalideerd op basis van het gemiddelde vochtgehalte dat gemeten is gedurende de MRI experimenten. De fitparameters waren de massaoverdrachtscoëfficiënt en de zelf-diffusiecoëfficiënt voor vaste componenten. De resultaten kwantificeren de verschillen in droogsnelheid van verse en voorbehandelde broccoli (zie **hoofdstuk 4**). Vergelijking van het drooggedrag tijdens de MRI experimenten toonde een goede overeenkomst met dat in een pilot drooginstallatie.

Hoofdstuk 6 betreft de dynamische optimalisatie voor het behoud van micronutriënten in combinatie met hoge energieefficiëntie bij het drogen van broccoli. Hiervoor was het nodig om de ruimtelijke verdeelde modellen te reduceren tot productgemiddelde modellen voor watertransport en afbraak van de micronutriënten glucosinolaten en vitamine C. Op basis van deze modellen bepaalt de optimalisatie de stuurpatronen voor luchttemperatuur en –debiet. Met de optimale sturing voor deze variabelen halveert het energieverbruik, neemt het vitamine C-gehalte aanzienlijk toe, en treedt er vrijwel geen afbraak van glucosinolaten op. Grafische weergave van de optimale sturingen in isokinetische temperatuur-vochtgehalte toestandsdiagrammen maakt inzichtelijk hoe de sturing afbraak van de micronutriënten voorkomt.

In het slothoofdstuk (**hoofdstuk** 7) worden de impact en perspectieven van dit werk voor het droogonderzoek en de kwaliteit van levensmiddelen beschreven. De aanpak van mechanistische modellen en optimalisatie is een fundamentele aanpak om micronutriënten op een energiezuinige manier te drogen. Met het gebruik van fysische en chemische eigenschappen is het mogelijk om de modellen voor een groot bereik van droogcondities toe te passen. De isokinetische temperatuur-vochtgehalte toestandsdiagrammen geven direct inzicht in de mogelijke manieren om temperatuurgevoelige componenten te behouden en zijn belangrijk in het maken van beslissingen bij het ontwerpen van verwerkingsprocessen met meervoudige doelen. Hoewel dit proefschrift een belangrijke bijdrage levert aan het droogonderzoek zijn er nog diverse mogelijkheden voor verdere ontwikkeling van de aanpak. Verdere ontwikkeling van monitoring methoden en modellen voor watertransport, en onderzoek naar de manier waarop micronutriënten afbreken in intacte levensmiddelen, zal de kwaliteit van gedroogde levensmiddelen nog verder verbeteren.

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The thesis book summaries my four years' PhD works in the group of Biomass Refinery and Process Dynamics Group (formerly Systems and Control Group) in Wageningen University. First of all, I would like to express my sincerely thank to the Dutch Ministry of Economic Affairs for funding this work under Project EOSL T07043 of its Energy Research Program.

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When talking about my academic path, it started from the time working with prof. Johan Grievink who is the emeritus professor from Delft University of Technology where I did my master study. Since the time working with him, I started to learn to work and think independently. My English has improved also from that period when he told me that I should think and write in English which has proved to be very helpful.

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About the Author

Xin Jin was born on April 13th, 1983, in Beijing, China. She got her bachelor degree in Pharmaceutical Engineering, in Beijing University of Chemical Technology, Beijing, China. Afterwards, she came to the Netherlands to pursue the MSc degree in Biochemical Engineering in Delft University of Technology (09.2006-03.2009), Delft, The Netherlands. During the MSc study she specialized in reactor and process design. She did the master thesis 'Scale-up and design of a new reactor concept with a retrofit into an industrial organic synthesis process' in Akzo Nobel Netherlands B.V. Besides, an internship was done in NPSP Composieten BV for the project of 'Technical and commercial feasibility study of the technology of 100% nature based composites'. Since April, 2009, she started the PhD project entitled 'Drying of healthy foods-from mechanism to optimization' in the group of Biomass Refinery and Process Dynamics (formerly Systems and control group), Wageningen University, Wageningen, The Netherlands. Since August 8th, 2013, she works in Innovative Chemical Engineering Laboratory, in Soochow University, Suzhou, Jiangsu Province, China.

List of Publications

Peer-reviewed International Journals

1. Jin, X., van der Sman, R. G. M., & van Boxtel, A. J. B. (2011). Evaluation of the Free Volume Theory to Predict Moisture Transport and Quality Changes during Broccoli Drying. *Drying Technology, 29*(16), 1963-1971.
2. Jin, X., van Boxtel, A. J. B., Gerkema, E., Vergeldt, F. J., Van As, H., van Straten, G., Boom, R. M., & van der Sman, R. G. M. (2012). Anomalies in moisture transport during broccoli drying monitored by MRI? *Faraday Discussions*, 158(0), 65-75.
3. Jin, X., Sman, R. G. M., Maanen, J. F. C., Deventer, H. C., van Straten, G., Boom, R. M., & van Boxtel, A. J. B. (2013). Moisture Sorption Isotherms of Broccoli Interpreted with the Flory-Huggins Free Volume Theory. *Food Biophysics*, 1-9.
4. Jin, X., Sman, R. G. M., van Straten, G., Boom, R.M., & van Boxtel, A.J.B. (2013). Energy Efficient Drying Strategies to Retain Nutritional Components in Broccoli (*Brassica oleracea var. italic*). Accepted by *Journal of Food Engineering.*
4. Jin, X., Sman, R.G.M., Gerkema, E., Vergeldt, F.J., Van As, H., van Straten, G., Boom, R.M., & van Boxtel, A.J.B. (2013). Quantifying Broccoli Drying Rates from MRI Measurements. *Submitted.*
5. Djaeni, M., Sasongko, S. B., Prasetyaningrum, A., Jin, X., & van Boxtel, A.J.B. (2012) Carrageenan Drying with Dehumidified Air: Drying Characteristics and Product Quality, *International Journal of Food Engineering*: Vol.8: Iss. 3, Article 32.

Peer-reviewed International Conferences

1. Jin, X., van der Sman, R. G. M., & van Boxtel, A. J. B. (2011). Evaluation of the Free Volume Theory to Predict Moisture Transport and Quality Changes during Broccoli Drying. In proceedings of the 17th *International Drying Symposium (IDS 2010)* Magdeburg Germany 3-6 October 2010.
2. Jin, X., van der Sman, R.G.M., Gerkema, E., Vergeldt, F.J., Van As, Henk., & van Boxtel, A.J.B. (2011) Moisture Distribution in Broccoli: Measurements by MRI Hot Air Drying Experiments. In proceedings of the 11th *International*

Congress on Engineering and Food (ICEF11), Athens, Greece, 22-26 May, 2011.

3. Jin, X., van der Sman, R.G.M., Gerkema, E., Vergeldt, F.J., Van As, Henk., van Straten, G., Boom, R.M., & van Boxtel, A.J.B. (2011) Investigation on the Influence of Pre-treatments on Drying Behaviour of Broccoli by MRI Experiments. In proceedings of the 7th *Asia-Pacific Drying Conference (ADC2011),* Tianjin, China, 18-20 September, 2011
4. Jin, X., van Boxtel, A.J.B., Gerkema, E., Vergeldt, F.J., Van As, Henk., van Straten, G., Boom, R.M., & van der Sman, R.G.M. (2012) Anomalies in moisture transport during broccoli drying monitored by MRI? In proceedings of *Faraday Discussions 158 (FD158)*, Wageningen, The Netherlands, 2-4 July, 2012.
5. Jin, X., van der Sman, R.G.M., van Straten, G., Boom, R.M., & van Boxtel, A.J.B. (2012) Optimization of Drying Trajectories to Retain Nutritional Components in Broccoli. In proceedings of the 18th *International Drying Symposium (IDS 2012)* Xiamen, China, 11-15 November, 2012.
6. Atuonwu, J.C., Jin, X., van Straten, G., van Deventer, H., & van Boxtel, A.J.B. (2011) Reducing Energy Consumption in Low Temperature Food Drying: An Assessment of Opportunities in Desiccant Adsorption and other Dehumidification Strategies. In proceedings of *the International Conference on Engineering and Food (ICEF11)*, Athens, Greece, 22-26 May, 2011.
7. Van der Sman, R.G.M., Jin, X., & Meinders, M.B.J. (2012) A Paradigm Shift in Drying of Food Materials via Free-Volume Concepts. In proceedings of the 18th *International Drying Symposium (IDS2012)* Xiamen, China, 11-15 November, 2012.

Other Conferences

1. Jin, X., van der Sman, R.G.M., Gerkema, E., Vergeldt, F.J., Van As, Henk., & van Boxtel, A.J.B. (2010) Characterization of Water Diffusion in Food Products from MRI Experiments. *Netherlands Process Technology Symposium (NPS 2010)*, Veldhoven, the Netherlands.

Overview of Completed Training Activities

Course	Graduate School/Institute	Year
Discipline Specific Activities		
Physical modelling	SENSE	2009
Reaction kinetics in food science	VLAG	2009
Spatial modelling with Comsol	Comsol Inc	2009
Sustainable Process & Product design	WUR	2012
Spatial modelling of food products	Cornell University	2010
Modelling with gProms	PSE LtD	2010
International Congresses		
International Drying Symposium	IDS	2010
International Congress on Engineering and Food	ICEF	2011
Asia-Pacific Drying Symposium	ADC	2011
International Drying Symposium	IDS	2012
Faraday Discussions	FD158	2012
General Courses		
VLAG PhD week	VLAG	2009
Academic writing II	CENTA	2009
Techniques for Writing and Presenting a Scientific Paper	WGS	2010
Project and time management	WGS	2010
Career Perspectives	WGS	2013
Optional		
Writing/updating project proposal	SCO/BRD	2009
PhD-trip US	FPE	2010
Discussion groups	SCO/BRD/PRE	2009-2013
NPS symposium	NPS	2010
Organization support, young scientist program	IDS	2012

Teaching Support

Signals and systems modelling	SCO/BRD	2009
Control engineering	SCO/BRD	2010-2013
Thesis supervision	SCO/BRD	2009-2012